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ATOMIC PHYSICS

Photo-Detachment of a Noncollinear Triatomic Anion

A. Afaq · K. Farooq

Abstract Photo-detachment of a noncollinear triatomic anion is investigated by considering each atom of the molecular anion as a coherent source of detached-electron waves, originating in all possible directions. The waves traveling along three different trajectories result in a quantum interference that displays on a screen placed at a very large distance from the system. To explain this quantum interference, an analytical formula of detached-electron flux is derived using a collinear three-center model recently published. The detached-electron flux versus laser photon energy expression displays molecular geometry-dependent oscillatory structures on an observation plane. This oscillatory behavior in the result can be explained using the semiclassical closed-orbit theory. The outgoing electron waves produced from one coherent center are propagated in the vicinity of the sources at two other coherent centers, which cause these oscillations. It is also observed that in a particular case, the noncollinear triatomic system reduces to the collinear three-center system.

Keywords Photo-detachment · Quantum interference · Molecular negative ion · Electron flux

A. Afaq (✉)
Centre of Excellence in Solid State Physics,
University of the Punjab, Lahore, 54590, Pakistan
e-mail: aafaq.cssp@pu.edu.pk

K. Farooq
School of Physics and Optoelectronic Technology,
Dalian University of Technology, 116024 Dalian, China

1 Introduction

The quantum interference phenomena of microscopic objects, like electrons and photons, have played a central role in the development of quantum mechanics. The phenomena of quantum interference of microscopic particles have always been a subject of prime interest in quantum mechanics not just because of its large applications but also due to its exceptionally interesting physics. Therefore, it has remained a subject of interest in experimental and theoretical studies. The waves associated with microscopic particles have been thoroughly investigated in the last century. The simplest of all the experiments describing the quantum interference phenomenon of microscopic objects is Young's double-slit experiment. Young's double-slit experiment explains in a simple manner the interference effects in the electrons. The similar interference phenomena are also observed in photo-detachment of negative molecular ion systems [1–7].

The photo-detachment of negative ions has been the focus area of research in the last few decades for structural and detached-wave function nature determination [8–15]. Photo-detachment microscopy of negative ions has established itself as a very sensitive technique for high-accuracy measurements of the electron affinities of atoms [13, 14]. Bryant et al. [8] were first to observe a ripple-like structure in the photo-detachment cross section of H^- in the presence of a static electric field of a few hundred kilovolts per centimeter above the threshold. Many theoretical studies have been presented to explain this ripple-like structure. Rau and Wong [9] used frame transformation theory, while Du and Delos [10–12] have developed a standard closed-orbit theory for the explanation of these oscillatory structures. Fabrikant [15] investigated the spatial distribution of electrons photo-detached from a polar molecular

anion in an external static electric field that opens an opportunity for experimental investigation of collisions of ultra slow electrons by polar molecules.

Afaq and Du have developed a two-center model for the photo-detachment of H_2^- in free space [2, 3]. Wang used this model to study the polarization dependent effect on H_2^- photo-detachment [6]. Afaq et al. [5] have extended this idea to present a three-center model in order to explain collinearly organized triatomic anions such as $BeCl_2^-$, HCN^-, CS_2^-, and CO_2^- for z-polarized laser light. Recently, Yang and Du [7] generalized the colinear three-center model for an arbitrary laser polarization direction and showed strong oscillations when the laser polarization is parallel to the system axis and oscillation amplitude gradually decreases to zero as the laser polarization is directed perpendicular to the molecular axis.

In all previous research works, a particular colinear geometry of a homonuclear triatomic molecule has been considered for the detached-electron flux oscillations. To the best of our knowledge, no work has been reported about the photo-detachment of noncollinear triatomic negative ions in the literature. In this article, we take a noncollinear triatomic molecule and study, perhaps for the first time, the molecular geometry-dependent electron flux oscillations. We derive an analytical formula for detached-electron flux distributions on a distant screen for different photon energies, various geometries of the system, and for other parameters characterizing the molecular anion. To derive the formula, we take each atom of the system as a coherent source of detached-electron waves similar to the collinear three-center model [5]. The superposition of these three waves on an observation plane would result into quantum interferences. It will be shown that this detached-electron flux which is the differential cross section displays strong molecular geometry-dependent oscillations on an observation plane. These oscillations are explained according to the closed-orbit theory as follows: The outgoing detached-electron waves, produced from one center, are propagated in the vicinity of the sources at other centers which cause these oscillations. The structural information of noncollinear triatomic anions may be explained by analyzing these oscillations in electron flux spectra. Our derived formula for electron flux is universal, which may be applicable to any geometry of the triatomic molecular negative ion.

Noncollinear triatomic molecular ions like Si_2O^-, H_2O^-, NO_2^-, N_3^-, SO_2^-, ClO_2^-, CNS^-, and NH_2^- are attractive systems due to their unique structure and potential applications [18, 19]. These molecules are composed of a noncollinear chain of three atoms lying in the noncollinear pattern. The knowledge of the structure and dynamics of these fascinating noncollinear triatomic molecules is important in quantum chemistry and molecular physics. A noncollinear chain of three hydrogen-like atoms with an extra electron (D_3^-) is assumed to be a generic model for a noncollinear triatomic negative ion. In this article, the idea of quantum interference is applied to an electron detached from the system.

This article is organized as follows: In Section 2, a theoretical study is presented for the photo-detachment of a noncollinear triatomic negative ion, which is then applied on H_3^- anion. The results and discussions for various detached energies are presented in Section 3. Conclusions are given in Section 4. Atomic units have been used unless otherwise noted.

2 Theory

The noncollinear triatomic anion interacting with a z-polarized laser light is shown schematically in Fig. 1. The numbers 1, 2, and 3 represent three atomic centers in the system. It is convenient to fix atoms 1 and 2 on the y-axis while the position of the third atom is taken as variable on the z-axis. The origin of coordinates is marked as O. Let 2d be the distance between two adjacent atoms on y-axis and X be the distance between fixed to variable atoms. The laser polarization is along the z-axis.

We suppose that there is only one active electron in our noncollinear triatomic system for the photo-detachment process. The active electron is loosely bound by a short-range spherically symmetric molecular core potential $V(r)$, where r is the distance between the active electron and origin of the system. The photo-detached-electron wave function satisfies the Schrodinger equation with a source and is given by

$$(E - H)\psi_D = D\psi_I, \qquad (1)$$

where E is the detached-electron energy, D is the dipole operator that explains the interaction of laser light with noncollinear molecular negative system, $D = z$ for z-polarized light, H is the Hamiltonian that describes the behavior of our system, and ψ_I is the initial wave function of the detached electron. It is also assumed that the normalized bounded initial wave function for the active electron in the system can be written as a linear combination of an atomic orbital of H^--like bounded state [16] at the three centers $\psi_I = \frac{1}{\sqrt{3}} \sum \phi_i$, where $\phi_i = B \frac{\exp(-k_b r_i)}{r_i}$ $(i = 1, 2, 3)$ are the normalized wave functions for H^- but centered at 1, 2, and 3 as shown in Fig. 1, in which B is the normalization constant [10] and k_b is related to the binding energy E_b of H^- by $E_b = k_b^2/2$. The photo-detachment process happens in two steps: in the first step, the photon energy E_{ph} is absorbed by an active electron and then it escapes from the negative ion as an electron wave. In the second step, the outgoing wave propagates out to a large distance. This electron wave may originate from each center of the system but with

a different phase. The quantum interference of these outgoing waves at a large distance would result in the oscillations in the electron flux spectra.

Let ψ_1, ψ_2, and ψ_3 be the detached-electron waves from the centers 1, 2, and 3, respectively, as shown in Fig. 1. Following the previous approach given in Ref. [5], the resultant outgoing detached-electron wave ψ_D can be written as linear combination of individual waves as

$$\psi_D = \frac{1}{\sqrt{3}} \sum_1^3 c_i \psi_i, \tag{2}$$

where c_i $(i = 1, 2, 3)$ are the normalization constants of our system and can be calculated using the molecular orbit theory. In the case of homonuclear triatomic negative ion, $c_i = 1$ for all $i = 1, 2, 3$. Let (r_i, θ_i, ϕ_i) represent the spherical coordinates of the detached electron relative to each center. Therefore, the outgoing detached-electron wave generated from each center is given by [17]

$$\psi_i = \frac{4ik^2 B}{(k_b^2 + k^2)^2} \cos \theta_i \frac{\exp(ikr_i)}{kr_i}, \tag{3}$$

where $k = \sqrt{2E}$ and E is the detached-electron energy and it is equal to $E_{ph} - E_b$, where E_b is the binding energy of the molecule which is different for each molecule. By substituting (3) in (2), we get the explicit expression for the detached-electron wave function. We can further simplify this expression by applying the large distance approximation: the distances r_i, are much greater than the interatomic
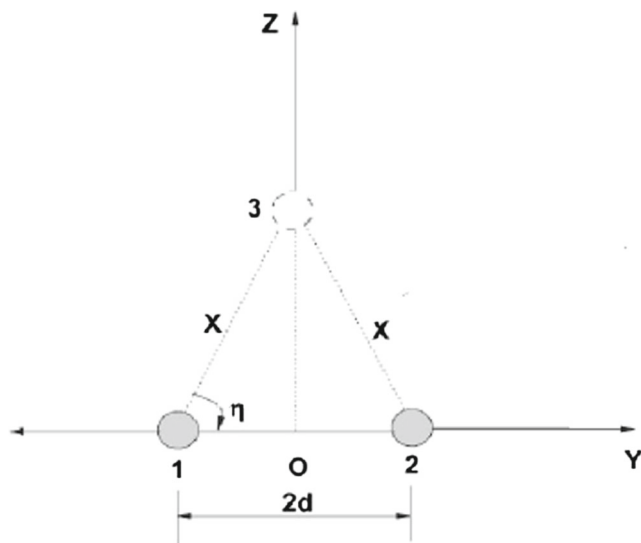

Fig. 1 The schematic diagram of the noncollinear three-center system. The two centers represented by *solid spheres* are fixed on *y*-axis separated by interatomic distance 2d, while the third center represented by a *broken sphere* is on *z*-axis and is separated by distance *x* from each center; *x* can be changed with changing angle η. The laser is polarized along the *z*-direction. The screen is placed at a very large distance from the system. The distance between 1 and 3 or 2 and 3 can be varied by the equation $X = d \sec \eta$

distances of our system. Let (r, θ, ϕ) be spherical polar coordinates of the detached-electron with respect to the origin. Then we approximate the phase terms in (3) using

$$r_1 \approx r + d \sin \theta \sin \phi,$$

$$r_2 \approx r - d \sin \theta \sin \phi,$$

$$r_3 \approx r - d \cos \theta \tan \eta.$$

All other places we can set $r \approx r_1 \approx r_2 \approx r_3$ and $\theta_1 \approx \theta_2 \approx \theta_3 \approx \theta$. With these approximations, the detached-electron wave function ψ_D in (2) becomes

$$\psi_D = \frac{1}{\sqrt{3}} \frac{4ik^2 B}{(k_b^2 + k^2)^2} \cos \theta [\exp(-iF) + 2\cos(kd \sin \theta \sin \phi)] \frac{\exp(ikr)}{r}, \tag{4}$$

where $F = kd \cos \theta \tan \eta$ is a dimensionless quantity, describing the shape of the molecule. For $\eta = 0^0$, i.e., for linear shape of the molecule, we get $F = 0$, then the wave function in (4) reduces exactly to the wave function given in Ref. [5] ((3) therein).

In order to find the detached-electron flux in the radial direction for the noncollinear triatomic negative ion, the wave function obtained in (3) is treated quantum mechanically with the following relation:

$$J_r(r, \theta, \phi) = \mathbf{J} \cdot \hat{r} = \frac{i}{2} (\psi_D \overrightarrow{\nabla} \psi_D^* - \psi_D^* \overrightarrow{\nabla} \psi_D) \cdot \hat{r}. \tag{5}$$

The relation for flux in the radial direction is

$$J(r, \theta, \phi) = \frac{J_0(r, \theta)}{3} [1 + 4\cos(kd \sin \theta \sin \phi) \cos(F) + 4\cos^2(kd \sin \theta \sin \phi)], \tag{6}$$

where $J_0(r, \theta) = k |\frac{4ik^2 B}{(k_b^2 + k^2)^2}|^2 \frac{\cos^2 \theta}{r^2}$ is the electron flux in the radial direction for H^- as a one center system, and $F = kd \cos \theta \tan \eta$.

The detached-electron flux at any point $\rho = \sqrt{x^2 + y^2}$ on the screen placed in the XY-plane at a distance L from the system is

$$J_z(\rho) = \frac{J_0(\rho)}{3} [1 + 4\cos(\frac{kdy}{\sqrt{\rho^2 + L^2}}) \cos(\frac{kdL \tan \eta}{\sqrt{\rho^2 + L^2}}) + 4\cos^2(\frac{kdy}{\sqrt{\rho^2 + L^2}})], \tag{7}$$

with $J_0(\rho) = k |\frac{4ik^2 B}{(k_b^2 + k^2)^2}|^2 \frac{L^3}{(\rho^2 + L^2)^{5/2}}$ as the electron flux of H^- in free space.

3 Results and Discussions

In (7), the parameter η defines the shape of a molecular negative ion, and the system would be noncollinear geometrical shape for $\eta \neq 0$. The different photo-detachment spectra

Fig. 2 The detached-electron flux given as in (7) is plotted versus ρ. The energy of $E_{ph} = 30$ eV, $L = 1,000$ a.u, and $d = 4$ a.u., but the geometry of the noncollinear molecule is different. At $\eta = 0^0$, we obtained the same result as in Ref. [5]
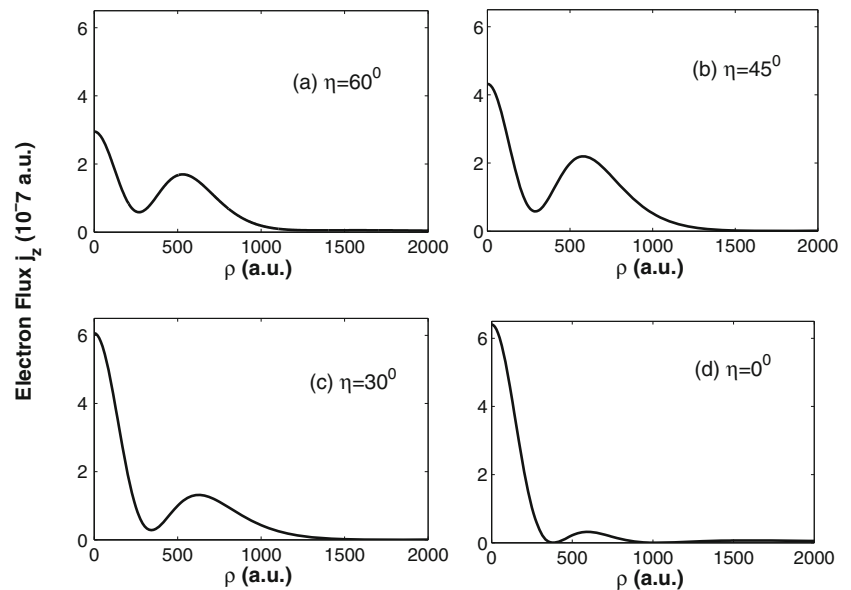

would be obtained for different η values by plotting photon versus ρ values using (7), and these plots are presented in Figs. 2 and 3.

Figure 2 displays quantum interferences for different geometrical shapes of a triatomic molecule keeping photon energy constant $E_{ph} = 30$ eV. When the η value decreases and becomes 0, the geometry of the triatomic molecule goes from a noncollinear to collinear shape, and we observe that the central maxima increases and it becomes maximum for collinear geometrical shape as it is clear from

Fig. 2a–d. These quantum interferences are due to the electron waves that originate from each atom of the system and travel along three different classical trajectories that meet at the single point on the observation plane. The geometrical shape-dependent quantum interferences are important in order to investigate the structure of a noncollinear molecule. For a particular η value and the photon energy, one can obtain a particular photo-detachment spectrum on an observation plane. So by observing the spectra, one can find the geometrical shape of the molecular negative ion.

Fig. 3 The detached-electron flux with different energies and for fixed $\eta = 45^0$, i.e., for a fixed geometrical shape of the molecule
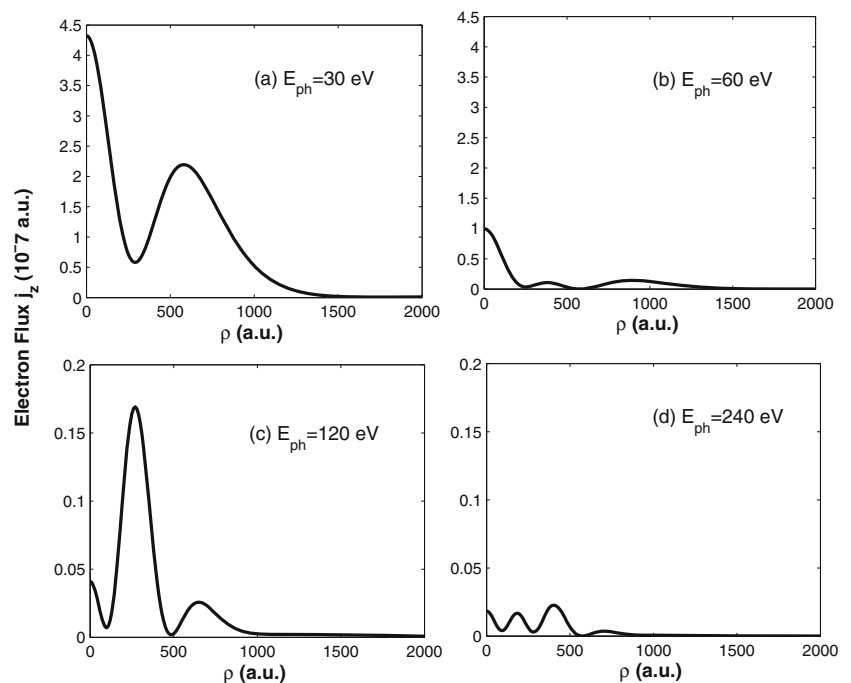
Equation (7) can be reduced to a collinear form by taking $\eta = 0^0$ in it; the second term reduces to $4\cos\left(\frac{kdy}{\sqrt{\rho^2+L^2}}\right)$. So a new expression becomes exactly the same as for the collinear triatomic negative ion as in Ref. [5] ((9) therein). The same result has been shown in Fig. 2d for a fixed photon energy of 30 eV.

We calculate the electron flux distributions of a noncollinear triatomic negative ion on a given observation plane for different energies $E = 30, 60, 120, 240$ eV with a fixed geometrical shape of the molecule for $\eta = 45^0$ as shown in Fig. 3. From the figures, we can see that this η-value has a great influence on the electron flux distribution. Figure 2d shows the case when $\eta = 0^0$. Under this condition, the molecule looks like a collinear molecule [5]. These oscillations in the electron flux are due to the interference of three trajectories, where each is coming from each center of the noncollinear molecule. As the detached-electron energy increases, the electron flux is shown to exhibit the damped oscillations as is clear from the Fig. 3.

4 Conclusion

In conclusion, we have studied the photo-detachment of noncollinear triatomic homonuclear anion using a three-center model, particularly discussing the influence of a geometrical shape on the electron flux distribution. We have derived a general relation for the detached-electron flux distribution for z-polarized laser light. The results show that the geometrical shape has an important effect on the electron flux distributions. The interference in the electron flux is because of three different trajectories originating from each atom of the system. When these impinge on a sensitive detector with a different phase, the interference phenomenon is observed. Our study suggests that we can estimate the shape of the molecule by analyzing the photo-detachment spectra. The oscillations in the present noncollinear three-center system can be explained using the closed-orbit theory as interference between detached-electron waves produced from one center and the sources at the other centers. We hope that this model may be helpful to understand noncollinear triatomic molecule in photo-detachment microscopy experiments.

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