

## Theory of inner-shell photoionization of fixed-in-space molecules

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A theory is presented for the calculation of molecular inner-shell photoionization near thresholds and electron-molecular-ion elastic scattering. The interaction of the incoming/outgoing electron with each atom of the formation (except for the ionized atom) is accounted for by suitable boundary conditions imposed on the electron wave function at nuclei of these atoms in the system. The theory is applied to calculations of the form of the photoelectron angular distribution for  $1s$  photoionization of the C atom in the CO diatomic molecule, as well as for the photoelectron angular distribution due to photodetachment from a quasimolecular negative ion consisting of a  $C^-$  ion located near a neutral O atom.

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### I. INTRODUCTION

Inner-shell photoionization is a method of investigating the electronic states of molecules. Molecules give rise to photoionization cross sections that are rather different from free atoms due to loss of spherical symmetry. For example, the inner-shell photoabsorption spectra of diatomic molecules exhibit broad resonances, quite different from the monotonically decreasing atomic-photoionization cross section [1]. The main difficulty in calculating cross sections for molecular photoionization is a realistic description of the motion of an unbound photoelectron in the continuum of a molecule or a molecular ion, whereas an initial molecular state of a deep inner-shell level remains essentially atomic-like. Dill and Dehmer [2] combined the multiple-scattering technique for treating nonseparable eigenvalue problems with electron-scattering theory to construct continuum electronic wave functions for molecules. Since Ref. [2] is the starting point for our consideration, we briefly recap the general ideas of this method. The molecular potential of a heteronuclear diatomic molecule is represented as a cluster of nonoverlapping spherical potentials with effective radii  $\rho_1$  and  $\rho_2$  centered at the atomic sites (regions I<sub>1</sub> and I<sub>2</sub>). Inside each sphere, the molecular potential is approximated as the sum of a central atomic potential of the particular atom, and the monopole term of the expansion of the potential of the other atom about the center of the given atom. In the space outside the atomic spheres, but inside the molecular sphere that embraces the atoms (region II) the molecular potential is taken to be a constant. And in the region outside the molecular sphere with radius  $R_m \geq \rho_1 + \rho_2$  (region III), the molecular potential is considered to be Coulombic, centered on the center of the molecular sphere. The matching conditions for logarithmic derivatives of the electron wave function on the surfaces of atomic and molecular spheres give a set of inhomogeneous linear equations that defines the phase shifts and

amplitudes of the molecular continuum wave functions. Built in such a way, the wave functions can be used to describe both the electron-molecule scattering [3,4] and molecular photoionization [5–11].

The method of Ref. [2] is a generalization of the augmented-plane-waves (APW) approach [12] for molecular systems. The APW method, widely used in solid-state physics, is usually applied to calculate the bound structure of solids whereas the muffin-tin potential covers all space. For the molecular case the situation is quite different, because the muffin-tin potential here is due to a finite number of the atomic spheres, and, therefore, it is impossible to neglect the existence of the molecular boundary. Thus, the traditional APW method must be adapted for molecular photoionization. In Ref. [2] this adaptation consists in introducing a molecular sphere and assuming a Coulomb potential outside this sphere.

The solution of the molecular-photoionization problem in the framework of the method of Ref. [2] leads to the following principal difficulties. First, the molecular potential exhibits unphysical discontinuities at the molecular sphere; this is connected with the assumption of a constant potential in region II. Second, the center of Coulomb potential in region III does not coincide with the nucleus of the ionized atom. Third, in the method of Ref. [2] the asymptotic of the photoelectron wave function far from the molecule is a superposition of a plane wave plus a spherical wave convergent on the molecular center. In fact, because of the multicentered character of the problem, the asymptotic form of the molecular continuum wave function must include two spherical waves with centers on the nuclei of the atoms that form the diatomic molecule. In the case of an  $N$ -atom molecule, we must evidently deal with  $N$  spherical waves, one generated by each of the atoms of the molecule. Finally, in Ref. [2] the question of how matching wave functions of different Hamiltonians at the surface of the molecular sphere influences amplitudes and phase shifts of continuum wave functions is not entirely clear.

A method for the calculation of molecular photoionization is presented in this paper. It is based on an idea developed by

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Fermi [13] investigating the shift of the higher spectral lines of an excited atom under gas pressure. For the description of the interaction of a Rydberg electron with the atoms of the buffer gas, a pseudopotential as an equivalent of the boundary conditions imposed on the wave function of excited electron was used [13,14]. We employ this idea to construct the molecular continuum wave function. It is crucial that within the framework of the pseudopotential method the effects connected with electron multiple-scattering by the various potential centers be taken into account accurately. However, the use of this method is limited to low photoelectron energies. Within the framework of this method elastic electron scattering by molecules and molecular ions, and molecular-photoionization cross sections near thresholds can be calculated, which obviate some of the difficulties inherent in the method of Ref. [2].

## II. THEORY AND RESULTS

### A. Molecular continuum wave functions

Suppose that the nucleus of the atom in a molecule being ionized is located in the origin of the coordinate system and a set of vectors  $\{\mathbf{R}_1, \dots, \mathbf{R}_N\} \equiv \vec{\mathcal{R}}$  defines the positions of the nuclei of the other atoms of the molecule. These  $N$  atoms shall be termed atom scatterers. The molecular field in which the photoelectron moves is a sum of two potentials; the potential generated by the ionized atom, which we approximate as a central field  $V(r)$ , which is slowly varying (except the region near the atomic residual), and the potentials  $V_j(|\mathbf{r} - \mathbf{R}_j|)$  of the atom scatterers, which we also approximate to be central fields about their respective nuclei. For example, in the case of the photoionization of a hydrogen atom confined in a molecule,  $V(r) = -1/r$  and  $V_j(|\mathbf{r} - \mathbf{R}_j|)$  are short-range potentials of the atoms surrounding the H atom. Here and below we use atomic units ( $\hbar = m = e = 1$ ). The Schrödinger equation for the photoelectron wave function in this multicenter system takes the form

$$\left[ -\frac{1}{2}\Delta + V(r) - E \right] \Phi_E(\mathbf{r}, \vec{\mathcal{R}}) = -\Phi_E(\mathbf{r}, \vec{\mathcal{R}}) \sum_{j=1}^N V_j(|\mathbf{r} - \mathbf{R}_j|). \quad (1)$$

The potentials  $V_j(|\mathbf{r} - \mathbf{R}_j|)$  are further approximated as non-overlapping and equal to zero for  $|\mathbf{r} - \mathbf{R}_j| > \rho_j$ , where  $\rho_j$  is the radius of atom scatterer  $j$ . Then in the region between the atom scatterers the photoelectron wave function is a solution of the homogeneous equation (1) with the right side equal to zero, i.e.,

$$\hat{H}_0 \Phi_E(\mathbf{r}, \vec{\mathcal{R}}) = \left[ -\frac{1}{2}\Delta + V(r) - E \right] \Phi_E(\mathbf{r}, \vec{\mathcal{R}}) = 0. \quad (2)$$

It is clear that the behavior of the electron wave function in this region that covers all space, except the spheres of atom scatterers, plays the primary role in the description of photoionization of deep atomic subshells because the dipole-matrix elements are generated near the nucleus of the ionized atom at distances of  $\sim I_{nl}^{-1/2}$ , where  $I_{nl}$  is the ionization potential of the deep  $nl$ -atomic level. The size of this region is

much less than interatomic distances and therefore in this region all potentials  $V_j(|\mathbf{r} - \mathbf{R}_j|) = 0$ . Consequently, to describe molecular photoionization it is sufficient to construct the photoelectron wave function correctly in this region where Eq. (2) is valid. Near the origin of the coordinate system the photoelectron wave functions of initial and final states coincide with the regular solutions of Eq. (2) to within constants, while for large  $r$  the continuum wave function must correctly describe elastic photoelectron scattering by a positive molecular ion that contains the atom with a hole in the  $nl$  subshell.

Qualitatively, the behavior of the wave functions describing the motion of an electron in the molecular field with energy  $E = k^2/2 > 0$ , the solutions of Eq. (1), is as follows: near each of the atoms of the molecule, the functions  $\Phi_{\mathbf{k}}^{\pm}(\mathbf{r}, \vec{\mathcal{R}})$  are close to the wave functions of that atom; in interatomic space they coincide with the electron wave functions in the field of the residual ion; and wave functions  $\Phi_{\mathbf{k}}^{\pm}(\mathbf{r}, \vec{\mathcal{R}})$  must satisfy the so-called outgoing-wave and incoming-wave boundary conditions. Using the Green's function of Eq. (2),

$$\Phi_{\mathbf{k}}^{\pm}(\mathbf{r}, \vec{\mathcal{R}}) = \Psi_{\mathbf{k}}^{\pm}(\mathbf{r}) - \sum_{j=1}^N \int G_{\mathbf{k}}^{\pm}(\mathbf{r}, \mathbf{r}') V_j(|\mathbf{r}' - \mathbf{R}_j|) \times \Phi_{\mathbf{k}}^{\pm}(\mathbf{r}', \vec{\mathcal{R}}) d\mathbf{r}'. \quad (3)$$

Here, the functions  $\Psi_{\mathbf{k}}^{\pm}(\mathbf{r})$  are the solutions of homogeneous Equation (2), with boundary conditions that describe the elastic electron scattering by isolated potential  $V(r)$  and is given by the expression [15]

$$\Psi_{\mathbf{k}}^{\pm}(\mathbf{r}) = 4\pi \sum_{l,m} i^l e^{\pm i\Delta_l} Y_{lm}(\mathbf{r}) Y_{lm}^*(\mathbf{k}) \varphi_{kl}(r). \quad (4)$$

Here,  $\varphi_{kl}(r)$  is the regular-at-zero solution of the radial Schrödinger equation (2), which has the asymptotic form

$$\varphi_{kl}(r)|_{r \rightarrow \infty} \approx \frac{1}{kr} \sin\left(kr - \frac{\pi l}{2} + \frac{z}{k} \ln 2kr + \Delta_l\right), \quad (5)$$

where  $z$  is the charge of the residual atomic ion created by the photoionization process and  $\Delta_l(k)$  is the phase shift of the wave function in the potential field of this ion, including the Coulomb phase. The spherical functions  $Y_{lm}(\mathbf{r}) \equiv Y(\Omega)$  and  $Y_{lm}(\hat{\mathbf{k}}) \equiv Y(\Omega_k)$  are defined by the spherical coordinates of vectors  $\mathbf{r}$  and  $\mathbf{k}$ , respectively.  $\Psi_{\mathbf{k}}^{-}(\mathbf{r})$  and  $\Psi_{\mathbf{k}}^{+}(\mathbf{r})$  [Eq. (4)] are characterized by the following asymptotic behavior: at  $r \rightarrow \infty$  they contain the plane wave  $\exp(i\mathbf{k} \cdot \mathbf{r})$ , as well as, respectively, converging and diverging spherical waves of  $s, p, d$  etc. types. The Green's functions in Eq. (3) are defined by

$$\hat{H}_0 G_{\mathbf{k}}^{\pm}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (6)$$

and they can be expressed as expansion in terms of spherical harmonics [16]

$$G_k^\pm(\mathbf{r}, \mathbf{r}') = \sum_{l,m} G_{kl}^\pm(r, r') Y_{lm}(\mathbf{r}) Y_{lm}^*(\mathbf{r}'). \quad (7)$$

The radial parts of the Green's functions, Eq. (7), can be written as

$$G_{kl}^\pm(r, r') = 2k \begin{cases} \varphi_{kl}(r) \chi_{kl}^\pm(r'), & r < r' \\ \varphi_{kl}(r') \chi_{kl}^\pm(r), & r > r'. \end{cases} \quad (8)$$

Here,  $\chi_{kl}^\pm(r) = \pm i \varphi_{kl}(r) - \chi_{kl}(r)$  are linear combinations of regular  $\varphi_{kl}(r)$  and irregular-at-zero  $\chi_{kl}(r)$  solutions of the radial Schrödinger equation (2). The latter solution has the asymptotic form

$$\chi_{kl}(r)|_{r \rightarrow \infty} \approx -\frac{1}{kr} \cos\left(kr - \frac{\pi l}{2} + \frac{z}{k} \ln 2kr + \Delta_l\right). \quad (9)$$

According to these formulas, the Green's functions, Eq. (7), have asymptotic forms [16]

$$G_k^\pm(\mathbf{r}, \mathbf{r}')|_{r \rightarrow \infty} = \frac{\exp\left[\pm i\left(kr + \frac{z}{k} \ln 2kr\right)\right]}{2\pi r} \Psi_{\pm \mathbf{k}'}^{\mp*}(\mathbf{r}), \quad (10)$$

where the vector  $\mathbf{k}'$  is defined by  $\mathbf{k}' = k\mathbf{r}/r$ .

Using Eq. (10), it is seen that the asymptotic large- $r$  behavior of the second term in Eq. (3) has the form

$$\begin{aligned} & \sum_{j=1}^N \int G_k^\pm(\mathbf{r}, \mathbf{r}') V_j(|\mathbf{r}' - \mathbf{R}_j|) \Phi_{\mathbf{k}}^\pm(\mathbf{r}', \vec{\mathcal{R}}) d\mathbf{r}'|_{r \rightarrow \infty} \\ & \rightarrow \frac{\exp\left[\pm i\left(kr + \frac{z}{k} \ln 2kr\right)\right]}{2\pi r} \\ & \times \sum_{j=1}^N \int \Psi_{\pm \mathbf{k}'}^{\mp*}(\mathbf{r}') V_j(|\mathbf{r}' - \mathbf{R}_j|) \Phi_{\mathbf{k}}^\pm(\mathbf{r}', \vec{\mathcal{R}}) d\mathbf{r}'. \end{aligned} \quad (11)$$

According to Eq. (11), the Green's functions in Eq. (3) asymptotically generate  $N$  spherical waves. The coefficient of wave  $j$  is the amplitude for elastic electron scattering by atom scatterer  $j$ . This amplitude depends on vectors  $\mathbf{k}, \mathbf{k}'$  and  $\vec{\mathcal{R}}$ .

We now restrict our theoretical method to low electron energies. Since we have assumed nonoverlapping potentials  $V_j(|\mathbf{r} - \mathbf{R}_j|)$ , the region of integration in Eq. (11) is divided into  $N$  isolated spheres with radii  $\rho_j$ . If the wavelength of the photoelectron is much greater than any of radii of potential wells  $1/k \gg \rho_j$ , then the integrand in Eq. (11) is a product of two functions: smoothly changing functions  $\Psi_{\mathbf{k}}^\pm(\mathbf{r})$  and rapidly changing functions  $V_j(|\mathbf{r} - \mathbf{R}_j|) \Phi_{\mathbf{k}}^\pm(\mathbf{r}, \vec{\mathcal{R}})$ . This makes it possible to remove the function  $\Psi_{\mathbf{k}}^\pm(\mathbf{r})$  from under the integral and, to an excellent approximation for low energies, Eq. (11) becomes

$$\begin{aligned} & \frac{\exp\left[\pm i\left(kr + \frac{z}{k} \ln 2kr\right)\right]}{2\pi r} \sum_{j=1}^N \int \Psi_{\pm \mathbf{k}'}^{\mp*}(\mathbf{r}') \\ & \times V_j(|\mathbf{r}' - \mathbf{R}_j|) \Phi_{\mathbf{k}}^\pm(\mathbf{r}', \vec{\mathcal{R}}) d\mathbf{r}' \\ & \approx \frac{\exp\left[\pm i\left(kr + \frac{z}{k} \ln 2kr\right)\right]}{2\pi r} \sum_{j=1}^N \Psi_{\pm \mathbf{k}'}^{\mp*}(\mathbf{R}_j) \\ & \times \int V_j(|\mathbf{r}' - \mathbf{R}_j|) \Phi_{\mathbf{k}}^\pm(\mathbf{r}', \vec{\mathcal{R}}) d\mathbf{r}' \\ & = \sum_{j=1}^N \left[ \int V_j(|\mathbf{r}' - \mathbf{R}_j|) \Phi_{\mathbf{k}}^\pm(\mathbf{r}', \vec{\mathcal{R}}) d\mathbf{r}' \right] G_{kl}^\pm(\mathbf{r}, \mathbf{R}_j)|_{r \rightarrow \infty}. \end{aligned} \quad (12)$$

To calculate the square bracket in Eq. (12) we need to know the wave function  $\Phi_{\mathbf{k}}^\pm(\mathbf{r}, \vec{\mathcal{R}})$  and the potentials of the atom scatterers  $V_j(|\mathbf{r} - \mathbf{R}_j|)$ . However, the direct calculation of the integrals in Eq. (12) can be avoided and the coefficients of the Green's functions in this equation can be expressed via  $s$ -wave phase shifts for electron scattering by each atom scatterer. Consider the wave function  $\Phi_{\mathbf{k}}^\pm(\mathbf{r}, \vec{\mathcal{R}})$  in the form

$$\Phi_{\mathbf{k}}^\pm(\mathbf{r}, \vec{\mathcal{R}}) = \Psi_{\mathbf{k}}^\pm(\mathbf{r}) + \sum_{j=1}^N C_j^\pm(\mathbf{k}) G_k^\pm(\mathbf{r}, \mathbf{R}_j), \quad (13)$$

where the  $C_j^\pm(\mathbf{k})$  are to be determined from the solution of the problem of elastic electron scattering by a positive molecular ion. By comparison with Eq. (12), it is seen that these wave functions, defined by Eq. (13), satisfy the necessary boundary conditions. It is also clear that these wave functions are solutions of Eq. (2) in the region between atom scatterers. It is evident, however, that these functions, in contrast to exact solutions defined by Eq. (3), do not describe correctly the electron behavior inside the atomic spheres; moreover, they diverge as  $1/|\mathbf{r} - \mathbf{R}_j|$  at the centers of these spheres. This divergence, however, plays no role in the photoionization problem because the dipole-matrix element is generated near the origin of the coordinate system, quite far from the atom scatterer spheres.

The functions (13), have especially simple forms in the case of  $V(r) \equiv 0$ . In this case the wave function (13) takes the form

$$\Phi_{\mathbf{k}}^\pm(\mathbf{r}, \vec{\mathcal{R}}) = e^{i\mathbf{k} \cdot \mathbf{r}} + \frac{1}{2\pi} \sum_{j=1}^N C_j^\pm(\mathbf{k}) \frac{e^{\pm i\mathbf{k} \cdot |\mathbf{r} - \mathbf{R}_j|}}{|\mathbf{r} - \mathbf{R}_j|}. \quad (14)$$

Using the summation theorem for spherical Bessel functions [17], we can easily show that Eq. (14) is a solution of Eq. (2) in interatomic space for  $V(r) \equiv 0$ . For large  $r$ , Eq. (14) is a superposition of a plane wave and  $N$  spherical  $s$  waves generated by the atom scatterers.

In order to find the coefficients  $C_j^\pm(\mathbf{k})$  defining the linear combination of the Green's functions in Eq. (13), we consider elastic electron scattering by a positive molecular ion.

Solutions of the Schrödinger equation  $\Phi_{\mathbf{k}}^{\pm}(\mathbf{r}, \vec{\mathcal{R}})$  for an electron moving with energy  $E > 0$  in the interatomic region must satisfy the boundary conditions on the surfaces of the atomic spheres [18]. However, since we only need the wave function to be correct in the neighborhood of the initial state of the photoelectron, the boundary conditions can be imposed at the nuclei of the atom scatterers [19]. This means that the wave function will be incorrect inside the atom scatterer spheres; but this is of no consequence for the photoionization calculation. Furthermore, by imposing the boundary conditions at the nuclei, the real atomic potentials can be replaced by point pseudopotentials that are equivalents of the boundary conditions [20,21].

The main idea of the pseudopotential method is to take into account the boundary conditions that are imposed on the wave function [Eq. (13)] by means of a transition from Eq. (2) to an inhomogeneous wave equation. This method is well known in electrodynamics where for calculation of the electrostatic potential of a charge located near a metallic sphere, for example, the potential is represented by a corresponding charge distribution on the sphere's surface. Then the surface charges can be replaced by a system of fictional electrical multipoles located at the center of the sphere. Solving the Poisson equation with these sources, the exact electrostatic potential outside the metallic sphere is obtained [22]. Similar to this, in the pseudopotential method, the boundary conditions on the wave function on the surface of the atomic spheres are replaced by fictional point potentials at the centers of these spheres.

In order to find these potentials, we operate with  $\hat{H}_0$  on the wave function, Eq. (13), and obtain, instead of Eq. (1), an inhomogeneous equation with pseudopotentials on the right-hand side,

$$\left[ -\frac{\Delta}{2} + V(r) - \frac{k^2}{2} \right] \Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}}) = \sum_{j=1}^N C_j^+(\mathbf{k}) \delta(\mathbf{r} - \mathbf{R}_j). \quad (15)$$

The methods of solving the problem of electron scattering using zero-range potentials have been developed in detail [14,23,24], where it was shown that the general solution of Eq. (15) near the points  $\mathbf{R}_j$  has the form

$$\Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}})|_{\mathbf{r} \rightarrow \mathbf{R}_j} \rightarrow \lambda_j (|\mathbf{r} - \mathbf{R}_j|^{-1} + k \cot \delta_0^j). \quad (16)$$

Here,  $\lambda_j$  are constants and  $\delta_0^j$  is the  $s$ -wave phase shift generated by atom scatterer  $j$ , which we approximate as the solution of the problem of slow electron scattering by an isolated  $j$  atom.

The boundary conditions, (16) involve the phase shift  $\delta_0^j$  of the wave function representing elastic electron scattering by the  $\delta$  potential. The phase-shift problem is simplified by considering electron scattering by a zero-range potential located at the coordinate origin. If all the phases except the  $s$  phase are vanishingly small, then the wave function  $\Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}})$  has the form

$$\Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}}) = e^{i\mathbf{k} \cdot \mathbf{r}} + f_0^j \frac{e^{ikr}}{r}, \quad (17)$$

where  $f_0^j$  is the  $s$ -wave scattering amplitude. Going to the  $r \rightarrow 0$  limit in Eq. (17) yields

$$\Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}})|_{r \rightarrow 0} \rightarrow 1 + f_0^j \left[ \frac{1}{r} + ik \right] = f_0^j \left[ \frac{1}{r} + ik + \frac{1}{f_0^j} \right]. \quad (18)$$

Comparing Eqs. (16) and (18), we obtain the well-known formula that connects the scattering amplitude with the  $s$ -wave phase shift  $f_0^j = [\exp(2i\delta_0^j) - 1]/2ik$  [15]. For coefficients  $C_j^+(\mathbf{k})$  we obtain  $C_j^+(\mathbf{k}) = 2\pi f_0^j$ .

In the case of  $N$  zero-range potentials the wave function, defined by Eq. (13), must satisfy the boundary conditions, (16) at each of the points  $\mathbf{r} = \mathbf{R}_j$ ,  $j = 1, \dots, N$ . From here we obtain the following set of algebraic equations for the coefficients

$$2\pi f_0^j \Psi_{\mathbf{k}}^+(\mathbf{R}_j) = C_j^+(\mathbf{k}) - 2\pi f_0^j \sum_{i \neq j}^N C_i^+(\mathbf{k}) G_{\mathbf{k}}^+(\mathbf{R}_i, \mathbf{R}_j). \quad (19)$$

When deriving Eq. (19) it is taken into account that the Green's functions  $G_{\mathbf{k}}^+(\mathbf{r}, \mathbf{R}_j)$  for close values of the arguments are approximately equal to the Green's function of a free particle [16]. Note that, according to Eq. (19), the coefficient  $C_j^+(\mathbf{k})$  of the  $j$ th zero-range potential, depends not only on vector  $\mathbf{R}_j$ , but also on vectors that define the positions of other  $\delta$  potentials. This means that the wave function, (13) with coefficients defined by Eq. (19) accounts for electron multiple-scattering by the potentials of this multi-center system. The solutions of Eq. (19) are reduced to calculating the corresponding determinants. The resulting coefficients  $C_j^+(\mathbf{k})$  can also be used to calculate the cross sections for elastic scattering by molecules or clusters and their positive ions.

## B. Elastic electron scattering

The elastic-scattering amplitude for slow electrons on a molecular ion is defined by the asymptotic behavior of the wave function, (13) as  $r \rightarrow \infty$  and has the form

$$F(\vartheta) = F^{\text{ion}}(\vartheta) + \frac{1}{2\pi} \sum_{j=1}^N C_j^+(\mathbf{k}) \Psi_{\mathbf{k}'}^{-*}(\mathbf{R}_j). \quad (20)$$

Here,  $F^{\text{ion}}(\vartheta)$  is the amplitude for elastic electron scattering by a free positive ion located at the coordinate origin,  $\vartheta$  is the angle of scattering, and  $\mathbf{k}' = k\mathbf{r}/r$  is the momentum of the scattered electron.

The case of diatomic molecules is especially simple where we have a two-centered system composed of one positive ion and one  $j$ -scattering center. The set of equations, (19), for this system is transformed into one equation

$$C_j^+(\mathbf{k}) = 2\pi f_0^j \Psi_{\mathbf{k}}^+(\mathbf{R}_j), \quad (21)$$



and the amplitude, (20) for electron scattering by molecular ions takes the form

$$F(\vartheta) = F^i(\vartheta) + f_0^j \Psi_{\mathbf{k}}^+(\mathbf{R}_j) \Psi_{-\mathbf{k}'}^+(\mathbf{R}_j). \quad (22)$$

According to Eq. (22), the cross section for elastic scattering by a fixed-in-space molecular ion at an angle  $\vartheta$  is defined, as it should be, by the mutual orientation of the vectors  $\mathbf{k}$ ,  $\mathbf{k}'$ , and  $\mathbf{R}_j$ . Note that the product of two spherical harmonics  $Y_{lm}(\mathbf{R}_j)$  in Eq. (22) can be reduced to one spherical harmonic by using the Clebsch-Gordan expansion [25]. If potential  $V(r) \equiv 0$  then we deal with only one  $j$ -scattering center. In this case  $F^{\text{ion}}(\vartheta) = 0$  and instead of Eq. (22) we have the following expression for the amplitude of scattering by an isolated potential at point  $\mathbf{R}_j$ ,

$$F(\vartheta) = f_0^j \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_j].$$

The total cross section  $\sigma_{\text{mol}}(k)$  for the oriented molecular ion is obtained from Eq. (22) with the help of the optical theorem [15]

$$\begin{aligned} \sigma_{\text{mol}}(k) &= 4\pi \frac{\text{Im} F(0)}{k} \\ &= \sigma_{\text{ion}}(k) + \Psi_{\mathbf{k}}^+(\mathbf{R}_j) \Psi_{-\mathbf{k}}^+(\mathbf{R}_j) \frac{4\pi}{k^2} \sin^2 \delta_0^j. \end{aligned} \quad (23)$$

If  $V(r) \equiv 0$  then we obtain the total cross section for scattering by a short-range potential  $V_j(|\mathbf{r} - \mathbf{R}_j|)$ . As it must be, this cross section has the form  $\sigma_{\text{mol}}(k) = (4\pi/k^2) \sin^2 \delta_0^j$ .

### C. Photoionization cross section

The differential cross section of molecular photoionization is defined by [26]

$$\frac{d\sigma}{d\Omega} = \frac{k\omega}{2\pi c} \left| \int \Phi_{\mathbf{k}}^{-*}(\mathbf{r}, \vec{\mathcal{R}}) (\mathbf{e} \cdot \mathbf{r}) \Phi_{nl}(\mathbf{r}, \vec{\mathcal{R}}) d\mathbf{r} \right|^2. \quad (24)$$

Here,  $c$  is the velocity of light,  $\mathbf{e}$  is the photon polarization vector, and  $\omega = I_{nl} + k^2/2$  is the photon energy. For the photoionization of a deep atomic subshell of an atom located at the coordinate origin, the photoelectron wave function of the initial state  $\Phi_{nl}(\mathbf{r}, \vec{\mathcal{R}})$  is located near the coordinate origin, within a region of approximate size of order  $\sim I_{nl}^{-1/2}$ . This value is much less than interatomic distances in the molecule. Therefore, to an excellent approximation, we can neglect the effect of the surrounding atoms of the molecule on the initial-state wave function of the photoelectron  $\Phi_{nl}(\mathbf{r}, \vec{\mathcal{R}})$  and approximate it as the wave function of the  $nl$  subshell of a free ionized atom, i.e., this wave function is the regular-at-zero solution of Eq. (2) with energy  $E = -I_{nl}$ ,

$$\Phi_{nl}(\mathbf{r}, \vec{\mathcal{R}}) = \varphi_{nl}(r) Y_{lm}(\mathbf{r}). \quad (25)$$

The relation  $\Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}}) = \Phi_{-\mathbf{k}}^{-*}(\mathbf{r}, \vec{\mathcal{R}})$  [15] connects the wave function of a photoelectron  $\Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}})$  in the molecular continuum with the function  $\Phi_{\mathbf{k}}^+(\mathbf{r}, \vec{\mathcal{R}})$  that describes the elastic electron scattering by the molecular ion. Hence, the coeffi-

cients of the Green's functions in Eq. (13) are defined by the expression  $C_j^{-*}(-\mathbf{k}) = C_j^+(\mathbf{k})$ . According to the dipole-selection rules a transition is possible from the  $nl$  subshell to states with orbital angular momenta  $l \pm 1$ . Therefore, in the expansion of the continuum wave function  $\Phi_{\mathbf{k}}^-(\mathbf{r}, \vec{\mathcal{R}})$ , Eq. (13), in spherical harmonics, it is sufficient to consider only partial waves with  $l \pm 1$ . The radial part of these wave functions is defined by

$$\begin{aligned} & \int \Phi_{\mathbf{k}}^-(\mathbf{r}, \vec{\mathcal{R}}) Y_{l\pm 1m}^*(\mathbf{r}) d\Omega \\ &= 4\pi i^{l\pm 1} e^{-i\Delta_{l\pm 1}} Y_{l\pm 1m}^*(\mathbf{k}) \varphi_{kl\pm 1}(r) \\ &+ \sum_{j=1}^N C_j^-(\mathbf{k}) G_{kl\pm 1}^-(r, R_j) Y_{l\pm 1m}^*(\mathbf{R}_j). \end{aligned} \quad (26)$$

Near the coordinate origin, the inequality  $r < R_j$  is valid for all vectors  $\mathbf{R}_j$ . Hence, Eq. (26), taking into account Eq. (8), can be rewritten in the form

$$\int \Phi_{\mathbf{k}}^-(\mathbf{r}, \vec{\mathcal{R}}) Y_{l\pm 1m}^*(\mathbf{r}) d\Omega = D_{l\pm 1}(\mathbf{k}, \vec{\mathcal{R}}) \varphi_{kl\pm 1}(r), \quad (27)$$

where amplitude  $D_{l\pm 1}(\mathbf{k}, \vec{\mathcal{R}})$  is defined by

$$\begin{aligned} D_{l\pm 1}(\mathbf{k}, \vec{\mathcal{R}}) &= 4\pi i^{l\pm 1} e^{-i\Delta_{l\pm 1}} Y_{l\pm 1m}^*(\mathbf{k}) \\ &+ 2k \sum_{j=1}^N C_j^-(\mathbf{k}) \chi_{kl\pm 1}^-(R_j) Y_{l\pm 1m}^*(\mathbf{R}_j). \end{aligned} \quad (28)$$

From Eq. (27), the radial parts of the photoelectron continuum wave functions differ only by amplitude  $D_{l\pm 1}(\mathbf{k}, \vec{\mathcal{R}})$  from the radial parts of the wave functions for the free atom. Equation (28) is physically obvious; the change in the wavefunction amplitude near the nucleus of the ionized atom is due to multiple reflection of the electron wave from atom scatterers. It is natural that the amplitudes of reflected waves depend on the electron momentum  $\mathbf{k}$  and vectors  $\mathbf{R}_j$ .

Taking into account Eqs. (13) and (25), the photoionization amplitude becomes

$$\begin{aligned} A_{nl \rightarrow \epsilon l \pm 1} &= \int \Phi_{\mathbf{k}}^{-*}(\mathbf{r}, \vec{\mathcal{R}}) (\mathbf{e} \cdot \mathbf{r}) \Phi_{nl}(\mathbf{r}, \vec{\mathcal{R}}) d\mathbf{r} \\ &= 4\pi \sum_{\lambda, \mu} d_{\lambda\mu} \left[ (-i)^\lambda e^{i\Delta_\lambda} Y_{\lambda\mu}(\mathbf{k}) \right. \\ &\quad \left. + \frac{k}{2\pi} \sum_{j=1}^N C_j^+(-\mathbf{k}) \chi_{k\lambda}^+(R_j) Y_{\lambda\mu}(\mathbf{R}_j) \right], \end{aligned} \quad (29)$$

where  $d_{\lambda\mu}$  is the dipole-matrix element for the free atom

$$d_{\lambda\mu} = \int \varphi_{k\lambda}(r) Y_{\lambda\mu}^*(\mathbf{r}) (\mathbf{e} \cdot \mathbf{r}) \varphi_{nl}(r) Y_{lm}(\mathbf{r}) d\mathbf{r}. \quad (30)$$

Thus, the calculation of the photoionization cross section for a deep subshell of an atom bound in a molecule is reduced to calculating dipole amplitudes for the free atom and the function in square brackets in Eq. (29). The representation of the molecular amplitude in this form, (29) is a result of Eqs. (27) and (28), which show that the molecular continuum wave function differs only by an amplitude factor from the atomic wave function. It is evident that connection between the dipole amplitudes (29) in a molecule and atom cannot be found in a closed form if the molecular continuum wave function is expressed using the free-particle Green's function, as done in Ref. [27]. Note that in the calculation of the dipole-matrix element, Eq. (30), both initial- and final-state wave functions are eigenfunctions of Eq. (2) to an excellent approximation. Therefore, the *length* and *velocity* forms of the dipole-matrix elements lead to nearly identical results.

Equation (24) and (29) for arbitrary initial-state orbital angular momenta  $l$  are complicated. Therefore, to illustrate the essential features of this theory, we consider the particular case of atomic  $s$ -level photoionization from a diatomic molecule. In this case, the general formulas for the differential-photoionization cross section can be greatly simplified. The amplitude, (29) for a dipole transition in this case takes the form

$$A_{nl \rightarrow \epsilon l \pm 1} = r_{\text{sp}} \sqrt{4\pi} \left[ -i e^{i\Delta_1} (\mathbf{e} \cdot \mathbf{n}) + \frac{k}{2\pi} C_j^+(-\mathbf{k}) \chi_{k1}^+(R_j) (\mathbf{e} \cdot \boldsymbol{\rho}) \right], \quad (31)$$

where the unit vectors  $\mathbf{n} = \mathbf{k}/k$ ,  $\boldsymbol{\rho} = \mathbf{R}_j/R_j$ , and the matrix element  $r_{\text{sp}}$  is

$$r_{\text{sp}} = \int \varphi_{k1}(r) r \varphi_{n0}(r) dr. \quad (32)$$

From Eqs. (24) and (31), the photoelectron angular distribution becomes

$$\frac{d\sigma}{d\Omega} = \frac{2\omega}{ck} r_{\text{sp}}^2 |(\mathbf{e} \cdot \mathbf{k}) + H_1(\mathbf{k}, \mathbf{R}_j) (\mathbf{e} \cdot \boldsymbol{\rho})|^2. \quad (33)$$

In this formula,

$$H_1(\mathbf{k}, \mathbf{R}_j) = i e^{-i\Delta_1} f_0^j k^2 \chi_{k1}^+(R_j) \Psi_{-\mathbf{k}}^+(\mathbf{R}_j). \quad (34)$$

It is very important to note that the differential-photoionization cross section, Eq. (33), is a product of two factors. The first depends on the ground atomic state and is defined by the integral, (32). The second is connected only with the molecular continuum characteristics and depends on mutual position of vectors  $\mathbf{e}$ ,  $\mathbf{k}$ , and  $\mathbf{R}_j$ . This second factor, referred to as a structural function  $S(\mathbf{k})$ ,

$$S(\mathbf{k}) = |(\mathbf{e} \cdot \mathbf{k}) + H_1(\mathbf{k}, \mathbf{R}_j) (\mathbf{e} \cdot \boldsymbol{\rho})|^2, \quad (35)$$

defines the form of the differential cross section for the molecular photoionization. The investigation of the structural function is, thus, of importance.

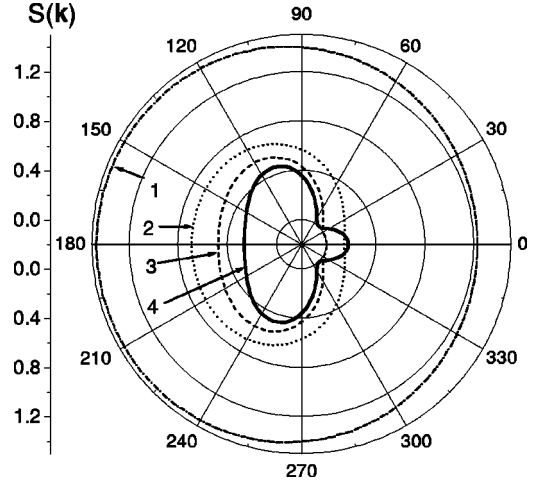


FIG. 1. Structural function  $S(\mathbf{k})$  for the photoionization of the  $1s$  level of the C atom in the CO molecule showing the dependence on the angle between the photoelectron momentum  $\mathbf{k}$  and the molecular axis  $\mathbf{R}_j$  in the case when  $\mathbf{R}_j$  is parallel to the photon polarization vector  $\mathbf{e}$ . Calculated results are for  $k=0.1$  (curve 1),  $k=0.3$  (curve 2),  $k=0.5$  (curve 3), and  $k=0.7$  a.u. (curve 4). Note that in this figure as well as in Figs. 2, 3, and 4 below, for clarity, when the value of  $S(\mathbf{k})$  is small, the zero of the radial coordinate on the polar plot is not at the origin, but on the circumference of the innermost circle.

To demonstrate the use of Eqs. (33)–(35), we calculate the form of the photoelectron angular distribution. As an example, we consider the photoionization of the  $1s$  level of the C atom in the CO molecule. This calculation will be carried out by performing preliminary radical simplification in Eq. (34) in which we approximate the exact wave functions of the electron moving in the field of the positive  $\text{C}^+$  ion with a hole in the  $1s$  subshell by plane waves and their spherical components,

$$\Psi_{\mathbf{k}}^+(\mathbf{R}_j) \rightarrow e^{i\mathbf{k} \cdot \mathbf{R}_j}, \quad (36a)$$

$$\chi_{k1}^+(R_j) \rightarrow i j_1(kR_j) - n_1(kR_j). \quad (36b)$$

Here,  $j_1(kR_j)$  and  $n_1(kR_j)$  are spherical Bessel functions [17]. In this approach, the phase shift of the wave function  $\Delta_1(k) = 0$ . The amplitude of the  $s$ -wave elastic scattering by the free O atom and the corresponding phase shift  $\delta_0^j$ , along with the ionization potential of the  $1s$  level ( $I_{1s} \approx 308$  eV) of the C atom are calculated in the Hartree-Fock approximation using the codes of Ref. [28]. The interatomic distance in the CO molecule is known to be  $R_j = 2.13$  au [29]. The coordinate system is chosen so that  $\mathbf{R}_j$  is directed along the  $z$  axis, and vectors  $\mathbf{e}$  and  $\mathbf{k}$  are located in the same plane; the C atom is located at the origin of the polar system of coordinates.

The results of the numerical calculations of  $S(\mathbf{k})$  as a function of the angle between  $\mathbf{k}$  and  $\mathbf{R}_j$  for various values of the photoelectron momentum  $k$  are given in Figs. 1 and 2. The atom scatterer O is on the  $z$  axis at point  $R_j$ . For low momenta (Fig. 1) the behavior of the structural function  $S(\mathbf{k})$  is defined by the second term in Eq. (35) because the first

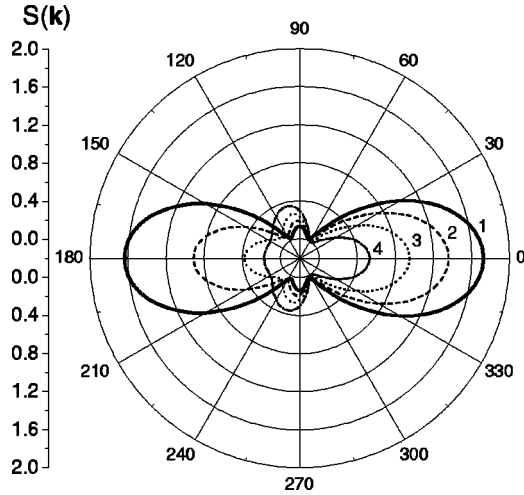


FIG. 2. As Fig. 1 but for  $k=1.5$  (curve 1),  $k=1.3$  (curve 2),  $k=1.1$  (curve 3), and  $k=0.9$  a.u. (curve 4).

term vanishes for  $k \rightarrow 0$ . Therefore, for  $k \rightarrow 0$  the photoelectron angular distribution is close to isotropic. With the increase of momentum  $k$  both terms in Eq. (35) become comparable and the photoelectron angular distribution (Fig. 2) has a more complicated form. For  $k \rightarrow \infty$  the second term remains finite while the first increases. In this case, the structural function is transformed into the angular distribution  $S(\mathbf{k}) \sim (\mathbf{e} \cdot \mathbf{n})^2$  that is typical for the dipole photoionization of a free atom. The same result occurs, of course, for  $R_j \rightarrow \infty$ .

In Fig. 3 the dependence  $S(\mathbf{k})$  on the angle between vectors  $\mathbf{e}$  and  $\mathbf{R}_j$  for fixed photon energy  $\omega = 334$  eV, the same as chosen in Ref. [11], is presented. This figure allows the observation of the evolution of the differential cross section for the molecular photoionization with the variation of this angle. As seen from this figure, the photoelectrons are emit-

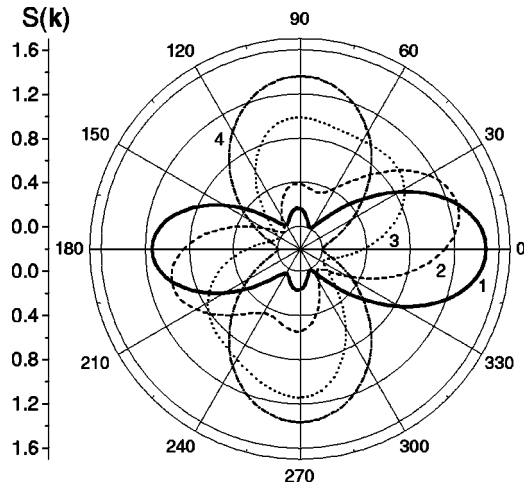


FIG. 3. Structural function  $S(\mathbf{k})$  for the photoionization of the 1s level of the C atom in the CO molecule at  $\omega = 334$  eV showing the dependence on the angle between the photoelectron momentum  $\mathbf{k}$  and the molecular axis  $\mathbf{R}_j$ . Calculated curves are for various values of the angle  $\theta_e$  between the photon polarization vector  $\mathbf{e}$  and the molecular axis  $\mathbf{R}_j$ :  $\theta_e = 0^\circ$  (curve 1),  $\theta_e = 30^\circ$  (curve 2),  $\theta_e = 60^\circ$  (curve 3), and  $\theta_e = 90^\circ$  (curve 4).

ted mainly, as expected, along the  $\mathbf{e}$  vector. The orientations of the curves  $S(\mathbf{k})$  follow the change in the orientation of the vector-polarization polar angle. This result qualitatively agrees with the experimental data [10] and calculations [11] for the photoelectron angular distribution from CO.

#### D. Photodetachment of a negative ion near a neutral atom

Consider the photodetachment of a quasimolecular system that consists of a negative ion located at the coordinate origin and a neutral atom at point  $\mathbf{R}$ . In this case, in Eq. (2), the potential is  $V(r) \equiv 0$ . Therefore, in interatomic space, the molecular continuum wave function is built from the regular  $j_1(kr)$  and irregular  $n_1(kr)$  solutions for a free particle. The simplicity of this two-center model system allows the calculation of the differential photoionization cross section of a quasimolecular negative ion in analytical form.

As in the case of the deep atomic-subshell photodetachment, we approximate the initial state of this molecular system with the wave function of the free negative ion. Then in interatomic space, outside the range of the atomic forces with radii  $\rho_1$  and  $\rho_2$ , the wave function of the ground state is defined by expression  $\Phi_{nl}(\mathbf{r}, \mathbf{R}_j) \propto \exp(-\kappa r)/r$  [14], with the electron affinity  $I_1 = \kappa^2/2$ . The relation  $\tan \delta_0^1(k) = -k/\kappa$  defines the  $s$ -phase shift for electron scattering by the atom that forms the negative ion.

From Eq. (14), the molecular continuum wave function is the superposition of the plane wave and two Green's functions for free motion

$$\Phi_{\mathbf{k}}^-(\mathbf{r}, \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{r}} + C_1^-(\mathbf{k}) \frac{e^{-ikr}}{2\pi r} + C_2^-(\mathbf{k}) \frac{\exp(-ik|\mathbf{r}-\mathbf{R}|)}{2\pi|\mathbf{r}-\mathbf{R}|}. \quad (37)$$

The set of equations for the coefficients, Eq. (19), acquires the form

$$C_1^+(\mathbf{k}) = 2\pi f_0^1 + C_2^+(\mathbf{k}) f_0^1 \frac{e^{ikR}}{R}, \quad (38a)$$

$$C_2^+(\mathbf{k}) = 2\pi f_0^2 e^{i\mathbf{k} \cdot \mathbf{R}} + C_1^+(\mathbf{k}) f_0^2 \frac{e^{ikR}}{R}. \quad (38b)$$

Here,  $f_0^1$  and  $f_0^2$  are the scattering amplitudes by the first and second atoms, which are defined by the  $s$ -phase shifts  $\delta_0^1$  and  $\delta_0^2$ . Note that the formulas similar to Eqs. (37) and (38) but with  $f_0^1 = f_0^2$  were used by Brueckner [30] to describe elastic pion scattering by deuterium, and also by Subramanyan [31] to consider electron scattering by diatomic molecules. The solution of Eqs. (38) is simple. Since, owing to the dipole-selection rules, the first of the coefficients  $C_1^+(\mathbf{k})$  drops out of the dipole-matrix element, we are left with only  $C_2^+(\mathbf{k})$ , which is

$$C_2^+(\mathbf{k}) = \frac{2\pi R \{1 + A_1 \exp[i(\mathbf{k} \cdot \mathbf{R} - kR - \delta_0^1)]\}}{A_1 A_2 \exp[-i(kR + \delta_0^1 + \delta_0^2)] - \exp(ikR)}, \quad (39)$$

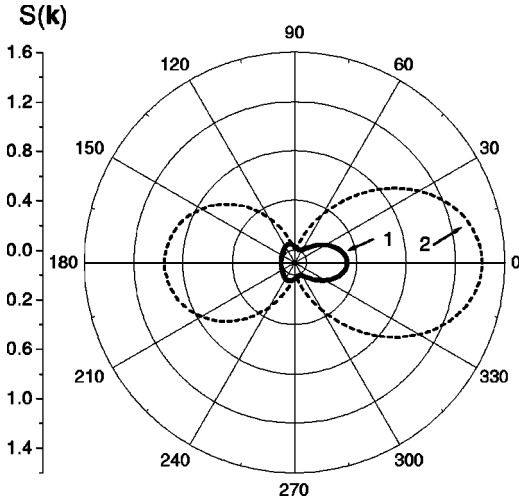


FIG. 4. Structural function  $S(\mathbf{k})$  for the photodetachment of the  $\text{C}^-\text{O}$  quasimolecular ion showing the dependence on the angle between the photoelectron momentum  $\mathbf{k}$  ( $k=0.55$  a.u.) and the molecular axis  $\boldsymbol{\rho}$  in the case when  $\boldsymbol{\rho}$  is parallel to the photon polarization vector  $\mathbf{e}$ . Calculated results are for positive  $a_1$  and  $a_2$  (curve 1) as well as for positive  $a_1$  and negative  $a_2$  (curve 2).

where  $A_i = kR/\sin \delta_0^i$ . Calculating the dipole-matrix element for the transition from the initial state to the continuum, Eq. (37), we obtain

$$S(\mathbf{k}) = \left| \mathbf{e} \cdot \mathbf{k} - \frac{k^2}{2\pi} C_2^+(-\mathbf{k}) [j_1(kR) + in_1(kR)] (\mathbf{e} \cdot \boldsymbol{\rho}) \right|^2. \quad (40)$$

Since the first atom has the extra bound electron, the scattering length of this atom is  $a_1 = -k^{-1} \tan \delta_0^1 > 0$ . The scattering length of the second atom can be either positive or negative.

In Fig. 4, the dependence of  $S(\mathbf{k})$  on the angle between  $\mathbf{k}$  and  $\boldsymbol{\rho}$  for the  $1s$  photodetachment of  $\text{C}^-$  located a distance  $R=2.13$  a.u. from the neutral O atom (referred to as the  $\text{C}^-\text{O}$  quasimolecule), for two different combinations of scattering lengths at fixed  $k=0.55$  a.u., are presented. In these numerical calculations, the scattering lengths  $a_1$  and  $a_2$  were found from the electron affinities of C ( $I_1=1.25$  eV) and O ( $I_2=1.46$  eV) [29]. To investigate  $S(\mathbf{k})$  with different signs of  $a_i$ , the same scattering lengths were used with the sign of  $a_2$  changed. In Fig. 4, the case of the photon polarization vector  $\mathbf{e}$  parallel to the molecular axis  $\boldsymbol{\rho}$  (along the  $z$  axis) is considered. Both curves in this figure are asymmetric. In the first case ( $a_1 > 0, a_2 > 0$ ) this asymmetry is more pronounced. The photoelectrons in the photodetachment of  $\text{C}^-$  are emitted mainly in the direction of the O atom. For  $a_1 > 0$  and  $a_2 < 0$  the curves in the right and left semiplanes are more symmetric. But the photoelectron emission in the direction of the O atom is preferred. It is also found that the curves in Fig. 4 are transformed in a similar manner to those in Fig. 3 when the angle between the vectors  $\mathbf{e}$  and  $\boldsymbol{\rho}$  changes in the interval from  $0$  to  $90^\circ$ , i.e., upon the evaluation from parallel excitation of the quasimolecule to perpendicular (not shown).

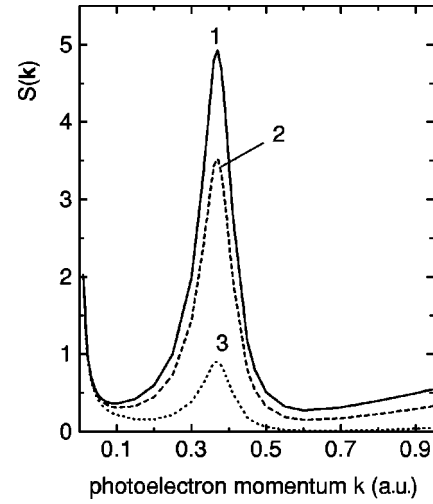


FIG. 5. Structural function  $S(\mathbf{k})$  for the photodetachment of the  $\text{C}^-\text{O}$  quasimolecular ion showing the dependence on  $k$  in the case when the photon polarization vector  $\mathbf{e}$  is parallel to the molecular axis  $\boldsymbol{\rho}$ . Calculated curves are for various values of the angle  $\theta$  between the photoelectron momentum  $\mathbf{k}$  and the molecular axis  $\boldsymbol{\rho}$ :  $\theta=0^\circ$  (curve 1),  $\theta=30^\circ$  (curve 2), and  $\theta=60^\circ$  (curve 3).

Finally, in Fig. 5 the dependence of  $S(\mathbf{k})$  of the photoelectron emission on  $k$  for fixed angles ( $0^\circ$ ,  $30^\circ$ , and  $60^\circ$ ) relative to the molecular axis for parallel molecular excitation ( $\mathbf{e} \parallel \boldsymbol{\rho}$ ) is presented. The curves have a pronounced resonance structure due to the diffraction of the photoelectrons by the neighbor scattering atom, as discussed in Ref. [32]. With increasing emission angle, the diffraction resonance becomes less pronounced, and it disappears completely when  $\mathbf{e}$  is perpendicular to  $\boldsymbol{\rho}$ , which follows from Eq. (40).

### III. CONCLUSION

We have developed a theory of deep-subshell photoionization of atoms confined in fixed-in-space molecules. The theory developed is a good approximation near the photoionization thresholds where the formulas derived are exact expressions within the framework of a non-overlapping central atomic-potential model. This method can be used to describe elastic electron scattering and the photoionization of molecules, clusters and their negative ions of any configuration. The calculated forms of the photoelectron angular distribution for diatomic molecules are in a qualitative agreement with experimental data and the results of other calculations. In contrast to Ref. [2], the present theory ultimately employs no arbitrary parameters, i.e., radii of atomic and molecular spheres. In addition, the constant potential of region II is avoided, and the molecular continuum wave functions (13), unlike Ref. [2], have the correct asymptotic behavior, i.e., the photoelectron wave function far from the molecule, as it should be, has the form of a superposition of the spherical waves generated by all molecular atoms.

Furthermore, it was shown that for initial  $s$  states, the differential cross section factors into two terms with all of the angular information in one of them, the structural function, thereby making it easier to understand the physics of



the situation. This structural function depends only upon the molecular continuum wave function.

It is also important to note that this theoretical methodology is applicable to any multi-atomic system, not only molecules. Thus, it can be applied to clusters and other nanostructures, along with atoms confined in various ways, e.g., inside a fullerene. This will allow the treatment of confined atoms to be extended so that intrinsic atomic resonances, molecular resonances, and confinement resonances [33] can be treated on the same footing.

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