

Rescattering of photodetached electrons from a polar molecule in a static electric field: Spatial distribution

Ilya I. Fabrikant

Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588-0111

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We investigate the spatial distribution of electrons photodetached from a polar molecular anion in an external static electric field. The large electron-molecule scattering amplitude strongly enhances the rescattering effect. This opens an opportunity for experimental investigation of collisions of ultraslow electrons (in the energy range below 0.1 meV) by polar molecules.

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The influence of a static electric field on photodetachment of negative ions has been studied experimentally since 1987 [1]. Theoretical description of spatial distribution of electrons photodetached in a static electric field [2–5] has stimulated first experiments [6,7] of this type. All theoretical treatments used so far neglected the final-state interaction between the electron and the atomic residue. Nevertheless they describe perfectly the existing experimental data [6,7]. This result agrees with the intuitive picture of photodetachment in a static field: if the field is not too strong, at the first stage of the process the spatial distribution is completely controlled by the photon-electron interaction. Very close to the photodetachment threshold this distribution is independent of the electron-atom interaction; in particular, it is spherically symmetric for photodetachment from a p state. At the second stage the electron current is redistributed due to the static field, and this process is independent of the electron-atom interaction. However, this simple picture does not take into account the rescattering effect: a part of the electron flux, moving initially in the direction of the static field, is reflected from the potential barrier and rescattered from the atomic residue. This effect was studied [8,9] for total photodetachment cross sections, and it was found that it becomes significant either for strong static fields or for atoms with large elastic scattering cross sections.

Typically, elastic cross sections for electron-atom scattering are not large enough to induce a substantial rescattering effect at moderate static fields [9]. This was recently confirmed by experimental studies [10] of photodetachment from S^- . The situation might be different for polar molecules due to the large values of electron-dipole scattering cross sections. This is also of a great interest with regard to the connection between negative-ion spectroscopy and electron collisions, since the investigation of electron scattering by polar molecules in the sub-meV range allows detection of very diffuse dipole-supported bound and virtual states [11]. A dipolar potential is an intermediate between a short-range and the Coulomb potential. Photoionization microscopy relevant to the second case was recently studied experimentally [12]. In the present paper we investigate the rescattering effect in spatial distribution of electrons photodetached from a dipolar anion.

Consider the current of photodetached electrons through a plane perpendicular to the static field at the distance z from the molecular anion. We will use atomic units and assume

that the force \mathbf{F} acting on the electron in the static field is directed along positive z axis. The center of mass of the molecular anion is placed at the origin. We start with the equation [2,5] for the ratio R of the electron current density to the photon current density

$$R = \frac{2\pi\omega}{c} \operatorname{Im} \left(u^*(\mathbf{r}) \frac{du(\mathbf{r})}{dz} \right), \quad (1)$$

where ω is the photon's frequency, c is the speed of light, and

$$u(\mathbf{r}) = \int G(\mathbf{r}, \mathbf{r}') (\mathbf{e}_{ph} \cdot \mathbf{r}') \psi_i(\mathbf{r}') d\mathbf{r}', \quad (2)$$

where $\psi_i(\mathbf{r})$ is the electron wave function for the initial state, and $G(\mathbf{r}, \mathbf{r}')$ is the retarded Green's function for the motion in the combined static electric and atomic fields. It satisfies the equation

$$G(\mathbf{r}, \mathbf{r}') = G_F(\mathbf{r}, \mathbf{r}') - \int G_F(\mathbf{r}, \mathbf{r}'') U(\mathbf{r}'') G(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'', \quad (3)$$

where $U(\mathbf{r})$ is the electron-molecule interaction potential, and $G_F(\mathbf{r}, \mathbf{r}')$ is the Green function calculated without the account of potential U . It can be expressed through the time-dependent propagator as [13]

$$G_F(\mathbf{r}, \mathbf{r}') = \frac{i}{(2\pi i)^{3/2}} \int_0^\infty \exp[iS_\tau(\mathbf{r}, \mathbf{r}')] \tau^{-3/2} d\tau, \quad (4)$$

where $S_\tau(\mathbf{r}, \mathbf{r}')$ is the classical action for the motion in the field \mathbf{F} as a function of coordinates \mathbf{r} , \mathbf{r}' , and time τ . Calculation of the integral in the right-hand side(rhs) of Eq. (4) by the stationary phase method leads to the following quasiclassical presentation for $G_F(\mathbf{r}, \mathbf{r}')$ [5]:

$$G_F(\mathbf{r}, \mathbf{r}') = \sum_{n=0}^1 g_n(\mathbf{r}) e^{-i\mathbf{p}_n \cdot \mathbf{r}'}, \quad (5)$$

where

$$g_n(\mathbf{r}) = (2\pi)^{-1} \tau_n^{-3/2} \exp[i(S_{\tau_n} - \pi n/2)] |S''_{\tau_n}|^{-1/2}, \quad (6)$$

and \mathbf{p}_n is the initial momentum of electron, escaping from the origin and arriving at point \mathbf{r} at time τ_n . Double prime in Eq. (6) designates the second derivative in time. Two terms in Eq. (6) correspond to two classical parabolic trajectories contributing to the electron current at point \mathbf{r} .

To solve Eq. (3), we find first a presentation for $G_F(\mathbf{r}, \mathbf{r}')$ and $G(\mathbf{r}, \mathbf{r}')$ near the origin where the effect of static field is small compared to the atomic potential. In addition we make the long-wave approximation, $pr_0 \ll 1$, where p is the momentum of the detached electron, and r_0 is the range of the potential U . Under these assumptions we can generalize previous results [8,9,14] obtained for the p -wave part and the s -wave part of $G_F(\mathbf{r}, 0)$. The result can be written as a sum of the Green function for $F=0$ and the rescattering correction due to the static field which is expressed as a bilinear combination of solutions of the Schrödinger equation with the atomic potential U .

To calculate the spatial distribution for a realistic experiment, we have to propagate this solution to macroscopic distances r . This can be accomplished by substituting the obtained result for G at small r, r' into Eq. (3) and using the quasiclassical representation for $G_F(\mathbf{r}, \mathbf{r}')$, Eq. (5). To present the result for the electron wave function, we introduce the electron momentum \mathbf{k}_0 , corresponding to propagation parallel to the vector \mathbf{F} , and the scattering amplitude $f(\mathbf{p}_n, \mathbf{k}_0)$ whose partial-wave expansion is

$$f(\mathbf{p}_n, \mathbf{k}_0) = \sum_l (2l+1) f_l P_l(\cos \theta_s), \quad (7)$$

where θ_s is the scattering angle, i.e., the angle between vectors \mathbf{p}_n and \mathbf{k}_0 . (We assume one-channel scattering without l mixing). For the wave function, Eq. (2), we obtain

$$u(\mathbf{r}) = \sum_n g_n(\mathbf{r}) \{ M(\mathbf{p}_n) + M(-\mathbf{k}_0) [cf(\mathbf{p}_n, \mathbf{k}_0) + c_0 f_0 + c_1 f_1 \cos \theta_s] \}, \quad (8)$$

where $M(\mathbf{p}_n)$ is the photodetachment matrix element in the absence of the electric field

$$M(\mathbf{p}) = \int \psi_{\mathbf{p}}^{(-)*}(\mathbf{r}) (\mathbf{e}_{ph} \cdot \mathbf{r}) \psi_i(\mathbf{r}) d\mathbf{r}, \quad (9)$$

and c, c_0, c_1 are coefficients depending on E and F . The physical meaning of this result can be seen from Fig. 1. While the first term in braces in Eq. (8) represents direct photodetachment into the state with the electron momentum \mathbf{p}_n , the second term represents photodetachment into the state with momentum $-\mathbf{k}_0$ with the following reflection by the potential barrier and rescattering into one the states \mathbf{p}_n ($n=0,1$).

We will specify now the dependence of the matrix element $M(\mathbf{p})$ on the angle χ between \mathbf{p} and the polarization vector \mathbf{e}_{ph} . For simplicity we will consider photodetachment from a molecular negative ion in the Σ electronic state and the ground rotational state below the threshold for rotational excitation of the neutral molecule whose ground electronic

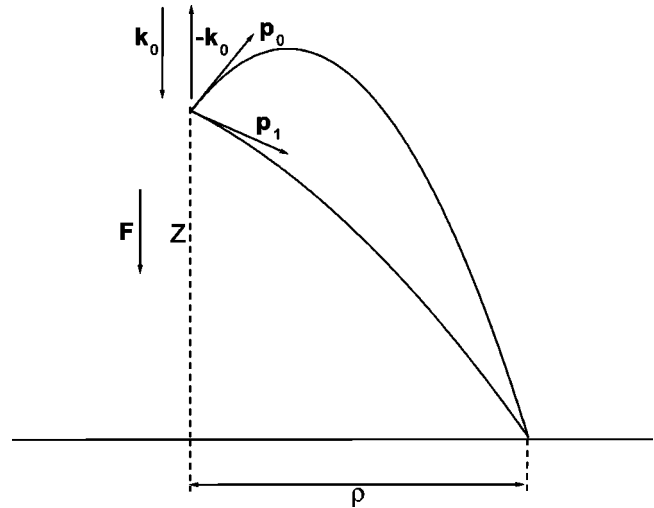


FIG. 1. Geometry of the problem. There are two parabolic trajectories leading to the arrival of electrons at point ρ, z in the observation plane. Electrons leaving the source with momentum $-\mathbf{k}_0$ return to the source with momentum \mathbf{k}_0 and are then rescattered.

state is also Σ . Due to conservation of total angular momentum and dipole selection rules, the photodetachment matrix element $M(\mathbf{p})$ has a p -wave character, that is $M(\mathbf{p}) = M_0(p) \cos \chi$. Furthermore, we will assume the case of so-called π polarization, that is \mathbf{e}_{ph} parallel to \mathbf{F} . Then the scattering amplitude entering Eq. (8) also can be written as a function of $\chi = \theta_s$. In spite of the dominance of the p wave in $M(\mathbf{p})$, the scattering amplitude in Eq. (8) contains, in general, *all* partial waves because of the l mixing due to the static field [8]. For the quantal generalization of the quasiclassical Eq. (8) we will assume that only s -wave and p -wave scattering is important. This is true at energies well below the rotational excitation threshold. In the two-wave approximation we have

$$u(\mathbf{r}) = M_0 \sum_n g_n(\mathbf{r}) (b_0 + b_1 \cos \chi_n), \quad (10)$$

where the coefficients b_0 and b_1 depend on E, F , and partial amplitudes f_0, f_1 . χ_n is the angle between the vectors \mathbf{e}_{ph} and \mathbf{p}_n . The quantal generalization of Eq. (10) follows from the exact integral representation of the Green function G_F , Eq. (4):

$$u(\mathbf{r}) = M_0 \left[b_0 + \frac{b_1}{ip} \left(2z \frac{\partial}{\partial x^2} - \frac{F}{2} \frac{\partial}{\partial E} \right) \right] G_F(\mathbf{r}, 0). \quad (11)$$

The quantal expression (11) should be used when either the parameter $\beta = 2p^3/3F$ is of the order of 2π or smaller [5] or for \mathbf{r} close to the classically forbidden region. For calculation of the rhs of Eq. (11) we use the analytical form of G_F given by Slonim and Dalidchik [15]. At large (macroscopic) distance r , the following representation is valid:

$$G_F(\mathbf{r},0) = -\frac{iz^{1/4}(2F)^{1/12}}{2\pi^{1/2}r} \exp\left[i\left(\frac{2}{3}z^{3/2}(2F)^{1/2} + \frac{\pi}{4}\right)\right] \text{Ai}\left((2F)^{1/3}\left(\frac{\rho^2}{4z} - \frac{E}{F}\right)\right), \quad (12)$$

where $\rho^2 = x^2 + y^2$. Using this representation and taking $b_1 = 0$ in Eq. (11), we can recover the result [7] for photodetachment from an atomic p state (isotropic angular distribution for $F=0$) without rescattering.

For presentation of results, it is convenient to introduce the quantity

$$P = R/\sigma_{F=0}, \quad (13)$$

where R is given by Eq. (1), and $\sigma_{F=0}$ is the total photodetachment cross section for the zero field. P does not depend on M_0 , therefore its calculation does not require the knowledge of the wave functions ψ_i and $\psi_p^{(-)}$.

For illustration of the theory we have chosen the process of photodetachment from LiF^- . The LiF molecule is known to have a positive electron affinity, 0.33 eV [16], and a fairly large dipole moment, 2.49 a.u. supporting two excited states of LiF^- [17]. The binding energy of the second excited state is very small, of the order of 10^{-5} eV or even less [18]. This leads to a very large elastic-scattering cross section, of the order of 10^{-10} – 10^{-9} cm² in the low-energy region, and makes the rescattering effect strong. It should be noted that such a large value of the cross section is a typical feature in electron scattering by polar molecules, since a partial cross section for a fixed dipole is formally divergent at zero energy, and only the inclusion of rotation makes it finite [17]. The scattering amplitude was obtained by numerical integration of the rotational close-coupling equations with a model potential fitted to reproduced the known electron affinity of LiF .

In Figs. 2 and 3 we present the normalized flux, Eq. (13), as a function of the distance ρ between the center of the observation plane and the observation point, for two values of the static field, 2 and 10 V/cm. The chosen values of the distance z , electric field F , and electron energy E are in the range used in experiments [7].

To understand the main features of the curves, note that in the absence of rescattering the outgoing electron flux in the quasiclassical approximation can be written as [5]

$$j(\mathbf{r}) = h_1(\mathbf{r}) - h_2(\mathbf{r})\sin[\Delta S(\mathbf{r})], \quad (14)$$

where $h_1(\mathbf{r})$, $h_2(\mathbf{r})$ are positive functions, and $\Delta S(\mathbf{r})$ is the difference between classical actions for the two interfering trajectories. At macroscopic distances between the anion and the observation screen $h_1 = h_2$, therefore we observe zeros in the flux distribution at $\Delta S = \pi/2 + 2\pi n$, $n = 0, 1, \dots$. At $\rho = 0$ $\Delta S \equiv \beta = 2p^3/3F$, and we observe a dark spot at the center if $\beta = \pi/2 + 2\pi n$, and the bright spot if $\beta = -\pi/2 + 2\pi n$. The presence of the rescattering term in Eq. (8) influences the flux distribution in two ways. First, functions h_1 and h_2 become unequal, therefore the flux does not reach zero at minima (a contrast reduction). Second, the complex

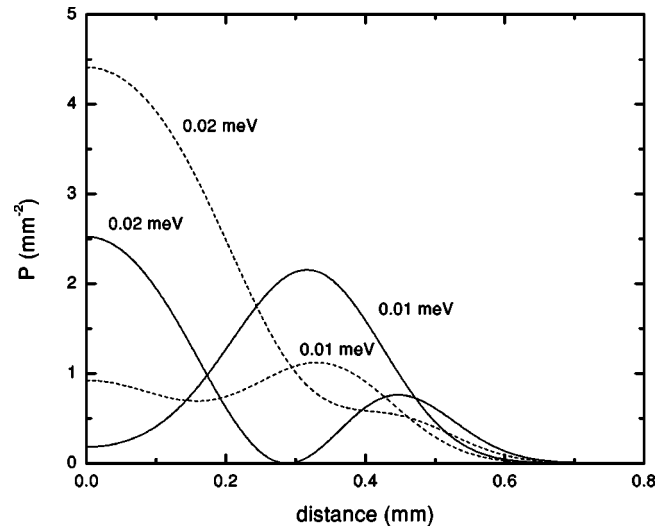


FIG. 2. The electron flux distribution, Eq. (13), as a function of the distance ρ between the center of the observation plane and the observation point, for photodetachment of LiF^- in parallel fields. The electric field is $F=2$ V/cm, the final-state electron energies are $E=0.01$ and 0.02 meV, and the distance between the interaction region and the observation plane is $z=50$ cm. Solid lines, calculation without rescattering; dashed line, calculation including the rescattering effect.

scattering amplitude creates a phase shift in the oscillating term that leads to shifting of maxima and minima. A combination of these two effects can lead to disappearance of a minimum, as, for example, in case $F=2$ V/cm, $E=0.02$ meV.

The rescattering effect decreases fast for higher energies and becomes weak when the number of interference rings reaches 3. This trend can be described by two parameters: the parameter β , introduced above, which characterizes the spreading of the reflected electron wave, and the rescattering parameter $\gamma = aF^{1/3}$, where a is the effective scattering length which can be estimated as $|f_0|$. The strength of the

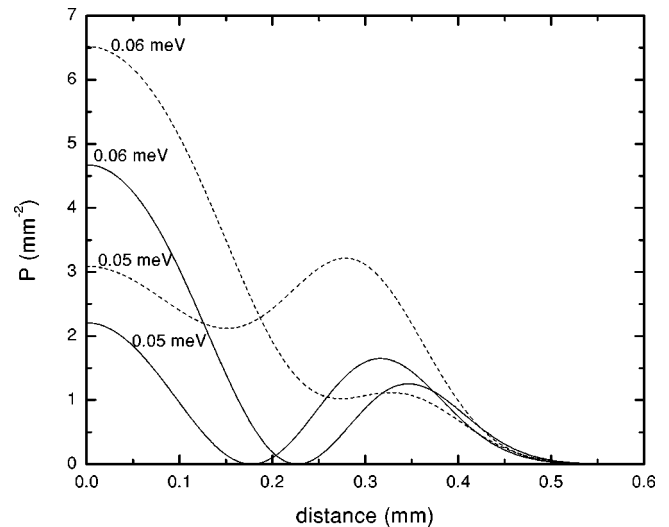


FIG. 3. The same as in Fig. 1 for $F=10$ V/cm, $E=0.05$ and 0.06 meV.

rescattering effect is characterized by $\gamma/\beta \approx aF/p^2$. This ratio varies between 1 and 0.28 in the examples presented in Figs. 1 and 2, and goes down to 0.077 at $F=2$ V/cm, $E=0.05$ meV.

Observations of the discussed features can provide information about scattering of ultraslow electrons by polar molecules. In fact, even the term “photodetachment microscopy” used in previous studies [3,6,7] was not completely

justified as long as they were dealing with a free electron wave propagating in a static field. The results obtained in the present paper indicate a direction in which future experiments should move towards practical realization of the “photodetachment microscope” [3].

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