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Interference in the molecular photoionization and Young's double-slit experiment

A S Baltenkov¹, U Becker², S T Manson³ and A Z Msezane⁴

¹ Arifov Institute of Electronics, 100125 Tashkent, Uzbekistan

² Fritz-Haber-Institute der Max-Planck-Gesellschaft, D-14195 Berlin, Germany

³ Department of Physics and Astronomy, Georgia State University, Atlanta, GA 30303, USA

⁴ Center for Theoretical Studies of Physical Systems, Clark Atlanta University, Atlanta, GA 30314, USA

E-mail: arkbalt@mail.ru

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Abstract

The photoabsorption by an electron bound by a two-centre potential has been investigated within the framework of the zero-range potential model. Expressions for total photoabsorption cross sections and for the photoelectron angular distributions have been derived for fixed-in-space and randomly oriented targets. The analytical formulae for gerade and ungerade molecular states have been used to analyse separately the molecular effects due to the two-centre ground state of quasi-molecule and diffraction effects that are connected with the spherical waves in the molecular continuum. It is shown that the interference of these waves significantly influences the magnitude of the cross sections near threshold but does not significantly distort the shape of the photoelectron angular distribution and it depends rather weakly on the character of the forces acting between the electron and molecular residue: Coulomb forces for neutral molecular photoionization or the short-range forces in the case of photodetachment of molecular negative ions. It is shown that despite the fact that the photoionization of diatomic molecules is reminiscent of Young's double-slit experiment, the similarity between these processes has been grossly exaggerated. This is confirmed by comparing the results of the classical interference of an electron scattered by two spatially separated centres with molecular photoelectron angular distributions.

(Some figures may appear in colour only in the online journal)

1. Introduction

In 1966, Cohen and Fano [1] discussed the photoionization of a homonuclear diatomic molecule and explained the oscillatory behaviour of the cross sections observed in the valence photoionization of N₂ and O₂ up to photon energy \sim 60 eV. Despite the fact that the process considered in [1] was based on a simple model of molecular ion H₂⁺, the formulae obtained in that paper describe the K-shell photoionization of some homonuclear diatomic molecules quite well.

More recently, the Cohen and Fano formulation has been of great interest in connection with developing spectrometric methods [2–5] in which the energy and momentum of the ejected electron correlate with both the polarization of ionizing photons as well as with the energy and momentum vectors of all of the remaining fragments after ionization. From these data, the mutual orientation of photoelectron momentum and molecular axes can be determined for each emission event detected. The use of these methods for homonuclear diatomics is of special interest because these molecules are characterized by the symmetry of their atomic constituents, which leads to considerable differences in photoelectron angular distributions between *gerade* and *ungerade* molecular states [6]. Measuring selectively the photoelectron angular distributions of these states avoids the cancelling out of diffraction effects [7].

Interpretation of these experiments assumes that the photoionization of the homonuclear diatomic molecule can be regarded as a molecular Young's double-slit experiment where the coherent emission of the spherical electron waves originating from two spatially separated sources gives the interference patterns. However, the analogy between these two processes cannot be considered as complete because the molecular photoionization is defined by the amplitude for a transition from the molecular ground state to the continuum, while the interference pattern in a Young-type experiment (YTE) has no connection with the molecular ground state but is formed due to the continuum wavefunction only. In this context, it is interesting to analyse how the diffraction pattern according to the Cohen and Fano model [1] is associated with the interference pattern in the YTE, i.e. the relative contributions of the initial discrete state and the final continuum state.

A qualitative picture of electron wave scattering by a two-centre target in YTE is shown in figure 1(a). On the left is the plane wave and on the right, according to the Huygens-Fresnel principle, there are two spherical waves; their interference creates the diffraction pattern. It is this picture of classical diffraction that is described in [1], 'Diffraction phenomena should occur when electrons released within a multi-center molecular field. From Huygens' point of view, the two atoms of N2 constitute two separate sources of photoelectrons. Superposition of the emission from these two sources produces an interference pattern whose properties should depend periodically on the ratio of the inter-nuclear distance to the photoelectron wavelength. This interference may modulate the cross section for photoabsorption by whole molecule'. However, the photoionization process is considered in [1] within the framework of zero-order Born approximation; the scattering picture in this approximation is given in figure 1(b). On the right and left of the target, there are plane waves only. In other words, using the Born approximation specifically omits any interferences in the final state of the molecular photoionization. As a result, in this approach electron wave diffraction similar to YTE, as described above, is omitted from the Cohen–Fano model [1]. Theoretical consideration of molecular photoionization within YTE evidently requires going beyond the ideas of the model [1]. The plane wavefunction for the molecular continuum would have to be replaced by a wavefunction that obeys the Huygens-Fresnel principle, i.e. beyond the target it should include, in addition to the plane wave, the spherical waves emitted from two atomic sites. It is precisely the existence of the spherical waves of the molecular continuum, which are absent in the zero-order Born approximation, that makes the molecular photoionization process similar to Young's doubleslit experiment.

In this paper, the aim is to analyse how the spherical waves generated in the process of scattering of the photoelectron waves by the molecular atoms influence the differential and total cross sections of molecular photoionization. In [8], we proposed a model of the molecular system that allowed this analysis to be analytical. This is a model of the two-centre quasimolecule formed by two zero-range potentials. These potentials provide an accurate description of the behaviour of particles interacting with one another through *shortrange* forces, e.g. a proton and a neutron in a deuteron



Figure 1. Qualitative picture of the electron wave crests for: (a) Young's double-slit diffraction; (b) the Cohen–Fano model; (c) the Dill–Dehmer model [16].

[9] or an electron in atomic or molecular negative ions [10]. The important advantage of these potentials is that the wave equation describing the electron in their field has exact analytical solutions for both the weakly bound electron and the low-energy continuum. These wavefunctions, unlike the system of the functions in the model of [1], (i) are mutually orthogonal, (ii) take into account exactly the multiple scattering of an electron by the two centres and (iii) meet the Huygens–Fresnel principle, i.e. they have the correct asymptotic behaviour.

In section 2, we present the general formulae for the cross section for molecular photoionization in *gerade* and *ungerade* states which follow from the Cohen and Fano model [1]. In section 3 within our model [8], the formulae for differential and total cross sections are derived, both for fixed-in-space molecules and for randomly oriented molecules. The cross sections resulting from these two models are compared in section 4. Next, section 5 presents the differential cross sections for electron elastic scattering and a comparison of the diffraction patterns of the classical Young's double-slit interference with the molecular photoelectron angular distributions is given. Finally, section 6 presents the summary and conclusions.

2. The Cohen and Fano model [1]

The wavefunctions used in [1] are defined as follows: the ground state wavefunction of the H_2^+ molecular ion is a linear combination of the wavefunctions of the separate H atoms with effective charges z^* . The *gerade* ground state of the system is described by

$$\psi_g(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}} [u(\mathbf{r} + \mathbf{R}/2) + u(\mathbf{r} - \mathbf{R}/2)].$$
(1)

The position of the electron is indicated by \mathbf{r} , vector \mathbf{R} is the internuclear distance (figure 1(a)), $u(\mathbf{r})$ is the ground-state electron wavefunction for an H atom, and S is the overlap integral. The final state wavefunction of the photoelectron in all space is a plane wave, which corresponds to the zero-order Born approximation. The dipole matrix element for molecular photoionization by photons with polarization \mathbf{e} is defined by (atomic units are used throughout the text)

$$M_g = -i \int e^{-i\mathbf{k}\cdot\mathbf{r}} (\mathbf{e}\cdot\nabla)\psi_g(\mathbf{r}) \,\mathrm{d}\mathbf{r},\tag{2}$$

with \mathbf{k} the wave vectors of the photoelectron. Integrating (2) by parts, we obtain the equalities

$$M_g = (\mathbf{e} \cdot \mathbf{k}) \int e^{-i\mathbf{k} \cdot \mathbf{r}} \psi_g(\mathbf{r}) \, \mathrm{d}\mathbf{r}$$

= $\sqrt{2} (\mathbf{e} \cdot \mathbf{k}) \cos(\mathbf{k} \cdot \mathbf{R}/2) \int e^{-i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}) \, \mathrm{d}\mathbf{r}/\sqrt{(1+S)}.$ (3

The differential photoionization cross section for the *gerade* state of a fixed-in-space molecule is defined by the absolute square of this matrix element:

$$\frac{\mathrm{d}\sigma_g(\omega, \mathbf{R})}{\mathrm{d}\Omega_k} \sim |J|^2 (\mathbf{e} \cdot \mathbf{n})^2 \cos^2(\mathbf{k} \cdot \mathbf{R}/2)/(1+S). \tag{4}$$

Here J is the integral in the last term of equation (3), and the unit vector $\mathbf{n} = \mathbf{k}/k$. The vector \mathbf{R} is introduced as an argument in the cross section $\sigma(\omega, \mathbf{R})$ to stress that we are dealing with a fixed-in-space molecular system. Averaging equation (4) over all possible directions of the molecular axis gives the differential photoionization cross section for randomly oriented molecules:

$$\frac{\mathrm{d}\sigma_g(\omega)}{\mathrm{d}\Omega_k} = \frac{1}{4\pi} \int \frac{\mathrm{d}\sigma_g(\omega, \mathbf{R})}{\mathrm{d}\Omega_k} \mathrm{d}\Omega_R$$
$$\sim |J|^2 (\mathbf{e} \cdot \mathbf{n})^2 \left(1 + \frac{\sin kR}{kR}\right) / (1+S). \tag{5}$$

The differential cross section, equation (5), can be written equivalently as

$$\frac{\mathrm{d}\sigma_g(\omega)}{\mathrm{d}\Omega_k} = \frac{\sigma_H(z^*)}{4\pi} [1 + 2P_2(\mathbf{e} \cdot \mathbf{n})] \left(1 + \frac{\sin kR}{kR}\right) \middle/ (1+S).$$
(6)

Here $\sigma_H(z^*)$ is the total photoionization cross section of a single H atom with effective charge z^* , and $P_2(\mathbf{e} \cdot \mathbf{n})$ is the Legendre polynomial of the second order. The total photoionization cross section of the *gerade* state of the molecule is then [1]

$$\sigma_{g}(\omega) = \int \frac{\mathrm{d}\sigma_{g}(\omega)}{\mathrm{d}\Omega_{k}} \mathrm{d}\Omega_{k}$$
$$= \sigma_{H}(z^{*}) \left(1 + \frac{\sin kR}{kR}\right) / (1+S). \tag{7}$$

Repeating the above development for the *ungerade* ground state

$$\psi_u(\mathbf{r}) = \frac{1}{\sqrt{2(1-S)}} [u(\mathbf{r} + \mathbf{R}/2) - u(\mathbf{r} - \mathbf{R}/2)], \quad (8)$$

we obtain instead of equations (4), (6) and (7) the following expressions:

$$\frac{\mathrm{d}\sigma_u(\omega, \mathbf{R})}{\mathrm{d}\Omega_k} \sim |J|^2 (\mathbf{e} \cdot \mathbf{n})^2 \sin^2(\mathbf{k} \cdot \mathbf{R}/2)/(1-S), \tag{9}$$

$$\frac{\mathrm{d}\sigma_u(\omega)}{\mathrm{d}\Omega_k} = \frac{\sigma_H(z^*)}{4\pi} [1 + 2P_2(\mathbf{e} \cdot \mathbf{n})] \left(1 - \frac{\sin kR}{kR}\right) \middle/ (1 - S),$$
(10)

$$\sigma_u(\omega) = \int \frac{\mathrm{d}\sigma_u(\omega)}{\mathrm{d}\Omega_k} \,\mathrm{d}\Omega_k$$
$$= \sigma_H(z^*) \left(1 - \frac{\sin kR}{kR}\right) / (1 - S). \tag{11}$$

Because of the similarity with the diffraction features of the two-centre systems, the modulation factors $F_{g,u} = [1\pm(\sin kR)/kR]$ in equations (7) and (11) are interpreted in [1] as a consequence of interference in molecular photoionization. However, these periodic modulations are not the result of the superposition *in the continuum* of the spherical waves emitted by the separate sources of photoelectrons, as is the case in YTE. They have a completely different nature. Their appearance in the photoionization cross sections 'is due to detailed properties of valence orbitals' [1], i.e. due to the multicentre structure of the *initial state* molecular wavefunction.

3. Photoabsorption of electron bound by two zero-range potentials

Consider the photoabsorption by a quasimolecular system in which an electron is bound by two identical short-range potentials separated by a distance R. We assume that the bound state wavefunction is localized about each of the centres and the region of its localization is small compared to R so that the initial state wavefunction remains essentially atomic-like. The character of this molecular system is in essence a model of the negative molecular ion. As in the model [1], the bound state wavefunctions in the field of two centres located at $\mathbf{r} = \pm \mathbf{R}/2$ are reasonably approximated as *gerade* and *ungerade* linear combinations of one-centre wavefunctions [8]:

$$\psi_{g}(\mathbf{r}) = \sqrt{\frac{q}{4\pi}} \left[\frac{\mathrm{e}^{-q|\mathbf{r} + \mathbf{R}/2|}}{|\mathbf{r} + \mathbf{R}/2|} + \frac{\mathrm{e}^{-q|\mathbf{r} - \mathbf{R}/2|}}{|\mathbf{r} - \mathbf{R}/2|} \right],$$

$$\psi_{u}(\mathbf{r}) = \sqrt{\frac{q}{4\pi}} \left[\frac{\mathrm{e}^{-q|\mathbf{r} + \mathbf{R}/2|}}{|\mathbf{r} + \mathbf{R}/2|} - \frac{\mathrm{e}^{-q|\mathbf{r} - \mathbf{R}/2|}}{|\mathbf{r} - \mathbf{R}/2|} \right].$$
(12)

Here it is assumed that $qR \gg 1$ so that the overlap-integral S = 0; the wave vector q is connected to the electron binding energy by the relation $I = q^2/2$.

The continuum wavefunction for *s*-wave scattering of a slow electron by two centres is given by [8]

$$\psi_{\mathbf{k}}^{+}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + C_{1}(\mathbf{k})\frac{e^{ik|\mathbf{r}+\mathbf{R}/2|}}{|\mathbf{r}+\mathbf{R}/2|} + C_{2}(\mathbf{k})\frac{e^{ik|\mathbf{r}-\mathbf{R}/2|}}{|\mathbf{r}-\mathbf{R}/2|}.$$
 (13)

The coefficients C_1 and C_2 in equation (13) have the form

$$C_1(\mathbf{k}) = \frac{ad - bd^*}{a^2 - b^2}, \qquad C_2(\mathbf{k}) = \frac{ad^* - bd}{a^2 - b^2}, \qquad (14)$$

where the parameters $a = \exp(ikR)/R$, $b = ik - k \cot \delta_0 =$ ik + q and $d = -\exp(i\mathbf{k} \cdot \mathbf{R}/2)$. The phase δ_0 here is the phase shift for s-wave scattering by the short-range potential and is connected with q by the relation $q = -k \cot \delta_0$ [8, 9]. Formally the second and third terms in the wavefunction, equation (13), look like the first-order terms of the Born approximation for electron scattering by a two-centre target. However, this is quite misleading since equation (13) represents the *exact* general solution of the continuum wave equation outside the range of the short-range potential. The situation can be clarified by operating on the wavefunction, equation (13), with the free-particle Hamiltonian, $\hat{H} = -(\nabla^2 + k^2)/2$. The result of this operation defines the right side of the inhomogeneous Schrödinger equation that this wavefunction obeys. Since the second and third terms in equation (13) are the free-particle Green's functions, we obtain on the right side of this equation a linear combination of the delta-functions, $\delta(\mathbf{r} \pm \mathbf{R}/2)$, which vanish beyond the region of the short-range potentials. Hence, the wavefunction, equation (13), is everywhere (beyond the cross-hatched spheres in figure 1(a)) a solution to the free particle wave equation.

Unlike the plane wave in the model of [1], the wavefunction, equation (13), is orthogonal to the ground state wavefunctions, equations (12). Being an exact solution of the wave equation, the function, equation (13), automatically takes into account exactly the multiple scattering of an electron by the two centres [8, 10], which is reflected in the amplitude dependence of the spherical waves on the *s*-wave scattering phase δ_0 . The second and third terms in equation (13) are two spherical *s*-waves generated by the scattering centres (figure 1(b)); thus, the wavefunction, equation (13), obeys the Huygens–Fresnel principle. It is precisely the presence of these spherical waves that makes the physical picture of molecular photoionization similar to that of Young's double-slit experiment.

The wavefunction $\psi_{\mathbf{k}}^{-}(\mathbf{r})$ describing the final state in the photoabsorption by the two-centre 'molecular' system is connected with the scattering function, equation (13), through

the relation $\psi_{\mathbf{k}}^{-}(\mathbf{r}) = \psi_{-\mathbf{k}}^{+*}(\mathbf{r})$ and has the form

$$\psi_{\mathbf{k}}^{-}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + C_{1}^{*}(-\mathbf{k})\frac{e^{-ik|\mathbf{r}+\mathbf{R}/2|}}{|\mathbf{r}+\mathbf{R}/2|} + C_{2}^{*}(-\mathbf{k})\frac{e^{-ik|\mathbf{r}-\mathbf{R}/2|}}{|\mathbf{r}-\mathbf{R}/2|}.$$
(15)

The initial and final state wavefunctions, equations (12) and (13), respectively, are then used to calculate the dipole matrix element corresponding to photoabsorption. Following the methodology of [8], equation (3), in the present case for the *gerade* state, is replaced by

$$M_g = 2\varphi\{(\mathbf{e} \cdot \mathbf{n})\cos(\mathbf{k} \cdot \mathbf{R}/2) - (\mathbf{e} \cdot \boldsymbol{\rho})\sin(\mathbf{k} \cdot \mathbf{R}/2)\Phi_g(k, R)\}.$$
(16)

Here the unit vector $\boldsymbol{\rho} = \mathbf{R}/R$ and the functions φ and $\Phi_g(k, R)$ are given by

$$\varphi = k\sqrt{4\pi q}(q^2 + k^2)^{-1}, \qquad \Phi_g(k, R) = ia(a-b)^{-1}.$$
 (17)

According to equation (16), the replacement of the plane wave by the exact wave function, equation (15), leads to the fact that the matrix element for molecular photoabsorption becomes a sum of two amplitudes. The first of them leads to Cohen–Fano diffraction and the second is connected to spherical molecular continuum wavefunctions defined by the $\Phi_g(k, R)$.

For the differential photoabsorption cross section for a fixed-in-space molecule in the ground *gerade* state, instead of equation (4), we now have

$$\frac{\mathrm{d}\sigma_g(\omega, \mathbf{R})}{\mathrm{d}\Omega_k} \sim 4|\varphi|^2 \{(\mathbf{e} \cdot \mathbf{n})^2 \cos^2(\mathbf{k} \cdot \mathbf{R}/2) - (\mathbf{e} \cdot \mathbf{n})(\mathbf{e} \cdot \boldsymbol{\rho}) \sin(\mathbf{k} \cdot \mathbf{R}) \mathrm{Re}\Phi_g + (\mathbf{e} \cdot \boldsymbol{\rho})^2 \sin^2(\mathbf{k} \cdot \mathbf{R}/2) |\Phi_g|^2 \}.$$
(18)

Averaging this cross section over all possible directions of the molecular axis (details of derivation and variables are given in the appendix) yields

$$\frac{\mathrm{d}\sigma_g(\omega)}{\mathrm{d}\Omega_k} = \frac{\sigma_A(\omega)}{4\pi} [F_g - 2\mathrm{Re}\Phi_g\varsigma_g + 2(\alpha_g + 2\eta_g)|\Phi_g|^2] \times [1 + \beta_g P_2(\mathbf{e} \cdot \mathbf{n})].$$
(19)

Here $\sigma_A(\omega)$ is the total cross section for negative ion photodetachment (see equation (6) of [8], equation (5) of [11]); the dipole angular distribution parameter in equation (19) is defined by

$$\beta_g = 2 \frac{F_g - 2 \operatorname{Re} \Phi_g \varsigma_g + 2 |\Phi_g|^2 (\alpha_g - \eta_g)}{F_g - 2 \operatorname{Re} \Phi_g \varsigma_g + 2 |\Phi_g|^2 (\alpha_g + 2\eta_g)}.$$
 (20)

The threshold behaviour of the dipole angular distribution parameter is determined by the limits

$$\Phi_g(k \to 0) = i(1 - qR)^{-1}, \qquad F_g = 2; \qquad \varsigma_g = 1/2, \alpha_g = 0 \quad \text{and} \quad \eta_g = 0,$$
(21)

which results in $\beta_g(k \to 0) = 2$. The total gerade cross section has the form

$$\sigma_g(\omega) = \sigma_A(\omega)[F_g - 2\operatorname{Re}\Phi_g\varsigma_g + 2(\alpha_g + 2\eta_g)|\Phi_g|^2], \quad (22)$$

where the factor multiplying the atomic cross section $\sigma_A(\omega)$ is the analogue of the Cohen–Fano two-centre modulation factor for the *gerade* state. Repeating the calculations for the *ungerade* ground state, equation (12), we have instead of equations (16)–(22)

$$M_{u} = 2i\varphi\{(\mathbf{e} \cdot \mathbf{n}) \sin(\mathbf{k} \cdot \mathbf{R}/2) + (\mathbf{e} \cdot \boldsymbol{\rho}) \cos(\mathbf{k} \cdot \mathbf{R}/2) \Phi_{u}(k, R)\}, \qquad (23)$$

where the function $\Phi_u(k, R)$ has the form $\Phi_u(k, R) = ia(a + b)^{-1}$. For the differential photoabsorption cross section for the fixed-in-space *ungerade* molecular state, instead of equation (18), we have

$$\frac{\mathrm{d}\sigma_{u}(\omega,\mathbf{R})}{\mathrm{d}\Omega_{k}} \sim 4|\varphi|^{2}\{(\mathbf{e}\cdot\mathbf{n})^{2}\sin^{2}(\mathbf{k}\cdot\mathbf{R}/2) + (\mathbf{e}\cdot\mathbf{n})(\mathbf{e}\cdot\boldsymbol{\rho})\sin(\mathbf{k}\cdot\mathbf{R})\mathrm{Re}\Phi_{u} + (\mathbf{e}\cdot\boldsymbol{\rho})^{2}\cos^{2}(\mathbf{k}\cdot\mathbf{R}/2)|\Phi_{u}|^{2}\}.$$
(24)

For the *ungerade* state of the molecule in the gas phase, averaging the cross section, equation (24), over all directions of the molecular axis leads to

$$\frac{\mathrm{d}\sigma_u(\omega)}{\mathrm{d}\Omega_k} = \frac{\sigma_A(\omega)}{4\pi} [F_u - 2\mathrm{Re}\Phi_u\varsigma_u + 2(\alpha_u + 2\eta_u)|\Phi_u|^2] \times [1 + \beta_u P_2(\mathbf{e}\cdot\mathbf{n})].$$
(25)

The total *ungerade* cross section is

$$\sigma_u(\omega) = \sigma_A(\omega)[F_u - 2\operatorname{Re}\Phi_u\varsigma_u + 2(\alpha_u + 2\eta_u)|\Phi_u|^2]. \quad (26)$$

The dipole angular distribution parameter in equation (25) is defined by

$$\beta_{u} = 2 \frac{F_{u} + 2\text{Re}\Phi_{u}\varsigma_{u} + 2|\Phi_{u}|^{2}(\alpha_{u} - \eta_{u})}{F_{u} + 2\text{Re}\Phi_{u}\varsigma_{u} + 2|\Phi_{u}|^{2}(\alpha_{u} + 2\eta_{u})}.$$
 (27)

The threshold behaviour of the parameter β_u is defined by the limits

$$\Phi_u(k \to 0) = i(1+qR)^{-1}, \quad F_u = 0, \quad \varsigma_u = 1/2,$$

$$\alpha_u = 1/3 \quad \text{and} \quad \eta_u = 1/3, \quad (28)$$

which yields the limit $\beta_u(k \to 0) = 0$.

Comparing the formulae for cross sections derived within the framework of the models of [1] and [8], we come to the following conclusions. The spherical waves in the model of [8] lead firstly to the dependence of the dipole angular distribution parameters, equations (20) and (27), on photon energy; in contrast, in the Cohen and Fano model [1], this parameter (the coefficient of the Legendre polynomial in equations (6) and (10)) is constant and equal to 2. Secondly, in the formulae derived in the model of [8], the diffraction effects are defined by the functions $\Phi_{g,u}(R)$, depending separately on *k* and *R*, while in the model of [1], the two-centre modulation factors are functions of the product *kR* only.

4. Numerical calculations

To determine the role of spherical waves in the formation of molecular photoionization spectra quantitatively, the total and differential cross sections of the process for different parameters of the models [1] and [8] are calculated. Using the molecular negative ion I_2 as a guide to choose the parameters, the electron affinity of this ion is equal to I = 2.58 eV [12] and the interatomic distance is R = 2.667 Å = 5.042 atomic units [13].

The calculated results for the two-centre amplitude (modulation) factors, F_g and F_u in the Cohen–Fano model and the ratios σ_g/σ_A and σ_u/σ_A in the present model, as a function of ε for different distances between the centres $2 \leq R \leq 5$ are presented in figure 2. The functions $\Phi_{g,u}(R)$, equations (16) and (23), connected with spherical wave interference decrease with increasing R; therefore, the results for the two models rapidly become closer with increasing R and for R > 5their effect on the behaviour of the amplitude factors defining the total cross sections for photoabsorption can be neglected. For smaller distances R, the differences in the factor shapes are especially noticeable for low photoelectron energy. For $\varepsilon = k^2/2 > 50$ eV, the results calculated within both the models practically coincide for all values of R considered. Furthermore, with increasing ε , the amplitude factors for gerade and ungerade states approach unity (dotted lines).

The evolution of the shapes of the differential photoabsorption cross sections for fixed-in-space molecules $d\sigma_{g/\mu}(\omega, \mathbf{R})/d\Omega_k$ for different internuclear distances R are given in figure 3 for $\mathbf{e} || \boldsymbol{\rho}$. The comparison of the formulae for these cross sections shows vivid differences in the calculated results in the models of [1] and [8] when the molecular axis is oriented along the photon polarization vector since for $\mathbf{e} || \boldsymbol{\rho}$ the coefficients of the functions $\Phi_{g,u}(R)$ reach the maximal values, while for $\mathbf{e} \perp \boldsymbol{\rho}$ these coefficients are equal to zero causing the cross sections in the two models to coincide. Of particular interest is that although the shapes of the photoelectron angular distributions (PADs) in the two models are practically the same, the inclusion of spherical waves in the present model decreases the absolute values of the cross sections for small inter-atomic distances considerably, as clearly seen in figure 3.

Figure 4 demonstrates the dependence of the shape of the PAD on the angle ϑ_e between the photon polarization vector **e** and the molecular axis ρ for a fixed distance between the atomic centres, R = 5.042, at photoelectron energy $\varepsilon =$ 10 eV. From these results, it is clear that the shape of the PAD is defined to a considerable extent by the photon polarization vector. The maxima in the differential cross sections are observed at the angles ϑ_k close to ϑ_e defining the position of the vector **e** relative to the polar axis **R**.

The angular distributions in figure 4 for $\mathbf{e} || \mathbf{R}$ and $\mathbf{e} \perp \mathbf{R}$ are qualitatively similar to the PADs for gerade/ungerade N(1s) core photoelectron emission of N₂ [6]. The measured data points in the interval 0° -90° are given in this figure by the full circles. The six-lobe structure of the PADs for \mathbf{e} || \mathbf{R} in both the *gerade* cases is transformed into two lobes for $\mathbf{e} \perp \mathbf{R}$, while the two-lobe structure PADs for both the *ungerade* states for $\mathbf{e} || \mathbf{R}$ become four-lobed for $\mathbf{e} \perp \mathbf{R}$. The similarity between the spectral shapes is surprising since the curves correspond to rather different molecular structures and spectral characteristics of the incident radiation. Besides in this calculation the photon energy was $\omega = 12.58$ eV, while the core photoelectron emission of N_2 [6] corresponds to $\omega = 419$ eV. The closeness of the spectral shapes serves as indirect evidence that the character of the forces acting between photoelectron and molecular residue-Coulomb forces (in the case of [6]) or short-range (in the model of [8])—has little effect on the shape of the PAD.



Figure 2. Two-centre modulation factors as a function of the photoelectron energy ε for different interatomic distances *R*. The left and the right panels correspond to the *gerade* and *ungerade* states, respectively. The dashed curves are Cohen–Fano functions F_g and F_u ; the solid curves are the calculated ratios σ_g/σ_A and σ_u/σ_A , i.e. using the expressions in square brackets in equations (21) and (26). The dotted line is the asymptotic value of the function, in each case.

More distinct differences in the two models are found in the behaviour of the dipole angular distribution parameters. The dependences of these parameters on photoelectron energy are presented in figure 5. The Cohen–Fano model gives for these parameters the constant value $\beta_{g,u} = 2$. The differences in the behaviour of the curves in the two models are due entirely to the presence of spherical waves in the molecular continuum wave function in the present model. As before, their role is particularly significant for low photoelectron energy. With increasing ε , both the *gerade* and *ungerade* β parameters tend to 2. Here the qualitative behaviour of the parameters in figure 5 is similar to both the experimental data [14] for



Figure 3. Photoelectron angular distributions (PADs) for *gerade* (left) and *ungerade* (right) states for electron energy $\varepsilon = 10$ eV. The PADs are shown in the plane perpendicular to the light propagation direction. The molecules are oriented parallel to the light polarization vector ($\mathbf{e} || \mathbf{R}$) as shown in the upper-right figure. The dashed lines are Cohen–Fano cross sections $d\sigma_{g/u}(\omega, \mathbf{R})/d\Omega_k$, equations (4) and (9), in which the constants $|J|^2/(1 \pm S)$, insignificant for the shape of the PADs, are omitted. The solid lines are the results of calculations using the expressions in brackets in equations (18) and (24).



Figure 4. The same as figure 3, but for the case when the photon polarization **e** is at various angles ϑ_e with respect to the molecular axis **R**. As in figure 3, the photoelectron energy $\varepsilon = 10$ eV and R = 5.042. For these values of *R* and ε , the curves calculated within both the models are similar and accurately coincide for $\mathbf{e} \perp \mathbf{R}$. The dashed lines correspond to equations (4) and (9). The solid lines are the results from equations (18) and (24). As in [6, 14], the open circles are the mirror images of the measured data points (full circles).



Figure 5. The dipole angular distribution parameters β_g and β_u as functions of photoelectron energy ε for various values of the internuclear distance *R*. The Cohen–Fano parameter is constant and equal to 2.



Figure 6. Electron angular distributions for R = 5.042 for various energies ε of electrons incident along the normal to the target axis ($\mathbf{k} \perp \mathbf{R}$), as shown in the upper figure on the right. The EADs are shown in the plane defined by the vectors \mathbf{k} , \mathbf{k}' and \mathbf{R} .

 $\beta_{g,u}$ in the case of N₂:N(1*s*) core photoelectron emission, and also previously calculated results [15]. We note that these calculations are based on significant approximations [16]; specifically, the potential of the multi-atomic system is taken as a cluster of non-overlapping spherical potentials centred on the atomic sites, along with a molecular sphere that embraces all of the atoms, as shown in figure 1(c). Beyond the molecular sphere the continuum wavefunction is approximated as the sum of a plane wave plus a single spherical wave emitted by the molecular centre. It is evident that owing to the absence



Figure 7. Electron and photoelectron angular distributions for R = 5.042 for various angles between the **k**, **e** and **R** vectors for 10 eV electrons. Solid lines are EADs, dashed lines are PADs for the *gerade* state and dotted lines for the *ungerade* state.

of spherical waves emitted by spatially separated sources in the outer region (figure 1(c)), this picture of the molecular photoionization process cannot be adequate to fully describe Young's double-slit diffraction.

5. Young's double-slit interference

Young-type interference patterns are observed in a doubleslit experiment in which the electron wave moving through the slits forms two spherical waves behind the screen. An exact analogue of this process in molecular physics is not molecular photoionization but elastic scattering of an electron by a diatomic homonuclear molecule. In the latter process, each of the two centres is an equivalent source of the spherical waves and the interference between these waves leads to a Young-type interference pattern. Within the present model, Young's double-slit experiment is described by the molecular continuum wavefunction, equation (13). The asymptotic form of this wavefunction as $r \rightarrow \infty$ defines the amplitude for elastic scattering of an electron wave by the two centres and has the form

$$F(\mathbf{k}, \mathbf{k}', \mathbf{R}) = \frac{2}{a^2 - b^2} \left\{ b \cos \left[(\mathbf{k} - \mathbf{k}') \cdot \frac{\mathbf{R}}{2} \right] - a \cos \left[(\mathbf{k} + \mathbf{k}') \cdot \frac{\mathbf{R}}{2} \right] \right\},$$
(29)

where the vector $\mathbf{k}' = k\mathbf{r}/r$ is the electron momentum after scattering. The differential cross section for electron elastic scattering within the solid angle $d\Omega_{k'}$ is defined by the absolute square of the scattering amplitude, equation (29),

$$\frac{\mathrm{d}\sigma(\mathbf{k},\mathbf{R})}{\mathrm{d}\Omega_{k'}} = |F(\mathbf{k},\mathbf{k}',\mathbf{R})|^2. \tag{30}$$

As in the case of the photo-process, the electron angular distribution (EAD) is a function of the mutual position of three vectors; in the photoabsorption cross sections, equations (18) and (24), these were the vectors \mathbf{e} , \mathbf{k} and \mathbf{R} , while for elastic scattering, equation (30), these are the vectors \mathbf{k} , $\mathbf{k'}$ and \mathbf{R} . It is evident that the direct comparison of the differential cross sections of these two processes does not make sense; the shape of the PAD is defined by the bound *gerade* or *ungerade* molecular state, while the elastic electron scattering EAD shape cannot, in principle, be treated in these terms because the angular distribution of electrons elastically scattered by a two-centre target is independent of the parity of the bound state that can be formed by these centres.

Choosing as in the PAD calculations **R** as the polar axis, the elastic cross section, equation (30), is calculated for a range of scattered electron energies, ε . Consider first the case of $\mathbf{k} \perp \mathbf{R}$. This corresponds to classical YTE in which the electron wave is incident onto the screen normal to its surface. The calculated EAD results are presented in figure 6. In this figure, the electron kinetic energies were chosen so that the value R = 5.042 au was within the range of electron wavelengths $\lambda = 2\pi/k$, and for one of these energies, $\varepsilon = 21.12$ eV, the electron wavelength is equal to the distance

between the atomic centres $\lambda \approx R$. With increasing electron energy, the angular distribution is transformed from two lobes into six lobes, both symmetrical relative to the vectors **k** and **R**.

The 10 eV EAD in figure 6, to some extent, can be compared with the lower *gerade* and *ungerade* PADs in figure 4. It is known that in the photoionization process, the electrons are emitted mainly along the photon polarization direction. For the above-mentioned PADs, the polarization vector is orthogonal to the molecular axis, i.e. the photoelectron wave moves, as in figure 6, mainly along the normal to the vector \mathbf{R} ($\vartheta_k \approx \vartheta_e = \pi/2$). The differences in the spectral shapes in these figures are evident.

An even more vivid illustration of the fact that the PADs in the model [1] have nothing in common with the classic two-slit-wave interference is presented in figure 7 where it is possible to see the evolution of the shapes of the $EAD(\vartheta_k)$ and the PAD(ϑ_e) as functions of the angles between the molecular axis **R** and vectors **k** and **e** for $\vartheta_e = \vartheta_k$. Here it is assumed that all photoelectrons are emitted along the polarization vector e and diffracted at the centres in the same way as electrons with momentum **k** elastically scattered by a target. Since in the EAD case we deal with the cross section of elastic electron scattering by a target and in the PAD case, with the cross section for ionic photodetachment, the EAD and PAD spectra are normalized so that their shapes can be compared directly. The energies of photoelectrons and elastically scattered electrons are the same and equal to $\varepsilon = 10$ eV. The first of the figures corresponds to $\vartheta_e = \vartheta_k = 0^\circ$ $(\mathbf{k} || \mathbf{R})$, and the next ones to 30° and 60°. The last figure corresponds to the case $\mathbf{e} \perp \mathbf{R}$ ($\mathbf{k} \perp \mathbf{R}$). The comparison of the PADs with the EADs shows that the shapes of the angular distributions and the character of their modifications for different mutual orientations of the vectors e, k and R are completely different. The angular distributions of scattered electrons (EADs) are symmetrical relative to the molecular axis for all the angles of electrons incident on a target. The PAD shapes (both for gerade and ungerade states), on the other hand, are defined to a considerable extent by the polarization vector; the shift of maxima of these angular distributions follows the polarization vector. The corresponding curves, therefore, are asymmetric relative to the polar axis **R**. Thus, the origin of the diffraction effects in the Cohen and Fano model [1] differs completely from the origins of the classic wave interference.

6. Discussion and conclusions

It has been demonstrated that a degree of similarity between homonuclear molecular photoionization and Young's doubleslit diffraction has been exaggerated. Specifically, the periodic modulations in molecular photoionization cross sections observed in experiments are due to the multicentre structure of the molecular *initial state*. While in YTE the diffraction effects are due to interference of the spherical waves emitted by the spatially separated sources of photoelectrons, i.e. they are connected with the multicentre structure of the molecular *continuum*. The fact that the interference in Young's double-slit experiments looks somewhat similar to diatomic molecular photoionization cross sections leads sometimes to mixing of the rather different pictures, detailed in figure 1. In [2], it is noted that '... Cohen and Fano [1] discussed the role of interference in the photoelectron spectra of valence electrons (*using the model of figure 1(b) for calculations*). Their theme was developed by Dehmer and Dill [16] into the K-shell spectroscopy of diatomic molecules (*using the model of figure 1(c) for calculations*). The idea behind it is sketched in *figure 1(a)*'.

Within the present molecular system model [8] it has been shown that the photoionization amplitude is a sum of the two terms. The first leads to Cohen-Fano effects and the second is responsible for spherical waves in the molecular continuum. Interference of these waves for low photoelectron energy crucially influences the absolute value of the cross sections but does not significantly distort the shape of the angular distribution. It has been shown that the angular distribution very weakly depends on the character of the forces acting between the photoelectron and the molecular residue: Coulomb forces for neutral molecular photoionization and short-range forces for photodetachment of molecular negative ions. The comparison of the interference patterns in molecular photoionization with those of electron scattering by two atomic molecules demonstrates that the interference patterns corresponding to these two processes are significantly different; this is because the former is essentially the initialstate effect, while the latter is a final-state effect.

Our consideration is based on using zero-range potentials. The well-known limitation of these potentials is that for scattering problems they are able to generate spherical *s*-waves only. Therefore, their application is restricted to the range of low kinetic energy of the colliding particles. The wavefunction for scattering by a target composed of zero-range potentials can be represented as a linear combination of Green's functions of free motion, equation (13); the coefficients of this linear combination $C_1(\mathbf{k})$ and $C_2(\mathbf{k})$ are defined by solving a system of the two linear algebraic equations.

The generalization of zero-range potentials for the case of non-zero orbital angular momenta and higher energy of particles is reduced to modifying the boundary conditions imposed on the wavefunction at the scattering centres and to representing the scattering wavefunction as a sum of plane wave and a linear combination of the derivatives of Green's functions; the derivatives of the first order for p-spherical waves, the second order for *d*-waves, *etc* (see [17-19]). Coefficients of this linear combination are defined by solving a system of the $2(l_{max} + 1)^2$ linear algebraic equations. Here, lmax is the maximal orbital angular momentum being taken into account [18]. For these spherical waves, the qualitative picture of scattering in figure 1(a) remains the same; the crests of the spherical waves in this figure will be those of s-, p-, d- etc spherical waves forming a diffraction pattern. The amplitudes of these waves will depend on the corresponding phases of elastic electron scattering by separate centres. If these phases are taken to be zero the spherical waves vanish and the picture in (a) goes to (b). Thus, inclusion of non-zero orbital angular momenta will not change the general conclusion of our paper: the origin of the diffraction effects in the Cohen and Fano model [1] are entirely different from the origin of the interference in Young's double-slit experiment.

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Appendix

Averaging in angles of the vector \mathbf{R} reduces to the calculation of the following integrals. For the *gerade* state:

$$\frac{1}{4\pi} \int \cos^2(\mathbf{k} \cdot \mathbf{R}/2) \, \mathrm{d}\Omega_{\rho} = \frac{1}{2} \left(1 + \frac{\sin \gamma}{\gamma} \right) = \frac{1}{2} F_g;$$

$$\gamma = kR; \tag{A.1}$$

$$\frac{1}{4\pi} \int (\mathbf{e} \cdot \boldsymbol{\rho}) \sin(\mathbf{k} \cdot \mathbf{R}) \, \mathrm{d}\Omega_{\rho} = (\mathbf{e} \cdot \mathbf{n}) \frac{1}{\gamma^2} (\sin \gamma - \gamma \cos \gamma)$$
$$= (\mathbf{e} \cdot \mathbf{n}) \varsigma_g; \qquad (A.2)$$

$$\frac{1}{4\pi} \int (\mathbf{e} \cdot \boldsymbol{\rho})^2 \sin^2(\mathbf{k} \cdot \mathbf{R}/2) d\Omega_{\boldsymbol{\rho}}$$

$$= \frac{(\mathbf{e} \cdot \mathbf{n})^2}{2} \left[\frac{1}{3} - \left(\frac{1}{\gamma} - \frac{2}{\gamma^3} \right) \sin \gamma - \frac{2}{\gamma^2} \cos \gamma \right]$$

$$+ \frac{1 - (\mathbf{e} \cdot \mathbf{n})^2}{4} \left\{ \left(1 - \frac{\sin \gamma}{\gamma} \right) - \left[\frac{1}{3} - \left(\frac{1}{\gamma} - \frac{2}{\gamma^3} \right) \sin \gamma - \frac{2}{\gamma^2} \cos \gamma \right] \right\}$$

$$= (\mathbf{e} \cdot \mathbf{n})^2 \alpha_g + [1 - (\mathbf{e} \cdot \mathbf{n})^2] \eta_g. \quad (A.3)$$

For the *ungerade* state:

$$\frac{1}{4\pi}\int\sin^2(\mathbf{k}\cdot\mathbf{R}/2)\,\mathrm{d}\Omega_\rho = \frac{1}{2}\left(1-\frac{\sin\gamma}{\gamma}\right) = \frac{1}{2}F_u;\qquad(A.4)$$

$$\frac{1}{4\pi} \int (\mathbf{e} \cdot \boldsymbol{\rho}) \sin(\mathbf{k} \cdot \mathbf{R}) \, d\Omega_{\rho} = (\mathbf{e} \cdot \mathbf{n}) \frac{1}{\gamma^2} (\sin \gamma - \gamma \cos \gamma)$$
$$= (\mathbf{e} \cdot \mathbf{n}) \varsigma_u; \qquad \varsigma_u = \varsigma_g \qquad (A.5)$$

$$\frac{1}{4\pi} \int (\mathbf{e} \cdot \boldsymbol{\rho})^2 \cos^2(\mathbf{k} \cdot \mathbf{R}/2) \, d\Omega_{\rho}$$

$$= \frac{(\mathbf{e} \cdot \mathbf{n})^2}{2} \left[\frac{1}{3} + \left(\frac{1}{\gamma} - \frac{2}{\gamma^3} \right) \sin \gamma + \frac{2}{\gamma^2} \cos \gamma \right]$$

$$+ \frac{1 - (\mathbf{e} \cdot \mathbf{n})^2}{4} \left\{ \left(1 + \frac{\sin \gamma}{\gamma} \right) - \left[\frac{1}{3} + \left(\frac{1}{\gamma} - \frac{2}{\gamma^3} \right) \sin \gamma + \frac{2}{\gamma^2} \cos \gamma \right] \right\}$$

$$= (\mathbf{e} \cdot \mathbf{n})^2 \alpha_u + [1 - (\mathbf{e} \cdot \mathbf{n})^2] \eta_u. \quad (A.6)$$

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