Dynamic two-center resonant photoionization in slow atomic collisions

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Abstract

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

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) [1, 2], molecular photodissociation [3], and nuclear photo-disintegration [4]—therefore deepen our understanding of the structure and dynamics of matter on a microscopic scale. Notably, photoionization and photodissociation allow to probe the fundamental role played by electron correlations.

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 [5, 6], can result in de-excitation reactions (e.g. Penning effect) in slow atomic collisions [7] and in ultracold quantum gases [8], govern energy transfer between chromophores [9] and lattice dynamics in polymers [10], and are even responsible for magnetism and superconductivity [11]. Electron correlations between atoms in bound systems with more than one atomic center lead to inter-atomic Coulombic decay (ICD) [12] observed in dimers and clusters [13–16] and water molecules [17]. Inter-atomic electron correlations can greatly enhance recombination processes [18, 19] and lead to resonances in electron scattering on two-atomic systems [19].

Particularly clean manifestations of electron correlations are revealed in some PI processes, e.g. in single-photon double ionization [20], non-sequential double ionization in strong laser fields [21] and resonant two-center PI [22]. 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 leading to its ionization. This two-center ionization channel can be remarkably effective and strongly dominate over the usual direct single-center PI. It was experimentally observed in helium–neon dimers using synchrotron radiation [23].

In this communication we study a dynamic variant of resonant two-center PI occurring in slow atomic collisions (see figure 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 $R^{-6}$ [22]. Therefore, it might seem at first sight that in collisions the two-center ionization channel becomes completely negligible. However, it turns out, quite unexpectedly, that it can dominate PI also in collisions.

Atomic units are used throughout unless otherwise stated.

Let us consider a collision between two atoms, A and B, which are initially (at $t \to -\infty$) 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 \( \omega fi A_0 / \nu \gg 1 \) (Massey adiabatic criterion, see e.g. [24]), where \( \omega fi \) and \( A_0 \) are typical transition frequency and linear size, respectively, of A and/ or B and \( \nu \) is the collision velocity. (We note that the condition \( \omega fi A_0 / \nu \gg 1 \) roughly corresponds to impact energies below 1 keV u \(^{-1} \).) 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 undected. In distant collisions electron transfer processes are not very likely and can be neglected. Indeed, in such collisions the overlap of electronic states of their nuclei move practically unde

Moreover, due to the relative motion of the atoms this overlap effectively diminishes further since even in closer collisions there might be not enough time for an electron to make a transfer to the other atomic center.

Even though the collision velocity is low, we shall assume that the relative motion of the nuclei can still be regarded as classical (the corresponding conditions are discussed, for instance, on pp 108–111 of [25], they are fulfilled down to impact energies as low as \( \sim 1 \) eV u \(^{-1} \)).

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 \( \mathbf{v} = (0, 0, \nu) \) the collision velocity. In this frame the collision is described by the equation

\[
\frac{i \partial \Psi(t)}{\partial t} = \hat{H}(t) \Psi(t),
\]

where the total Hamiltonian is given by

\[
\hat{H}(t) = \hat{H}^A + \hat{H}^B + \hat{V}^{AB} + \hat{W}^A + \hat{W}^B.
\]

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

\[
\hat{V}^{AB} = \frac{\mathbf{r} \cdot \mathbf{\xi}}{R(t)^2} - \frac{3(\mathbf{R}(t) \cdot \mathbf{r})(\mathbf{R}(t) \cdot \mathbf{\xi})}{R^2(t)}
\]

is the interaction between A and B, where \( \mathbf{r} (\mathbf{\xi}) \) is the coordinate of the electron of A (B) with respect to the nucleus of A (B). The ’electrostatic’ approximation (3) for the inter-atomic interaction can be used if the distance \( R \) is not too large: \( R \ll c / \omega fi \), where \( c \) is the speed of light and \( \omega fi \), the frequency of the virtual photon transmitting the interaction (see e.g. [18, 22, 26]).

Further, \( \hat{W}^A (\hat{W}^B) \) in (2) is the interaction of A (B) with the external EM field which will be taken as a classical linearly polarized field \( \mathbf{F} = F_0 \cos(\omega t - \mathbf{k} \cdot (\mathbf{R} + \mathbf{r})) (\mathbf{F} = F_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{\xi})) \), where \( F_0 \) is the field strength, \( \omega \) the field frequency and \( \mathbf{k} \) the wave vector (\( F_0 \cdot \mathbf{k} = 0 \)). The interactions \( \hat{W}^A \) and \( \hat{W}^B \) read

\[
\hat{W}^A = \frac{A(\mathbf{r}, t) \cdot \hat{p}_r}{c} + \frac{A^2(\mathbf{r}, t)}{2c^2},
\]

\[
\hat{W}^B = \frac{A(\mathbf{\xi}, t) \cdot \hat{p}_\xi}{c} + \frac{A^2(\mathbf{\xi}, t)}{2c^2},
\]

where \( A(\mathbf{r}, t) = A_0 \sin(\omega t - \mathbf{k} \cdot (\mathbf{R} + \mathbf{r})) \) \( (A(\mathbf{\xi}, t) = A_0 \sin(\omega t - \mathbf{k} \cdot \mathbf{\xi})) \) with \( A_0 = -eF_0 / \omega \) is the vector potential of the EM field at the position of the electron of atom A (B) and \( \hat{p}_r (\hat{p}_\xi) \) is the momentum operator for...
the electron of atom A (B). Below these interactions are taken in the dipole approximation: \( \mathbf{k} \cdot \mathbf{r} = 0, \mathbf{k} \cdot \mathbf{\xi} = 0. \) Besides, since it is assumed that \( kr = R/(\epsilon/\omega) \approx R/(\epsilon/\omega_p) \ll 1, \) we also set \( \mathbf{k} \cdot \mathbf{R} = 0. \)

We first include the interaction between atom B and the EM field by replacing the ground state \( \phi_0 \) (with an energy \( \epsilon_0 \)) and the excited state \( \phi_1 \) (with an energy \( \epsilon_1 \)) of non-interacting atom B by its field-dressed bound states

\[
\phi^\pm(t) = \alpha_0^\pm(t) \phi_0 + \alpha_1^\pm(t) \phi_1,
\]

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 \( t \to -\infty \) and impose the boundary conditions

\[
\phi^\pm(t \to -\infty) = \phi_0 \exp(-i\epsilon_0 t), \phi^\pm(t \to -\infty) = \phi_1 \exp(-i\epsilon_1 t).
\]

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

\[
\alpha_0^\pm(t) = \frac{W_{01}^B}{(\Delta + i\Gamma_{\text{rad}}^B/2)} \exp(-i(\epsilon_0 + \omega) t)
\]

and

\[
\alpha_1^\pm(t) = -\frac{W_{01}^B}{(\Delta + i\Gamma_{\text{rad}}^B/2)} \exp(-i(\epsilon_1 - \omega) t)
\]

where \( \Delta = \epsilon_0 + \omega - \epsilon_1 \) is the detuning, \( \Gamma_{\text{rad}}^B \) the width of the excited state \( \phi_1 \) due to its spontaneous radiative decay and \( W_{01}^B = -\frac{1}{2} \langle \phi_1 | A_0 \cdot \hat{p}_z | \phi_0 \rangle = \frac{1}{2} \langle \phi_1 | F_0 \cdot \mathbf{\xi} | \phi_0 \rangle \) \( (W_{01}^B)^* = (W_{01}^B)^\ast \). Expressions (6), (7) can be used provided \( |W_{01}^B| \ll \Gamma_{\text{rad}}^B/2 \) \( (|W_{01}^B| \ll \Gamma_{\text{rad}}^B) \).

Using the states (5), the first order perturbation theory with respect to the interaction \( \hat{V}_{AB} \), and keeping in mind that at \( t \to -\infty \) both atoms were in the ground states we obtain that the two-center ionization amplitude for atom A reads

\[
a_{2c^\pm} \equiv i \int_{-\infty}^{+\infty} dt \exp(i(\epsilon_p - \epsilon_0) t) \langle \psi_p^\pm | \hat{V}_{AB} | \psi_0 \rangle ,
\]

where \( \psi_0 \) with an energy \( \epsilon_0 \) is the ground state of atom A, \( \psi_p \) with an energy \( \epsilon_p \) describes an electron emitted with an asymptotic momentum \( \mathbf{p} \), and \( \phi^\pm \) are determined by equations (5)–(7). We note that all these quantities refer to the rest frame of A. Besides, in our derivation we have neglected the Doppler shift and the coupling to the scalar potential which appears in a moving reference frame [27] that is justified due to the low collision velocity.

Performing the integration over time in (8) we obtain

\[
a_{2c^\pm} = \int_{-\infty}^{+\infty} \frac{2i\beta^\pm}{\nu} \left( \begin{array}{c} \mathbf{r}_{p,0} \cdot \mathbf{\xi}_{0,1} - \mathbf{z}_{p,0} \cdot \mathbf{\xi}_{z1} \\ b^2 \\ - i a \mathbf{z}_{p,0} \cdot \mathbf{b} \mathbf{z}_{z1} + (b \cdot \mathbf{\xi}_{0,1}) \mathbf{z}_{p,0} - a \mathbf{z}_{p,0} \cdot \mathbf{b} \cdot \mathbf{\xi}_{0,1} \end{array} \right) \frac{d\mathbf{r}_{p,0}}{b^2} + s_p N_p \left( \frac{r_{p,0} \cdot \mathbf{b} \cdot \mathbf{\xi}_{0,1}}{b^4} \right).
\]

Here, \( s_p = |\Delta_p|/\nu \) and \( a = \Delta_p/|\Delta_p| \) with \( \Delta_p = \epsilon_p - \epsilon_0 - \omega \). We note that \( \Delta_p/\nu \) represents the minimum momentum transfer in the collision. Further, \( r_{p,0} = \langle \psi_p | \mathbf{r} | \psi_0 \rangle, z_{p,0} = \langle \psi_p | \mathbf{z} | \psi_0 \rangle, \mathbf{\xi}_{0,1} = \langle \phi_0 \mathbf{\xi} | \phi_1 \rangle \), \( \mathbf{\xi}_{n} \) \( (n = 0, 1, 2) \) are the modified Bessel functions [28]. Besides, \( \beta^+ = W_{01}^B/(\Delta + i\Gamma_{\text{rad}}^B/2) \) and \( \beta^- \approx 0. \)

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

\[
d\sigma_{2c} = \int_{b_{\text{min}}}^{b_{\text{max}}} db \int_0^{2\pi} d\varphi \mathbf{b} |a_{2c^\pm}|^2 ,
\]

where the integrations run over the azimuthal angle \( \varphi \) of \( \mathbf{b} \) and its absolute value. In particular, if the field is polarized along the z-axis, we obtain after rather lengthy calculations that

\[
d\sigma_{2c} = \left| \frac{1}{2\pi} |\beta^\pm| |\mathbf{\xi}_{0,1}| f_{p,0}^2 \right|^2 \frac{f_p^2}{v^2} \left( \frac{b_{\text{min}}}{\nu^2} \right)^2 
\times \left( f_p^2 K_0(f_p) - K_1(f_p) \right) \cos \varphi \left( f_p K_1(f_p) K_0(f_p) - 0.5 f_p^2 K_1^2(f_p) K_0^2(f_p) \right) \sin^2 \varphi ,
\]

where \( f_p = s_p(b = b_{\text{min}}), r_{p,0} = \int_{-\infty}^{+\infty} dr r^1 u_{p,0}(r) \) is the radial matrix element for transitions between the ground and continuum states of atom A with \( u_{p,0} \) 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, \( \zeta_{01} = \frac{1}{\sqrt{3}} \int_{0}^{+\infty} d\xi \xi^2 d_{0}(\xi) d_{1}(\xi) \) where \( d_{0} \) and \( d_{1} \) are the radial parts of the ground and excited states of atom B.

The functions \( K_{b}(x) (n = 0, 1, \ldots) \) diverge at \( x \to 0 \) and decrease exponentially at \( x \to 1 \) [28]. Therefore, in distant low-velocity collisions \( b \gg b_{\text{min}} \gg 1 \), the main contribution to the total cross section stems from a very small interval of emission energies centered at \( \varepsilon_{p,r} = \varepsilon_{0} + \omega \) with width \( \delta \varepsilon_{p} \sim v/b \). Since \( \delta \varepsilon_{p} \) is much less than a typical energy range \( \Delta \varepsilon_{p} \), in which the quantity \( r_{p}^{2}/p \) substantially varies \( (\Delta \varepsilon_{p} \sim 10 \text{ eV for atoms and} \Delta \varepsilon_{p} \sim 1 \text{ eV for negative ions}) \), \( r_{p}^{2}/p \) remains within \( \delta \varepsilon_{p} \) roughly a constant, \( r_{p}^{2}/p \approx r_{p,0}^{2}/p \) \( (p_r = \sqrt{2}(\varepsilon_{0} + \omega)) \). Then the contribution \( \sigma_{\text{2e}} \) to the total cross section from collisions with \( b \gg b_{\text{min}} \) is given by

\[
\sigma_{2e} = \frac{\pi^{2} \alpha}{8 \nu} |\beta_{+}^{0}|^{2} |\zeta_{01}|^{2} \frac{r_{p,0}^{2}}{p_{r}} \frac{1}{b_{\text{min}}},
\]

(12)

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

Since atom A moves in a gas of atoms B, the ionization rate per unit of time via the two-center channel reads

\[
\mathcal{K}^{2e} = \sigma_{2e} n_{B} v = \frac{\pi^{2} \alpha}{8} |\beta_{+}^{0}|^{2} |\zeta_{01}|^{2} \frac{r_{p,0}^{2}}{p_{r}} \frac{n_{B}}{b_{\text{min}}},
\]

(13)

where \( n_{B} \) is the density of atoms B. The velocity-independent rate \( \mathcal{K}^{2e} \) linearly increases with \( n_{B} \). However, there is an upper limit on the value of \( n_{B} \) because the gas has to remain transparent for the EM field. At the resonance the excitation cross section is very large (see e.g. [29]): \( \sigma_{\text{excit}} = 3\pi (c/\omega)^{2} \gg \pi a_{0}^{2} \). The mean free path for the EM field in the gas of atoms B is given by \( \lambda = 1/(n_{B} \sigma_{\text{excit}}) \) and it has to be larger than the size of the gas target.

Having derived the two-center ionization rate we shall now briefly discuss the single-center photoionization.

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

\[
a_{0}^{+} = \frac{-i}{2 \varepsilon} \int_{-\infty}^{+\infty} dt \exp(i(\varepsilon_{p} - \varepsilon_{0} - \omega) t) \langle \psi_{p}|A_{0} \cdot \hat{p}_{r}|\psi_{0}\rangle
\]

\[= \pi \langle \psi_{p}|F_{0} \cdot r|\psi_{0}\rangle \delta(\varepsilon_{p} - \varepsilon_{0} - \omega).
\]

(14)

This channel is described by the differential, \( d\mathcal{K}^{1e}/d\mathbf{p} \), and total, \( \mathcal{K}^{1e} \), decay rates per unit of time which read

\[
\frac{d\mathcal{K}^{1e}}{d\mathbf{p}} = \frac{1}{16\pi} \frac{r_{p,0}^{2}}{p_{r}^{2}} f(\varepsilon_{p}, \varphi_{p}) F_{0}^{2} \delta(\varepsilon_{p} - \varepsilon_{0} - \omega)
\]

and

\[
\mathcal{K}^{1e} = \frac{1}{12} \frac{r_{p,0}^{2}}{p_{r}} F_{0}^{2}.
\]

(16)

The angular distribution is given by the function \( f(\vartheta_{p}, \varphi_{p}) \) depending on the polar, \( \vartheta_{p} \), and azimuthal, \( \varphi_{p} \), emission angles of the electron. For instance, \( f = \cos^{2}\vartheta_{p} \) if \( F_{0} = (0, 0, F_{0}) \) and \( f = \sin^{2}\vartheta_{p} \cos^{2}\varphi_{p} \) if \( F_{0} = (F_{0}, 0, 0) \).

**Two-center versus single-center ionization.** The competition between the two-center and single-center ionizations can be characterized by the ratio \( \eta = \mathcal{K}^{2e}/\mathcal{K}^{1e} \). Using (16) and (13) we obtain

\[
\eta = \frac{3\pi^{2} \alpha}{2} |\beta_{+}^{0}|^{2} |\zeta_{01}|^{2} \frac{n_{B}}{b_{\text{min}}}. \]

(17)

Using the explicit form of \( \beta_{+}^{0} \) results in

\[
\eta = \frac{3\pi^{2} \alpha}{2} n_{B} \frac{|\zeta_{01}|^{4}}{b_{\text{min}}^{3}} \Delta^{2} + (\Gamma_{\text{rad}}^{B})^{2}/4.
\]

(18)

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

\[
\eta = \frac{27\pi^{2} \alpha}{32} \frac{n_{B}}{b_{\text{min}}^{3}} \left( \frac{c}{\omega} \right)^{6}.
\]

(19)

In stronger fields, where \( |W_{01}^{B}| > \Gamma_{\text{rad}}^{B}/2 \) \( (|W_{01}^{B} | > \Gamma_{\text{rad}}^{B}) \) and the first order of perturbation theory in the interaction \( \mathcal{W}_{\text{B}} \) is no longer valid, the so called rotating-wave approximation can be used instead [30]. One can show that in such fields the ratio \( \eta \) becomes smaller and decreases with increasing the field.
Let us now apply equation (19) to three collision systems.

(i) K(4s) (atom A, \( |\epsilon_0| \approx 4.3 \text{ eV} \))–Si (3p\(^2\)) (atom B): considering that the field is in resonance with the 3p–4s transition in silicon (\( \omega \approx 4.9 \text{ eV} \)) we obtain that \( n \geq 1 \) at \( b_{\text{min}} = 10 \text{ a.u.} \) if \( n_B \geq n_0^B = 4.2 \times 10^8 \text{ cm}^{-3} \). At \( n_B = n_0^B \) the mean free path \( \lambda \) 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 \( \sim 2 \text{ cm} \).

(ii) Li(2s) (atom A, \( |\epsilon_0| \approx 5.39 \text{ eV} \))–Mg(3s) (atom B): assuming that the field is resonant to the 3s–4p transition in magnesium (\( \omega \approx 6.1 \text{ eV} \)) we reach \( n \geq 1 \) at \( b_{\text{min}} = 10 \text{ a.u.} \) and \( n_B \geq n_0^B = 1.56 \times 10^{10} \text{ cm}^{-3} \). Now, at \( n_B = n_0^B \) \( \lambda \approx 0.65 \text{ cm} \) which means that the size of the target should not exceed \( \sim 6–7 \text{ mm} \) in order that the two–center contribution from distant collisions doubles the ionization rate.

(iii) H\(^-\) (1s 1s\(^-'\)) (atom A, \( |\epsilon_0| \approx 0.7 \text{ eV} \))–Rb(5s) (atom B): considering that the field is resonant to the 5s\(_{1/2}\)–5p\(_{1/2}\) transition in rubidium (\( \omega \approx 1.59 \text{ eV} \)) we obtain that \( n \geq 1 \) at \( b_{\text{min}} = 10 \text{ a.u.} \) provided \( n_B \geq n_0^B = 4.88 \times 10^6 \text{ cm}^{-3} \). At \( n_B = n_0^B \) the mean free path of the radiation in rubidium is \( \lambda \approx 140 \text{ cm} \). Since the typical size of targets in experiments with lasers is normally of the order of 1 mm \([31, 32]\), one can increase the target density by three orders of magnitude \( n_B^0 \sim 10^{10} \text{ cm}^{-3} \) which will reduce its size of transparency to the above 1 mm. Then \( n \approx 1.4 \times 10^3 \) with \( b_{\text{min}} = 10 \text{ a.u.} \) and even with \( b_{\text{min}} \) as large as 50 a.u. one still obtains \( n \approx 11 \). Thus, for the H\(^-\)–Rb system already very distant collisions may result in a strong enhancement of photo detachment from H\(^-\) caused by the two–center ionization channel.

Unlike the rates \( K^{X^2} \) and \( K^{Z^2} \) their ratio \( n \) does not depend on the transition matrix element of A. Therefore, we can apply \((18), (19)\) also if atom A is in fact a molecule. In particular, for photo-dissociation of I\(_2\) \( |\epsilon_0| \approx 1.57 \text{ eV} \) in collisions with Li (the 2s–2p transition, \( \omega \approx 1.85 \text{ eV} \)) we obtain an enhancement which is almost as strong as for the H\(^-\)–Rb system.

Since, according to our estimates, the inclusion of the contribution from collisions with \( b < b_{\text{min}} \) (not taken into account here) strongly increases \( n \), the effectiveness of the two–center channel may be regarded as spectacular: in a gas of atoms B with \( n_B \approx 10^{10} \text{ cm}^{-3} \) the average distance between the atoms A and B is about \( 2.5 \times 10^{-4} \text{ cm} \sim 10^3–10^5 \text{ a.u.} \) and nevertheless the two–center mechanism may still strongly dominate ionization of A.

We note in this context that within the present approach the magnitude of \( b_{\text{min}} \) cannot be strictly defined. As was just mentioned, closer collisions (with \( b < b_{\text{min}} \)) are expected to yield a very substantial contribution to two–center PI. Therefore, in an attempt to account for as much of the total rate as possible, in the above three examples the value of \( b_{\text{min}} \) was chosen to be close to the minimum possible value of the impact parameter which still enables one to fulfill the main assumptions of our approach: the nuclei of the colliding particles move along straight–line trajectories, the electrons of the colliding atomic particles essentially do not overlap and the interaction between them can be treated in the dipole–dipole approximation within the first order of perturbation theory.

Due to a steep dependence of the two–center channel on the inter–atomic distance the colliding atoms interact mainly in the vicinity of their closest rapprochement \( (R \sim b) \) that strongly reduces the effective distance. Because of the same reason the ‘electrostatic’ interaction \((\S)\) may be used if \( b_{\text{min}} \ll c/\omega \) (that, in particular, is the case in the examples (i)–(iii) where \( c/\omega \approx 760, 610 \) and 2340 a.u. respectively).

At a fixed interatomic distance \( R \) the two–center–to–single–center ionization ratio \( n_b \) (at the resonance) reads

\[
\eta_b \approx \left( \frac{\omega}{\omega_0} \right)^{1/3} \] [22]. Comparing it with equation (19) we see that the structure of both ratios is similar and that for ionization in atomic collisions the fixed interatomic distance \( R \) is replaced by the quantity \( R_{\text{eff}} \sim (b_{\text{min}} R)^{1/2} \), where \( R \sim n_b^{-1/3} \) is the average distance between the atoms. In this sense \( R_{\text{eff}} \) can be regarded as the ‘effective’ distance between the atoms in the process of collisional two–center PI.

If the density of atoms B is not very high (\( n_B \ll 1/b_{\text{min}}^3 \sim 10^{21}–10^{22} \text{ cm}^{-3} \)) the ‘effective’ distance \( R_{\text{eff}} \) turns out to be much less than the average distance \( R \). This explains why the two–center photoionization channel can still be so effective in collisions, where the average distance between A and B is enormous on the scale of a typical size of bound systems. Nevertheless, one should note that on this scale \( R_{\text{eff}} \) is quite large as well. For instance, taking \( b_{\text{min}} = 10 \text{ a.u.} \) and assuming that \( n_B \approx 10^{10} \text{ cm}^{-3} \) we obtain \( R_{\text{eff}} \approx 10^3 \text{ a.u.} \) which is much smaller than \( R \approx 10^4 \text{ a.u.} \) but still much larger than a typical size of bound atomic systems. This shows that the effectiveness of the two–center photoionization channel in collisions will be overall much weaker than in bound systems.

Compared to two–center PI in the ‘static’ case [22], this process in collisions attains new features. In particular, both angular and energy spectra of the emitted electrons change qualitatively. For instance, the emission cross section \((11)\) vanishes at an energy \( \varepsilon_p = \varepsilon_0 + \omega_0 \) i.e. exactly where its ‘static’ counterpart reaches
maximum [22]. This is caused by (destructive) interference between the contributions to the transition amplitude due to the incoming \((t < 0)\) and outgoing \((t > 0)\) parts of the trajectory \(R(t)\).

The present study focuses on slow collisions \((10 \text{ eV u}^{-1} \lesssim E_{\text{col}} \lesssim 1 \text{ keV u}^{-1})\) for which the connection with two-center reactions in bound systems is relatively close. In addition, using an approach in which all multipoles of the interatomic interaction as well as all impact parameters \((b_{\text{min}} = 0)\) are taken into account, we considered two-center PI in energetic \((\gtrsim 10 \text{ keV u}^{-1})\) collisions where the competing channels of direct impact ionization by the collision partner become effective. It turns out that two-center PI—due to comparatively very small momentum transfers involved in this process—can strongly outperform the ‘normal’ collisional ionization channels up to impact energies \(\approx 25 \text{ keV u}^{-1}\) and is very ‘visible’ at higher energies as well. Besides, since the total cross section for two-center PI scales roughly \(~1/\nu\) up to \(\approx 25 \text{ keV u}^{-1}\), the ratio \(\eta\) of two-center and direct PI remains a constant up to such rather large impact energies.

For collisions considered in this study the retardation effects have a minor impact on the cross section but with increasing the transition frequency they will eventually become of importance. However, as our analysis shows, the standard theoretical approaches being applied to the retarded interaction in collisions, where the minimum momentum transfer is zero, yield unphysical results and thus suitable treatments still have to be developed.

In conclusion, photoionization of an atom \(A\) in an external EM field can strongly increase if it traverses a gas of atoms \(B\) which are in a dipole resonance with this field. This enhancement is caused by the transmission of photo-excitation energy from atom \(B\) to atom \(A\) via dynamic two-center electron correlations.

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. Although in collisions the average distance between the atoms reaches tens of thousands of Bohr radii, the two-center correlations still turn out to be quite effective. This unexpected result forms an interesting connection between the area of interatomic phenomena and the field of atomic collisions: a large variety of interatomic processes extensively investigated in bound systems (e.g. various types of ICD [33], electron capture [34] and recombination [18, 19], resonance scattering [19]) may play a role in collisions as well.

A Rb gas target with a diameter of \(\approx 1.4 \text{ mm}\) and \(n_B \sim 10^{10} \text{ cm}^{-3}\) driven by three weak resonant \((\omega \approx 1.59 \text{ eV})\) continuous lasers currently functions at the Institute of Modern Physics. The lasers produce homogeneous (within a diameter of \(14 \text{ mm}\)) beams with intensity in the crossing area of \(\approx 1 \text{ W cm}^{-2}\) transferring up to 20% of the atoms from the ground 5s1/2 to the excited 5p3/2 state. It is planned to combine the target with a beam of \(\sim 100 \text{ eV H}^-\) (current \(\approx 10 \text{ pA}\), beam size \(\approx 1 \text{ mm}\)). Our estimates show that with the above parameters one can accumulate sufficient numbers of detachment events (with and without the Rb target) for measuring the predicted effects.

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