

Dynamic two-center resonant photoionization in slow atomic collisions.

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(Dated: June 16, 2022)

An additional channel opens for photoionization of atom A by an electromagnetic field if it traverses a gas of atoms B resonantly coupled to this field. We show that this channel, in which A is ionized via resonant photoexcitation of B with subsequent energy transfer to A through two-center electron correlations and which is very efficient when A and B constitute a bound system, can strongly dominate the ionization of A also in collisions where the average distance between A and B exceeds the typical size of a bound system by orders of magnitude.

PACS numbers: 34.10.+x 34.50.Fa 34.50.Rk 32.80.-t, 32.80.Hd,

INTRODUCTION

The breakup of bound microscopic systems by photoabsorption is characterized by well defined energy and momentum transfers, which often enables one to extract precise information about the process and the system itself. Studies of photo-induced breakup reactions – such as atomic photoionization (PI), molecular photodissociation, and nuclear photo-disintegration – have therefore played a key role in our understanding of the structure and dynamics of matter on a microscopic scale.

Electron correlations are omnipresent in the quantum world, ranging from atoms and small molecules to organic macromolecules and solids. They drive autoionization of atoms and ions and mutual electron transitions in high-energy ion-atom collisions [1]-[2], can result in de-excitation reactions in very slow atomic collisions [3] and in ultracold quantum gases [4], govern energy transfer between chromophores [5] and lattice dynamics in polymers [6], and are even responsible for magnetism and superconductivity [7]. Electron correlations coupling different atoms, which occur in bound systems with more than one atomic center, lead to inter-atomic Coulombic decay of inner-shell vacancies [8] – an autoionization-type reaction representing a kind of a two-center Auger decay – observed in dimers and clusters [9–11] and water molecules [12]. Inter-atomic electron correlations can greatly enhance recombination processes [13, 14] and lead to resonances in electron scattering on two-atomic systems [14].

Particularly clean manifestations of electron correlations are revealed in some PI processes, e.g. in single-photon double ionization [15], in atomic autoionization triggered by photoabsorption [16], in non-sequential double ionization in strong laser fields [17] and resonant two-center PI [18]. In the latter, ionization of a large-size molecule occurs via resonant photoabsorption by one of its atoms with subsequent transfer of excitation energy via two-center electron correlations to another atom lead-

ing to its ionization. This two-center ionization channel can be remarkably effective strongly dominating over the usual direct single-center PI and it was experimentally observed in helium-neon dimers using synchrotron radiation [19].

In this communication we study a dynamic variant of resonant two-center PI occurring in slow atomic collisions (see fig. 1). The average distance R between colliding atoms is (many) orders of magnitude larger than in a bound system and the probability for the two-center PI scales as R^{-6} [18]. Therefore, it might seem at first sight that in collisions the two-center ionization channel becomes already completely negligible. However, it turns out, quite unexpectedly, that it can dominate PI also in collisions.

Atomic units are used throughout unless otherwise stated.

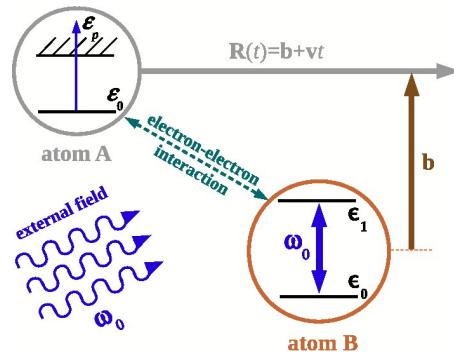


FIG. 1: Scheme of photoionization in atomic collisions.

GENERAL CONSIDERATION

Two-center ionization

Let us consider a collision between two atoms, A and B , which are initially (at $t \rightarrow -\infty$) in their ground states, supposing that the binding energy in the ground state of A is smaller than an excitation energy of a dipole allowed transition from the ground state in B .

We shall assume the collision to be slow enough such that practically no excitation (or ionization) of the colliding partners is possible if A and B enter the collision being in their ground states. This is the case if $\omega_{fi}a_0/v \gg 1$ (Massey adiabatic criterion, see e.g. [20]), where ω_{fi} and a_0 are typical transition frequency and linear size, respectively, of A and/or B and v is the collision velocity.

However, if atom B is coupled to an electromagnetic (EM) field resonant to a dipole transition between its ground and excited states, then the incident atom A can be ionized by absorbing the excitation energy of B via dynamic two-center electron correlations.

We shall consider only very distant collisions, in which the interaction between A and B is quite weak and their nuclei move practically undeflected, and assume that, although the collision velocity is low, the relative motion of the nuclei can still be regarded as classical. In a reference frame, where atom B is at rest and taken as the origin, atom A moves along a classical straight-line trajectory $\mathbf{R}(t) = \mathbf{b} + \mathbf{v}t$, where $\mathbf{b} = (b_x, b_y, 0)$ is the impact parameter and $\mathbf{v} = (0, 0, v)$ the collision velocity. In this frame the collision is described by the Schrödinger equation

$$i\frac{\partial\Psi(t)}{\partial t} = \hat{H}(t)\Psi(t), \quad (1)$$

where the total Hamiltonian is given by

$$\hat{H}(t) = \hat{H}^A + \hat{H}^B + \hat{V}^{AB} + \hat{W}^A + \hat{W}^B. \quad (2)$$

Here, \hat{H}^A (\hat{H}^B) is the Hamiltonian of a free (non-interacting) atom A (B), and

$$\hat{V}^{AB} = \frac{\mathbf{r} \cdot \boldsymbol{\xi}}{R^3(t)} - 3\frac{(\mathbf{R}(t) \cdot \mathbf{r})(\mathbf{R}(t) \cdot \boldsymbol{\xi})}{R^5(t)} \quad (3)$$

is the interaction between A and B , where \mathbf{r} ($\boldsymbol{\xi}$) is the coordinate of the electron of A (B) with respect to the nucleus of A (B). Further, \hat{W}^A (\hat{W}^B) is the interaction of A (B) with the external EM field which will be taken as a classical linearly polarized field $\mathbf{F}_0 \cos(\omega t - \mathbf{k} \cdot \boldsymbol{\xi})$ ($\mathbf{F} = \mathbf{F}_0 \cos(\omega t - \mathbf{k} \cdot (\mathbf{R} + \mathbf{r}))$), where \mathbf{F}_0 is the field strength, ω the field frequency and \mathbf{k} the wave vector ($\mathbf{F}_0 \cdot \mathbf{k} = 0$). The interactions \hat{W}^A and \hat{W}^B read

$$\begin{aligned} \hat{W}^A &= \frac{\mathbf{A}(\mathbf{r}, t) \cdot \hat{\mathbf{p}}_r}{c} + \frac{\mathbf{A}^2(\mathbf{r}, t)}{2c^2} \\ \hat{W}^B &= \frac{\mathbf{A}(\boldsymbol{\xi}, t) \cdot \hat{\mathbf{p}}_\xi}{c} + \frac{\mathbf{A}^2(\boldsymbol{\xi}, t)}{2c^2}, \end{aligned} \quad (4)$$

where $\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \sin(\omega t - \mathbf{k} \cdot (\mathbf{R} + \mathbf{r}))$ ($\mathbf{A}(\boldsymbol{\xi}, t) = \mathbf{A}_0 \sin(\omega t - \mathbf{k} \cdot \boldsymbol{\xi})$) with $\mathbf{A}_0 = -c\mathbf{F}_0/\omega$ is the vector potential of the EM field at the position of the electron of atom A (B) and $\hat{\mathbf{p}}_r$ ($\hat{\mathbf{p}}_\xi$) is the momentum operator for the electron of atom A (B). Below these interactions are taken in the dipole approximation: $\mathbf{k} \cdot \mathbf{r} = 0$, $\mathbf{k} \cdot \boldsymbol{\xi} = 0$.

We first include the interaction between atom B and the EM field by replacing the ground state ϕ_0 (with an energy ϵ_0) and the excited state ϕ_1 (with an energy ϵ_1) of non-interacting atom B by its field-dressed bound states,

$$\phi^\pm(t) = \alpha_0^\pm(t)\phi_0 + \alpha_1^\pm(t)\phi_1, \quad (5)$$

where $\alpha_0^\pm(t)$ and $\alpha_1^\pm(t)$ are time-dependent coefficients to be determined. We assume that the field is switched on adiabatically at $t \rightarrow -\infty$ and impose the boundary conditions $\phi^+(t \rightarrow -\infty) = \phi_0 \exp(-i\epsilon_0 t)$, $\phi^-(t \rightarrow -\infty) = \phi_1 \exp(-i\epsilon_1 t)$.

Using the first order of perturbation theory in the interaction \hat{W}^B we obtain

$$\begin{aligned} \alpha_0^+(t) &= \exp(-i\epsilon_0 t) \\ \alpha_1^+(t) &= \frac{W_{10}^B}{(\Delta + i\Gamma_{rad}^B/2)} \exp(-i(\epsilon_0 + \omega)t) \end{aligned} \quad (6)$$

and

$$\begin{aligned} \alpha_0^-(t) &= -\frac{W_{01}^B}{(\Delta + i\Gamma_{rad}^B/2)} \exp(-i(\epsilon_1 - \omega)t) \\ \alpha_1^-(t) &= \exp(-i\epsilon_1 t), \end{aligned} \quad (7)$$

where $\Delta = \epsilon_0 + \omega - \epsilon_1$ is the detuning, Γ_{rad}^B the width of the excited state ϕ_1 due to its spontaneous radiative decay and $W_{10}^B = 0.5 \langle \phi_1 | \mathbf{F}_0 \cdot \boldsymbol{\xi} | \phi_0 \rangle$ ($W_{01}^B = (W_{10}^B)^*$).

If $|W_{10}^B| > \Gamma_{rad}^B$ ($|W_{10}^B| \gg \Gamma_{rad}^B$) the first order perturbation theory is no longer valid and instead we may use the rotating wave-approximation [21] to get

$$\begin{aligned} \alpha_0^+(t) &= \sqrt{\frac{\Omega + |\Delta|}{2\Omega}} \exp(-i(\epsilon_+ - \omega)t) \\ \alpha_1^+(t) &= \frac{2W_{10}^B}{\sqrt{2\Omega(\Omega + |\Delta|)}} \frac{\Delta}{|\Delta|} \exp(-i\epsilon_+ t) \end{aligned} \quad (8)$$

and

$$\begin{aligned} \alpha_0^-(t) &= \sqrt{\frac{\Omega - |\Delta|}{2\Omega}} \exp(-i(\epsilon_- - \omega)t) \\ \alpha_1^-(t) &= -\frac{2W_{10}^B}{\sqrt{2\Omega(\Omega - |\Delta|)}} \frac{\Delta}{|\Delta|} \exp(-i\epsilon_- t), \end{aligned} \quad (9)$$

where $\epsilon_\pm = \epsilon_1 + 0.5(|\Delta| \pm \Omega) \Delta / |\Delta|$ are the quasi-energies of the field-dressed states.

Using the states (5), the first order perturbation theory with respect to the interaction \hat{V}^{AB} , and keeping in mind that at $t \rightarrow -\infty$ both atoms were in the ground states

we obtain that the two-center ionization amplitudes for atom A reads

$$a_{0 \rightarrow \mathbf{p}}^{2c,\pm} = i \int_{-\infty}^{+\infty} dt \exp(i(\varepsilon_p - \varepsilon_0)t) \langle \psi_{\mathbf{p}} \phi^{\pm} | \hat{V}_{AB} | \psi_0 \phi^+ \rangle (10)$$

where ψ_0 with an energy ε_0 is the ground state of atom A and $\psi_{\mathbf{p}}$ with an energy ε_p describes an electron emitted with an asymptotic momentum \mathbf{p} (all the quantities refer to the rest frame of A) [22].

Performing the integration over time in (10) we obtain

$$\begin{aligned} a_{0 \rightarrow \mathbf{p}}^{2c,\pm} = & \frac{2i\beta^{\pm}}{v} s_p^{\pm} \left(K_1(s_p^{\pm}) \frac{\mathbf{r}_{\mathbf{p},0} \cdot \boldsymbol{\xi}_{0,1} - z_{\mathbf{p},0} \xi_{z_{0,1}}}{b^2} \right. \\ & + s_p^{\pm} K_0(s_p^{\pm}) \frac{z_{\mathbf{p},0} \xi_{z_{0,1}}}{b^2} \\ & - i q s_p^{\pm} K_1(s_p^{\pm}) \frac{(\mathbf{r}_{\mathbf{p},0} \cdot \mathbf{b}) \xi_{z_{0,1}} + (\mathbf{b} \cdot \boldsymbol{\xi}_{0,1}) z_{\mathbf{p},0}}{b^3} \\ & \left. - s_p^{\pm} K_2(s_p^{\pm}) \frac{(\mathbf{r}_{\mathbf{p},0} \cdot \mathbf{b}) (\mathbf{b} \cdot \boldsymbol{\xi}_{0,1})}{b^4} \right). \end{aligned} \quad (11)$$

Here, $s_p^+ = |\varepsilon_p - \varepsilon_0 - \omega|b/v$, $s_p^- = |\varepsilon_p - \varepsilon_0 - \omega - \Omega\Delta/|\Delta||b/v$, $q = (\varepsilon_p - \varepsilon_0 - \omega)/|\varepsilon_p - \varepsilon_0 - \omega|$, $\mathbf{r}_{\mathbf{p},0} = \langle \psi_{\mathbf{p}} | \mathbf{r} | \psi_0 \rangle$, $z_{\mathbf{p},0} = \langle \psi_{\mathbf{p}} | z | \psi_0 \rangle$, $\boldsymbol{\xi}_{0,1} = \langle \phi_0 | \boldsymbol{\xi} | \phi_1 \rangle$, $\xi_{z_{0,1}} = \langle \phi_0 | \xi_z | \phi_1 \rangle$ and K_n ($n = 0, 1, 2$) are the modified Bessel functions [24]. In the first order perturbation theory in the interaction $\hat{W}^B \beta^+ = W_{10}^B / (\Delta + i\Gamma_{rad}^B/2)$ and $\beta^- \approx 0$. In the rotating-wave approximation $\beta^+ = W_{10}^B/\Omega$ and $\beta^- = \sqrt{(\Omega - |\Delta|)/(\Omega + |\Delta|)} W_{10}^B/\Omega$.

The differential, $\frac{dP^{2c}(b)}{d^3\mathbf{p}}$, and total, $P^{2c}(b)$, ionization probabilities are given by

$$\frac{dP^{2c}(b)}{d^3\mathbf{p}} = \frac{dP^{2c,+}(b)}{d^3\mathbf{p}} + \frac{dP^{2c,-}(b)}{d^3\mathbf{p}} \quad (12)$$

with

$$\frac{dP^{2c,\pm}(b)}{d^3\mathbf{p}} = \frac{1}{2\pi} \int_0^{2\pi} d\varphi_{\mathbf{p}} |a_{0 \rightarrow \mathbf{p}}^{2c,\pm}|^2, \quad (13)$$

where the integration runs over the azimuthal angle $\varphi_{\mathbf{p}}$ of the impact parameter \mathbf{b} , and

$$P^{2c}(b) = P^{2c,+}(b) + P^{2c,-}(b), \quad (14)$$

with

$$P^{2c,\pm}(b) = \int d^3\mathbf{p} \frac{dP^{2c,\pm}(b)}{d^3\mathbf{p}}. \quad (15)$$

The differential cross section, which describes the spectra of electrons emitted via the two-center channel in collisions with the impact parameters $b \geq b_{min} \gg 1$, read

$$\frac{d\sigma^{2c}}{d^3\mathbf{p}} = \frac{d\sigma^{2c,+}}{d^3\mathbf{p}} + \frac{d\sigma^{2c,-}}{d^3\mathbf{p}}, \quad (16)$$

where

$$\frac{d\sigma^{2c,\pm}}{d^3\mathbf{p}} = 2\pi \int_{b_{min}}^{+\infty} db b \frac{dP^{2c}(b)}{d^3\mathbf{p}}. \quad (17)$$

In (17) the integration runs over the absolute value of the impact parameter. In particular, after some rather lengthy calculations we obtain that

$$\begin{aligned} \frac{d\sigma^{2c,\pm}}{d^3\mathbf{p}} = & \frac{1}{2\pi} |\beta^{\pm}|^2 |\xi_{01}|^2 \frac{r_{p,0}^2}{p^2} \frac{(s_p^{\pm})^2 b_{min}^2}{v^4} \times \\ & ((s_p^{\pm})^2 (K_1^2(s_p^{\pm}) - K_0^2(s_p^{\pm})) \cos^2(\vartheta_p) \\ & + (s_p^{\pm} K_1(s_p^{\pm}) K_0(s_p^{\pm}) \\ & - \frac{(s_p^{\pm})^2}{2} (K_1^2(s_p^{\pm}) - K_0^2(s_p^{\pm}))) \sin^2(\vartheta_p) \end{aligned} \quad (18)$$

if the field is polarized along the z -direction (along the collision velocity) and

$$\begin{aligned} \frac{d\sigma^{2c,\pm}}{d^3\mathbf{p}} = & \frac{1}{2\pi} |\beta^{\pm}|^2 |\xi_{01}|^2 \frac{r_{p,0}^2}{p^2} \frac{(s_p^{\pm})^2 b_{min}^2}{v^4} \times \\ & (s_p^{\pm} K_0(s_p^{\pm}) K_1(s_p^{\pm}) \\ & - \frac{1}{2} (s_p^{\pm})^2 (K_1^2(s_p^{\pm}) - K_0^2(s_p^{\pm})) \cos^2(\vartheta_p) \\ & + \frac{1}{4} (s_p^{\pm})^2 (K_1^2(s_p^{\pm}) - K_0^2(s_p^{\pm})) \sin^2(\vartheta_p) \\ & + \left(\frac{1}{2} K_1^2(s_p^{\pm}) + \frac{1}{8} (s_p^{\pm})^2 (K_1^2(s_p^{\pm}) - K_0^2(s_p^{\pm})) \right) \\ & \times \sin^2(\vartheta_p) \end{aligned} \quad (19)$$

if the field is polarized along the x -direction. In (18)-(19) $r_{p,0} = \int_0^{+\infty} dr r^3 u_{p,1}(r) u_0(r)$ is the radial matrix element for transitions between the ground and continuum states of atom A with u_0 and $u_{p,1}$ being their radial parts (the ground state of atom A was assumed to be an s -state and $u_{p,1}$ denotes the continuum radial wave with the orbital quantum number $l = 1$). Further, $\xi_{01} = \frac{1}{\sqrt{3}} \int_0^{+\infty} d\xi \xi^3 d_0(\xi) d_1(\xi)$ where d_0 and d_1 are the radial parts of the ground and excited states of atom B .

The modified Bessel functions $K_n(x)$ ($n = 0, 1, 2, \dots$) diverge at $x \rightarrow 0$ and decrease exponentially at $x > 1$ [24]. Therefore, in distant low-velocity collisions ($b \geq b_{min} \gg 1, v \ll 1$) the main contribution to the total cross section is given by a small interval of emission energies $\delta\varepsilon_p \sim v/b \ll 1$ centred at $\varepsilon_{p,r} = \varepsilon_0 + \omega$. If this interval is much less than a typical energy range $\Delta\varepsilon_p$ in which the quantity $r_{p,0}^2/p$ substantially varies ($\Delta\varepsilon_p \sim 10$ eV for atoms and $\Delta\varepsilon_p \sim 1$ eV for negative ions), then $r_{p,0}^2/p$ remains within $\delta\varepsilon_p$ roughly a constant, $r_{p,0}^2/p \approx r_{p,r,0}^2/p_r$ where $p_r = \sqrt{2(\varepsilon_0 + \omega)}$, and we obtain that

$$P^{2c,\pm}(b) = \frac{3\pi\alpha}{16} |\beta^{\pm}|^2 |\xi_{01}|^2 \frac{r_{p,r,0}^2}{p_r} \frac{1}{v b^5}, \quad (20)$$

$$P^{2c}(b) = \frac{3\pi\alpha}{16} (|\beta^+|^2 + |\beta^-|^2) |\xi_{01}|^2 \frac{r_{p,r,0}^2}{p_r} \frac{1}{v b^5} \quad (21)$$

and

$$\sigma^{2c,\pm}(b) = \frac{\pi^2\alpha}{8v} |\beta^{\pm}|^2 |\xi_{01}|^2 \frac{r_{p,r,0}^2}{p_r} \frac{1}{b_{min}^3}, \quad (22)$$

$$\sigma^{2c}(b) = \frac{\pi^2 \alpha}{8v} (|\beta^+|^2 + |\beta^-|^2) |\xi_{01}|^2 \frac{r_{p_r,0}^2}{p_r} \frac{1}{b_{min}^3}, \quad (23)$$

where $\alpha = 1$ ($\alpha = \frac{3}{2}$) if the field is polarized along the z -axis (x - or y -axis).

Taking into account that atom A moves in a gas of atoms B , the total ionization rate per unit of time via the two-center channel is given by

$$\begin{aligned} \mathcal{K}^{2c} &= \sigma^{2c} n_B v \\ &= \frac{\pi^2 \alpha}{8} (|\beta^+|^2 + |\beta^-|^2) |\xi_{01}|^2 \frac{r_{p_r,0}^2}{p_r} \frac{n_B}{b_{min}^3}, \end{aligned} \quad (24)$$

where n_B is the density of atoms B . The rate \mathcal{K}^{2c} , which turned out to be velocity independent, is proportional to n_B and by increasing it the two-center ionization process can be made more effective. However, there is a limitation on the upper boundary of n_B set by the condition that the gas has to remain transparent for the EM field. At the resonance the excitation cross section reaches a large value: $\sigma_{excit} = 3\pi(c/\omega)^2 \gg \pi a_0^2$. The mean free path λ for the EM field in the gas of atoms B can be estimated according to $\lambda = 1/(n_B \sigma_{excit})$ and it has to be larger than the size l_B of the gas target, $\lambda > l_B$, in order that the target remains transparent for the EM field.

Single-center ionization

The amplitude for the direct (single-center) ionization of atom A is given by

$$\begin{aligned} a_0^{1c} \rightarrow \mathbf{p} &= \frac{i}{2} \int_{-\infty}^{+\infty} dt \exp(i(\varepsilon_p - \varepsilon_0 - \omega)t) \langle \psi_{\mathbf{p}} \phi^+ | \mathbf{F}_0 \cdot \mathbf{r} | \psi_0 \phi^+ \rangle \\ &= \pi i \langle \psi_{\mathbf{p}} | \mathbf{F}_0 \cdot \mathbf{r} | \psi_0 \rangle \delta(\varepsilon_p - \varepsilon_0 - \omega). \end{aligned}$$

This channel is described by the differential, $dK^{1c}/d^3\mathbf{p}$, and total, K^{1c} , decay rates per unit of time which read

$$\frac{dK^{1c}}{d^3\mathbf{p}} = \frac{1}{16\pi} \frac{r_{p_r,0}^2}{p_r^2} f(\vartheta_{\mathbf{p}}, \varphi_{\mathbf{p}}) F_0^2 \delta(\varepsilon_p - \varepsilon_0 - \omega) \quad (26)$$

and

$$K^{1c} = \frac{1}{12} \frac{r_{p_r,0}^2}{p_r} F_0^2, \quad (27)$$

where the value $p_r = \sqrt{2(\varepsilon_0 + \omega)}$ follows from the energy conservation expressed by the delta-function in (26). The angular distribution is given by the function $f(\vartheta_{\mathbf{p}}, \varphi_{\mathbf{p}})$ depended on the polar, $\vartheta_{\mathbf{p}}$, and azimuthal, $\varphi_{\mathbf{p}}$, emission angles of the electron. For instance, $f = \cos^2 \vartheta_{\mathbf{p}}$ if $\mathbf{F}_0 = (0, 0, F_0)$ and $f = \sin^2 \vartheta_{\mathbf{p}} \cos^2 \varphi_{\mathbf{p}}$ if $\mathbf{F}_0 = (F_0, 0, 0)$.

Two-center versus single-center ionization

The competition between the two-center and single-center ionizations is natural to characterize by the ratio

$\eta = \mathcal{K}^{2c}/\mathcal{K}^{1c}$. Using (27) and (24) we obtain

$$\begin{aligned} \eta &= \frac{K_{2c}}{K_{1c}} \\ &= \frac{3\pi^2 \alpha}{2} (|\beta^+|^2 + |\beta^-|^2) |\xi_{01}|^2 \frac{n_B}{b_{min}^3}. \end{aligned} \quad (28)$$

Inserting into (28) expressions for β^{\pm} , derived within the first order in the interaction \hat{W}^B , results in

$$\eta = \frac{3\pi^2 \alpha}{8} \frac{n_B}{b_{min}^3} \frac{|\xi_{01}|^4}{\Delta^2 + (\Gamma_{rad}^B)^2/4}. \quad (29)$$

Since $\Gamma_{rad}^B = \frac{4}{3} \frac{\omega^3}{c^3} |\xi_{01}|^2$, at the resonance ($\Delta = 0$) the ratio becomes

$$\eta = \frac{27\pi^2 \alpha}{32} \frac{n_B}{b_{min}^3} \left(\frac{c}{\omega} \right)^6. \quad (30)$$

In stronger fields, where the rotating-wave approximation should be used instead of the first-order perturbation theory, the ratio becomes smaller and decreases with increasing the field.

RESULTS AND DISCUSSION

Let us now apply formula (30) to the following collision systems:

- i) H(1s) (atom A , $|\varepsilon_0| \approx 13.6$ eV) – He(1s²) (atom B);
- ii) Li(1s² 2s) (atom A , $|\varepsilon_0| \approx 5.39$ eV) – H(1s) (atom B);
- iii) K(4s) (atom A , $|\varepsilon_0| \approx 4.3$ eV) – Si (3p²) (atom B);
- iv) Li(2s) (atom A , $|\varepsilon_0| \approx 5.6$ eV) – Mg(3s) (atom B);
- v) H⁻(1s 1s') ('atom' A , $|\varepsilon_0| \approx 0.7$ eV) – Li(2s) (atom B);
- vi) H⁻(1s 1s') ('atom' A , $|\varepsilon_0| \approx 0.7$ eV) – Rb(5s) (atom B).

i. H(1s) – He(1s²): Considering that the field is in resonance with the 1s² - 1s2p transition in helium ($\omega \approx 21$ eV) we obtain that at $b_{min} = 10$ a.u. $\eta \geq 1$ provided $n_B \geq 2.6 \times 10^{13} \text{ cm}^{-3}$. However, at $n_B = 6.76 \times 10^{13} \text{ cm}^{-3}$ the mean free path λ of the radiation in a gas of helium atoms would be merely 4.6×10^{-3} cm. Thus, for this collision system a substantial enhancement of photo ionization (by factor of 2) from distant collisions due to the two-center channel would be possible only for very small-size helium gas targets.

ii. Li(2s) – H(1s): Assuming that the field is resonant to the 1s - 2p transition in hydrogen ($\omega \approx 10$ eV) $\eta \geq 1$ with $b_{min} = 10$ a.u. is reached if $n_B \geq 3 \times 10^{11} \text{ cm}^{-3}$. At the density $n_B = 3 \times 10^{11} \text{ cm}^{-3}$ $\lambda \approx 0.09$ cm which means that the size of the target should not exceed 1 mm in order that the two-center correlations in distant collisions yield a substantial contribution to PI.

iii. K(4s) – Si (3p²): Considering that the field is in resonance with the 3p - 4s transition in silicon ($\omega \approx 4.9$ eV) we obtain that with $b_{min} = 10$ a.u. $\eta \geq 1$ if

$n_B \geq 4.2 \times 10^9 \text{ cm}^{-3}$. At $n_B = 4.2 \times 10^9 \text{ cm}^{-3}$ the mean free path λ of the radiation in a gas of silicon atoms is about 1.6 cm. Thus, for this collision system a substantial enhancement of PI from distant collisions due to the two-center channel would be possible for gas targets not exceeding ~ 2 cm.

iv. $\text{Li}(2s) - \text{Mg}(3s)$: Assuming that the field is resonant to the $3s - 4p$ transition in magnesium ($\omega \approx 6.1$ eV) we get that $\eta \geq 1$ at $b_{min} = 10$ a.u. provided $n_B \geq 1.56 \times 10^{10} \text{ cm}^{-3}$. At the density $n_B = 1.56 \times 10^{10} \text{ cm}^{-3}$ $\lambda \approx 0.65$ cm which means that the size of the target should not exceed 5-7 mm in order that the two-center contribution from distant collisions doubles the ionization rate.

v. $\text{H}^-(1s 1s') - \text{Li}(2s)$: Considering that the field is resonant to the $2s-2p$ transition in lithium ($\omega \approx 1.85$ eV) we obtain that $\eta \geq 1$ at $b_{min} = 10$ a.u. is reached at $n_B \geq 1.2 \times 10^7 \text{ cm}^{-3}$. At $n_B = 1.2 \times 10^7 \text{ cm}^{-3}$ the mean free path of the radiation in lithium is already rather large, $\lambda \approx 77$ cm. Since the typical size of targets in experiments with lasers is normally of the order of 1 mm, one can increase the target density by about 800 times which will reduce its size of transparency to the above 1 mm. Then $\eta \approx 800$ with $b_{min} = 10$ a.u. and even with b_{min} as large as 50 a.u. one still obtains $\eta \sim 6-7$. Thus, for $\text{H}^- - \text{Li}$ system already very distant collisions may result in a strong enhancement of photo detachment from H^- caused by the two-center ionization channel.

vi. $\text{H}^-(1s 1s') - \text{Rb}(5s)$: Considering that the field is resonant to the $5s_{1/2}-5p_{3/2}$ transition in rubidium ($\omega \approx 1.59$ eV) we obtain that at $b_{min} = 10$ a.u. $\eta \geq 1$ provided $n_B \geq 4.88 \times 10^6 \text{ cm}^{-3}$. At $n_B = 4.88 \times 10^6 \text{ cm}^{-3}$ the mean free path of the radiation in rubidium is $\lambda \approx 140$ cm. For rubidium targets with the size $l_B \approx 1$ mm the transparency condition ($\lambda \lesssim l_B$ cm) allows one to increase the target density up to $n_B \approx 1.4 \times 10^3 \times 4.88 \times 10^6 \approx 6.8 \times 10^9 \text{ cm}^{-3}$ resulting in $\eta \approx 1.4 \times 10^3$ with $b_{min} = 10$ a.u. and even with $b_{min} = 50$ a.u. the ratio is still quite large, $\eta \approx 11$. Thus, for $\text{H}^- - \text{Rb}$ collision system the effect is even larger than for $\text{H}^- - \text{Li}$ one.

Unlike the rates \mathcal{K}^{1c} and \mathcal{K}^{2c} their ratio η does not depend on the transition matrix element of A . Therefore, we can apply (29)-(30) also if 'atom' A is in fact a molecule. In particular, for photo dissociation of I_2 ($|\varepsilon_0| \approx 1.57$ eV) in collisions with Li ($\omega \approx 1.85$ eV) or Rb ($\omega \approx 1.59$ eV) we obtain the same enhancements as for the $\text{H}^- - \text{Li}$ and $\text{H}^- - \text{Rb}$ systems.

Since, according to our estimates, the inclusion of the contribution from collisions with $b < b_{min}$ (not taken into account here) strongly increases η , the effectiveness of the two-center channel seems to be really amazing. Indeed, let us put it into a perspective: in a gas of atoms B with $n_B \sim 10^{10} \text{ cm}^{-3}$ the average distance R_{av} between the atoms A and B ($R_{av} \sim 1/n_B^{1/3}$) is about $2.5 \times 10^{-4} \text{ cm} \sim 10^4\text{-}10^5$ a.u. and nevertheless the two-center mechanism

may still strongly dominate ionization of A . One of the reason for such a high effectiveness of this channel is that the effective mean distance R_{eff} between the atoms in the collision, where the energy exchange between them is most likely to occur, is given by $R_{eff} \sim \sqrt{b_{min}/n_B^{1/3}}$ and turns out to be much smaller than R_{av} .

CONCLUSION

In conclusion, photoionization of atom A in an external electromagnetic field can strongly increase if it moves with a low velocity in a gas of atoms B which are in a dipole resonance with this field. This enhancement is caused by the transmission – via the dynamic two-center electron correlations – of photo-excitation energy from atom B , which acts as a very efficient antenna absorbing quanta from the field, to atom A resulting in ionization of the latter.

Two-center correlations are already known as an extremely efficient mechanism of 'communication' between parts of a bound system whose size R is typically of the order of few or several Bohr radii. At $R \gg 1$ most of the two-center processes show the R^{-6} scaling and the largest distances probed so far ($R \lesssim 10^2$ a.u.) were in helium dimers [11].

In collisions the average distance between the atoms reaches tens of thousands of the Bohr radii. Nevertheless, the two-center correlations turn out to be quite effective also in collisions. This, in particular, suggests that a large variety of inter-atomic phenomena extensively investigated recently in bound systems, can play a role in collisions as well.

It is planned that a Rb gas target with up to 20% atoms transferred from the ground state ($5^2S_{1/2}$ to the excited $5^2P_{3/2}$ -state by a weak resonant ($\omega \approx 1.5$ eV) continuous laser field, which functions at the Institute of Modern Physics, will be combined in the near future with a beam of ~ 100 eV H^- in order to perform an experiment on the two-center PI in slow atomic collisions.

Acknowledgement.

We thank B. Kullmann for his contribution at an early stage of this study and J. Yang for useful conversations. We acknowledge the support from the National Key Research and Development Program of China (Grant No. 2017YFA0402300), the German Research Foundation (DFG) (the projects MU 3149/4-1 and VO 1278/4-1), the program "One Hundred Talented People" of the Chinese Academy of Sciences and the CAS President's Fellowship Initiative. A. B. V. is grateful for the hospitality of the Institute of Modern Physics.

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