Two-center dielectronic recombination and resonant photoionization

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We consider radiative recombination and photoionization in an atomic system, which consists of two subsystems A and B. These subsystems are well separated in space and it is supposed that A has a lower ionization potential. In such a case photoionization of A and recombination of an incident electron with A^+ can be strongly influenced, via two-center electron-electron correlations, by resonant electron dipole transitions induced in B. A theoretical description of these two-center resonant dielectronic processes is presented.

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I. INTRODUCTION

Photoionization of atoms and its inverse process of radiative recombination, in which an incident electron recombines with an ion by emitting a photon, are among the basic processes studied by atomic physics.

When an atom is not isolated in space but is a neighbor to another (distant) atom, the electronic structures of these two centers can be coupled by a long-range electromagnetic interaction that leads to a variety of interesting phenomena. For example, the interaction between electrons belonging to different atoms, separated by substantial distances, is responsible for deexcitation processes in slow atomic collisions [1] and the energy transfer in quantum optical ensembles [2] and cold Rydberg gases [3]. They also play an important role in biological systems as Förster resonances between chromophores [4] and represent the origin of magnetism and superconductivity [5].

Another interesting realization of two-center electron-electron coupling is represented by a process in which the electronic excitation energy of one of the atoms cannot be quickly released through a forbidden (single-center) Auger decay and is instead transferred to the partner atom, resulting in its ionization. This interatomic decay process, predicted in [6], has been observed in recent years in various systems such as van der Waals clusters [7], rare gas dimers [8], and water molecules [9].

In addition, a process was studied [10] in which a capture of an incident electron by an ion (or atom) proceeds via the Coulomb interaction of this electron with an electron of a neighboring atom, leading to ionization of the latter. Since the total charge of the two centers is unchanged, such a process effectively results in an interatomic electron exchange.

Very recently, two more processes were considered, in which the interaction between electrons belonging to different neighboring centers may play a prominent role [11,12]. One of them is a capture of an incident electron by a system of two neighboring atomic centers [11]. In this process, which may be termed two-center dielectronic recombination, the electron can be captured by one of the centers due to simultaneous (resonant) excitation of the other center, which subsequently deexcites via spontaneous radiative decay (see Fig. 1). In the other process, which was termed two-center resonant photoionization [12], two centers are irradiated by an electromagnetic field and one of the reaction pathways for ionization of one of the centers is radiationless transfer of excitation from a neighboring center, whose bound states are resonantly coupled by the field (see Fig. 2). In both cases it was found that the presence of a neighboring center can strongly enhance the corresponding process.

The emphasis in [11] and [12] was on the demonstration of the importance of these processes in various cases, whereas their theoretical treatments were outlined just very briefly. It is, therefore, the main intention of the present paper to discuss in some detail a theoretical description of these processes. Atomic units (a.u.) are used throughout unless otherwise stated.

II. GENERAL CONSIDERATION

We shall consider photoionization and radiative recombination in a simple atomic system, which consists of two subsystems (centers) A and B, each having just a single (active) electron. These subsystems are supposed to be separated by a distance R which is large enough in so that one can still speak about their individuality. In addition, this assumption also enables one to treat the electrons as distinguishable particles. Let, for definiteness, the ionization potential I_A of the subsystem A be smaller than the excitation energy ΔE_B of a dipole-allowed transition in the subsystem B. Under such circumstances, if the subsystem A is involved in a process, where it undergoes transitions with frequency close to ΔE_B, this process can be substantially influenced by the presence of the subsystem B.

For instance, if the system under consideration is irradiated by an electromagnetic field with frequency $\omega_0 \approx \Delta E_B$, the presence of the subsystem B may have a strong influence on ionization of the subsystem A. Indeed, in such a case A can be ionized not only directly but also via resonance photoexcitation of B with its consequent deexcitation through the transfer of energy ΔE_B via the electron-electron interaction to A, which results in ionization of the latter.

Another example is represented by a system which initially consists of an incident electron, an ion A^+, and the subsystem B. In such a case, recombination of the incident electron with A^+ can also be strongly influenced by the presence of B if the difference between the initial and final energies of the $(e^- + A^+)$ subsystem is close to ΔE_B.

Let us now turn to the description of the photoionization and recombination processes. Suppose, for simplicity, that the centers A and B are atoms (ions) and that their nuclei, which have charge numbers Z_A and Z_B, respectively, are at rest. We

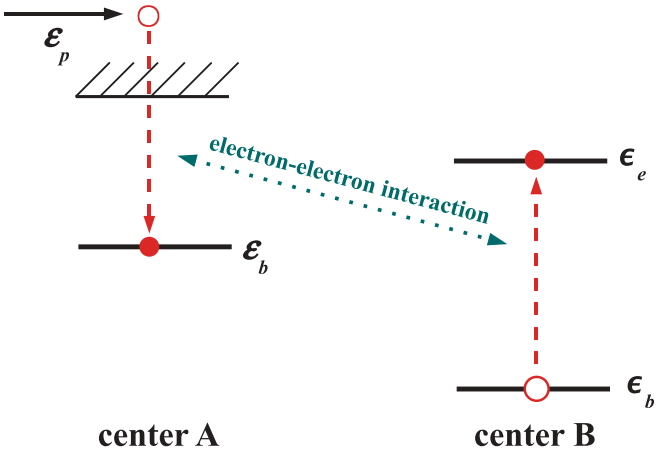

FIG. 1. (Color online) Scheme of two-center dielectronic recombination.

take the position of the nucleus Z_A as the origin and denote the coordinates of the nucleus Z_B, the electron of the atom A, and that of the atom B by $\mathbf{R}$, $\mathbf{r}_1$, and $\mathbf{r}_2 = \mathbf{R} + \boldsymbol{\xi}$, respectively, where $\boldsymbol{\xi}$ is the position of the electron of the atom B with respect to the nucleus Z_B.

In order to treat the processes we adopt the so-called noncovariant QED approach (see, e.g., [13]), which employs the radiation gauge. Within this approach the interaction between electric charges is regarded as occurring via both Coulomb (instantaneous) potentials and the coupling of these charges to the radiation field described by a vector potential.

For distances R much larger than the typical sizes of the centers A and B, which are of relevance for the present study, the two-center electron-electron coupling becomes most efficient when these electrons undergo dipole-allowed transitions. By restricting our attention only to such transitions, the Coulomb part of the electron-electron interaction, $\hat{V}_{AB}$, reduces to the instantaneous interaction between two electric dipoles,

$$V_{AB} = \frac{r_i \xi_j}{R^3}\left(\delta_{ij} - 3\frac{R_i R_j}{R^2}\right), \tag{1}$$

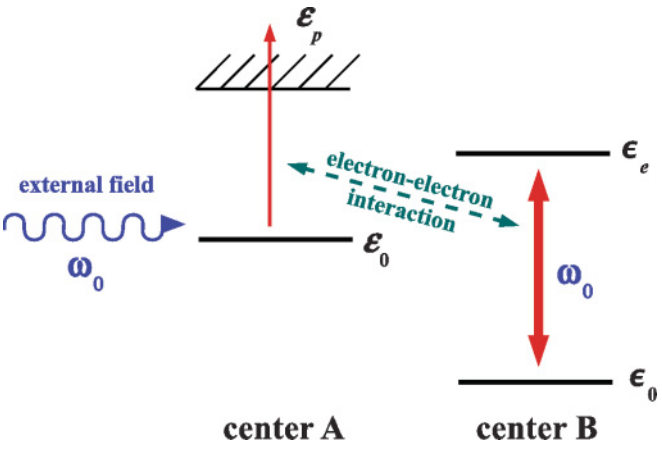

FIG. 2. (Color online) Scheme of two-center resonant photoionization.

where r_i and ξ_j $(i,j = 1,2,3)$ are the components of the coordinates of the electrons, δ_{ij} is 1 for $i = j$ and 0 otherwise, and a summation over the repeated indices is implied.

The vector potential, which describes the radiation field, reads

$$\hat{\mathbf{A}}(\mathbf{r},t) = \sum_{\mathbf{k},\lambda}\sqrt{\frac{2\pi c^2}{V_{\rm ph}\omega_k}}\mathbf{e}_{\mathbf{k},\lambda}[\hat{c}^\dagger_{\mathbf{k},\lambda}\exp(-i\mathbf{k}\cdot\mathbf{r}) + \hat{c}_{\mathbf{k},\lambda}\exp(i\mathbf{k}\cdot\mathbf{r})]. \tag{2}$$

Here $\hat{c}^\dagger_{\mathbf{k},\lambda}$ and $\hat{c}_{\mathbf{k},\lambda}$ are the operators for creation and destruction, respectively, of a photon with momentum $\mathbf{k}$ and polarization λ $(\lambda = 1,2)$, $\mathbf{e}_{\mathbf{k},\lambda}$ is the photon polarization vector ($\mathbf{e}_{\mathbf{k},\lambda_1}\cdot\mathbf{e}_{\mathbf{k},\lambda_2} = \delta_{\lambda_1,\lambda_2}$, $\mathbf{e}_{\mathbf{k},\lambda}\cdot\mathbf{k} = 0$), $\omega_k = c|\mathbf{k}| = ck$ is the photon frequency, c is the speed of light, and $V_{\rm ph}$ is the normalization volume for the field. The sum in Eq. (2) runs over all photon modes.

While the process of recombination involves just one (real) photon, an arbitrary number of photons, depending on the intensity of the electromagnetic field, can, in general, participate in the process of photoionization. In this paper, however, we shall restrict our attention to ionization in a weak field, where only one real photon is initially present (and where the enhancement of the photoionization due to the presence of the center B is largest [12]). In such a case photoionization and recombination are very closely interrelated and can both be treated in a unified manner. In particular, for both radiative recombination and photoionization, the coupling of the electrons to the radiation field is given by

$$\begin{aligned}\hat{W} &= \hat{W}_A + \hat{W}_B \\ &= \frac{1}{c}[\hat{\mathbf{A}}(\mathbf{r}_1,t)\cdot\hat{\mathbf{p}}_1 + \hat{\mathbf{A}}(\mathbf{r}_2,t)\cdot\hat{\mathbf{p}}_2],\end{aligned} \tag{3}$$

where $\hat{\mathbf{p}}_j$ $(j = 1,2)$ is the momentum operator for the jth electron.

By taking into account what has been discussed previously, our consideration of the photoionization and recombination processes shall be based on the equation

$$i\frac{\partial}{\partial t}|\Psi\rangle = (\hat{H}_0 + \hat{V}_{AB} + \hat{W})|\Psi\rangle. \tag{4}$$

Here, $|\Psi\rangle$ is the state vector of the system consisting of the centers A and B and the radiation field, and $\hat{H}_0$ is the sum of the Hamiltonians for the noninteracting centers A and B and the free radiation field. Further, $\hat{V}_{AB}$ and $\hat{W}$ are defined by Eqs. (1) and (3), respectively.

Both in the photoionization and in the recombination processes we have essentially four different basic two-electron configurations: (i) $\psi_g = u_0(\mathbf{r}_1)\chi_0(\boldsymbol{\xi})$ in which both electrons are in the corresponding ground states u_0 and χ_0 with energies ε_0 and ϵ_0, respectively; (ii) $\psi_a = u_0(\mathbf{r}_1)\chi_e(\boldsymbol{\xi})$, in which the electron of the center A is in the ground state, while the electron of the center B is in the excited state χ_e with an energy ϵ_e; (iii) $\psi_{\mathbf{p},g} = u_{\mathbf{p}}(\mathbf{r}_1)\chi_0(\boldsymbol{\xi})$, in which the electron of the center A is in a continuum state $u_{\mathbf{p}}$ with an energy ε_p and the electron of the center B is in the ground state; and (iv) $\psi_{\mathbf{p},e} = u_{\mathbf{p}}(\mathbf{r}_1)\chi_e(\boldsymbol{\xi})$, in which the electron of the center A is in a state $u_{\mathbf{p}}$, while the electron of the center B is in the state χ_e.

Taking also into account that the radiation field can be either in its vacuum state $|0\rangle$ or in a state $|\mathbf{k},\lambda\rangle$, in which one photon with momentum $\mathbf{k}$ and polarization λ is present, one can look for the solution of Eq. (4) by expanding $|\Psi\rangle$ into a "complete"

set of quantum states according to

$$|\Psi\rangle = \left(g\psi_g + a\psi_a + \int d^3\mathbf{p}\,\alpha_{\mathbf{p}}\psi_{\mathbf{p},g} + \int d^3\mathbf{p}\beta_{\mathbf{p}}\psi_{\mathbf{p},e}\right)|0\rangle + \sum_{\mathbf{k},\lambda}\left(g_{\mathbf{k},\lambda}\psi_g + a_{\mathbf{k},\lambda}\psi_a + \int d^3\mathbf{p}\,\alpha_{\mathbf{p}}^{\mathbf{k},\lambda}\psi_{\mathbf{p},g} + \int d^3\mathbf{p}\beta_{\mathbf{p}}^{\mathbf{k},\lambda}\psi_{\mathbf{p},e}\right)|\mathbf{k},\lambda\rangle. \quad (5)$$

By inserting Eq. (5) into Eq. (4) we obtain a system of differential equations for the unknown time-dependent coefficients g, a, $\{\alpha_{\mathbf{p}}\}$, $\{\beta_{\mathbf{p}}\}$, $\{g_{\mathbf{k},\lambda}\}$, $\{a_{\mathbf{k},\lambda}\}$, $\{\alpha_{\mathbf{p}}^{\mathbf{k},\lambda}\}$, and $\{\beta_{\mathbf{p}}^{\mathbf{k},\lambda}\}$. Because of reasons that will soon become clear, it is convenient to write down this system by splitting it into two parts:

$$\begin{aligned}
i\frac{dg}{dt} - E_g g &= \int d^3\mathbf{p}\langle\psi_g|\hat{V}_{AB}|\psi_{\mathbf{p},e}\rangle\beta_{\mathbf{p}} + \sum_{\mathbf{k},\lambda}\left(\langle\chi_0;0|\hat{W}_B|\mathbf{k},\lambda;\chi_e\rangle a_{\mathbf{k},\lambda} + \int d^3\mathbf{p}\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}}\rangle\alpha_{\mathbf{p}}^{\mathbf{k},\lambda}\right),\\
i\frac{d\beta_{\mathbf{p}}}{dt} - E_{p,e}\beta_{\mathbf{p}} &= \langle\psi_{\mathbf{p},e}|\hat{V}_{AB}|\psi_g\rangle g + \sum_{\mathbf{k},\lambda}\left(\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle\alpha_{\mathbf{p}}^{\mathbf{k},\lambda} + \langle u_{\mathbf{p}};0|\hat{W}_A|\mathbf{k},\lambda;u_0\rangle a_{\mathbf{k},\lambda}\right),\\
i\frac{da_{\mathbf{k},\lambda}}{dt} - E_a^k a_{\mathbf{k},\lambda} &= \langle\chi_e;\mathbf{k},\lambda|\hat{W}_B|0;\chi_0\rangle g + \int d^3\mathbf{p}\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle\beta_{\mathbf{p}} + \int d^3\mathbf{p}\langle\psi_a|\hat{V}_{AB}|\psi_{\mathbf{p},g}\rangle\alpha_{\mathbf{p}}^{\mathbf{k},\lambda},\\
i\frac{d\alpha_{\mathbf{p}}^{\mathbf{k},\lambda}}{dt} - E_{p,g}^k\alpha_{\mathbf{p}}^{\mathbf{k},\lambda} &= \langle u_{\mathbf{p}};\mathbf{k},\lambda|\hat{W}_A|0;\chi_0\rangle g + \langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle\beta_{\mathbf{p}} + \langle\psi_{\mathbf{p},g}|\hat{V}_{AB}|\psi_a\rangle a_{\mathbf{k},\lambda}
\end{aligned} \quad (6)$$

and

$$\begin{aligned}
i\frac{da}{dt} - E_a a &= \int d^3\mathbf{p}\langle\psi_a|\hat{V}_{AB}|\psi_{\mathbf{p},g}\rangle\alpha_{\mathbf{p}} + \sum_{\mathbf{k},\lambda}\left(\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle g_{\mathbf{k},\lambda} + \int d^3\mathbf{p}\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}}\rangle\beta_{\mathbf{p}}^{\mathbf{k},\lambda}\right),\\
i\frac{d\alpha_{\mathbf{p}}}{dt} - E_{p,g}\alpha_{\mathbf{p}} &= \langle\psi_{\mathbf{p},g}|\hat{V}_{AB}|\psi_a\rangle a + \sum_{\mathbf{k},\lambda}\left(\langle\chi_0;0|\hat{W}_B|\mathbf{k},\lambda;\chi_e\rangle\beta_{\mathbf{p}}^{\mathbf{k},\lambda} + \langle u_{\mathbf{p}};0|\hat{W}_A|\mathbf{k},\lambda;u_0\rangle g_{\mathbf{k},\lambda}\right),\\
i\frac{dg_{\mathbf{k},\lambda}}{dt} - E_g^k g_{\mathbf{k},\lambda} &= \langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle a + \int d^3\mathbf{p}\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle\alpha_{\mathbf{p}} + \int d^3\mathbf{p}\langle\psi_g|\hat{V}_{AB}|\psi_{\mathbf{p},e}\rangle\beta_{\mathbf{p}}^{\mathbf{k},\lambda},\\
i\frac{d\beta_{\mathbf{p}}^{\mathbf{k},\lambda}}{dt} - E_{p,e}^k\beta_{\mathbf{p}}^{\mathbf{k},\lambda} &= \langle u_{\mathbf{p}};\mathbf{k},\lambda|\hat{W}_A|0;\chi_0\rangle a + \langle\chi_e;\mathbf{k},\lambda|\hat{W}_B|0;\chi_0\rangle\alpha_{\mathbf{p}} + \langle\psi_{\mathbf{p},e}|\hat{V}_{AB}|\psi_g\rangle g_{\mathbf{k},\lambda}.
\end{aligned} \quad (7)$$

Note that in Eqs. (6) and (7) the following notation has been introduced: $E_g = \varepsilon_0 + \epsilon_0$, $E_a = \varepsilon_0 + \epsilon_e$, $E_{p,g} = \varepsilon_p + \epsilon_0$, $E_{p,e} = \varepsilon_p + \epsilon_e$, $E_g^k = \varepsilon_0 + \epsilon_0 + \omega_k$, $E_a^k = \varepsilon_0 + \epsilon_e + \omega_k$, $E_{p,g}^k = \varepsilon_p + \epsilon_0 + \omega_k$, and $E_{p,e}^k = \varepsilon_p + \epsilon_e + \omega_k$.

These differential equations have to be supplemented with appropriately chosen initial conditions. Indeed, as was already mentioned, in our consideration radiative recombination and photoionization are described in a similar manner and the only formal difference between them within this description lies in these conditions.

In the case of photoionization they are given by $g_{\mathbf{k},\lambda}(t_0) = \delta_{\mathbf{k}\mathbf{k}_i}\delta_{\lambda\lambda_i}$ and $g(t_0) = a(t_0) = \alpha_{\mathbf{p}}(t_0) = \beta_{\mathbf{p}}(t_0) = a_{\mathbf{k},\lambda}(t_0) = \alpha_{\mathbf{p}}^{\mathbf{k},\lambda}(t_0) = \beta_{\mathbf{p}}^{\mathbf{k},\lambda}(t_0) = 0$, where t_0 is the initial moment of time and $\mathbf{k}_i$ and λ_i are the momentum and polarization of the incident photon. On the other hand, for recombination such conditions are formulated as follows: $g(t_0) = a(t_0) = \beta_{\mathbf{p}}(t_0) = g_{\mathbf{k},\lambda}(t_0) = a_{\mathbf{k},\lambda}(t_0) = \alpha_{\mathbf{p}}^{\mathbf{k},\lambda}(t_0) = \beta_{\mathbf{p}}^{\mathbf{k},\lambda}(t_0) = 0$ and $\alpha_{\mathbf{p}}(t_0) = \delta^3(\mathbf{p} - \mathbf{p}_0)$, where $\mathbf{p}_0$ is the initial momentum of the incident electron.

Inspection of Eqs. (6) and (7) easily shows that these two subsystems do not contain the same coefficients and, thus, are mutually independent. In particular, it is obvious that both for photoionization and recombination the coefficients $a(t)$, $\alpha_{\mathbf{p}}(t)$, $g_{\mathbf{k},\lambda}(t)$, and $\beta_{\mathbf{p}}^{\mathbf{k},\lambda}(t)$ remain zero for any time t and all the necessary information is contained solely in the subsystem (7) and the initial conditions. For definiteness, in the following we shall give in some detail the derivation for recombination only.

A. Radiative recombination

In the case of recombination it is natural to set $t_0 = -\infty$. Then, by assuming that the interactions resulting in recombination are switched on and off adiabatically at $t = -\infty$ and $t = +\infty$, respectively, it is convenient to use the Fourier transformation in order to obtain the unknown coefficients $a(t)$, $\alpha_{\mathbf{p}}(t)$, $\beta_{\mathbf{p}}^{\mathbf{k},\lambda}(t)$, and $g_{\mathbf{k},\lambda}(t)$.

Applying the Fourier transformation to both sides of Eqs. (7) we obtain

$$
\begin{aligned}
(\omega - E_a)\widetilde{a} &= \int d^3\mathbf{p}\langle\psi_a|\hat{V}_{AB}|\psi_{\mathbf{p},g}\rangle\widetilde{\alpha}_{\mathbf{p}} + \sum_{\mathbf{k},\lambda}\left(\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle\widetilde{g}_{\mathbf{k},\lambda} + \int d^3\mathbf{p}\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}}\rangle\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda}\right),\\
(\omega - E_{p,g})\widetilde{\alpha}_{\mathbf{p}} &= \langle\psi_{\mathbf{p},g}|\hat{V}_{AB}|\psi_a\rangle\widetilde{a} + \sum_{\mathbf{k},\lambda}\left(\langle\chi_0;0|\hat{W}_B|\mathbf{k},\lambda;\chi_e\rangle\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda} + \langle u_{\mathbf{p}};0|\hat{W}_A|\mathbf{k},\lambda;u_0\rangle\widetilde{g}_{\mathbf{k},\lambda}\right),\\
\left(\omega - E_g^k\right)\widetilde{g}_{\mathbf{k},\lambda} &= \langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle\widetilde{a} + \int d^3\mathbf{p}\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle\widetilde{\alpha}_{\mathbf{p}} + \int d^3\mathbf{p}\langle\psi_g|\hat{V}_{AB}|\psi_{\mathbf{p},e}\rangle\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda},\\
\left(\omega - E_{p,e}^k\right)\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda} &= \langle u_{\mathbf{p}};\mathbf{k},\lambda|\hat{W}_A|0;\chi_0\rangle\widetilde{a} + \langle\chi_e;\mathbf{k},\lambda|\hat{W}_B|0;\chi_0\rangle\widetilde{\alpha}_{\mathbf{p}} + \langle\psi_{\mathbf{p},e}|\hat{V}_{AB}|\psi_g\rangle\widetilde{g}_{\mathbf{k},\lambda},
\end{aligned}
\tag{8}
$$

where the unknown coefficients $\widetilde{a}$, $\widetilde{\alpha}_{\mathbf{p}}$, $\widetilde{g}_{\mathbf{k},\lambda}$, and $\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda}$ are related to those in Eqs. (7) according to

$$
\widetilde{b}(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} dt\, b(t)\exp(i\omega t), \quad b(t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} d\omega\,\widetilde{b}(\omega)\exp(-i\omega t). \tag{9}
$$

Using the last two equations of the system (8) we now express the coefficients $\widetilde{g}_{\mathbf{k},\lambda}$ and $\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda}$ as follows:

$$
\begin{aligned}
\widetilde{g}_{\mathbf{k},\lambda} &= \frac{\langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle\widetilde{a} + \int d^3\mathbf{p}\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle\widetilde{\alpha}_{\mathbf{p}} + \int d^3\mathbf{p}\langle\psi_g|\hat{V}_{AB}|\psi_{\mathbf{p},e}\rangle\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda}}{\omega - E_g^k + i0},\\
\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda} &= \frac{\langle u_{\mathbf{p}};\mathbf{k},\lambda|\hat{W}_A|0;\chi_0\rangle\widetilde{a} + \langle\chi_e;\mathbf{k},\lambda|\hat{W}_B|0;\chi_0\rangle\widetilde{\alpha}_{\mathbf{p}} + \langle\psi_{\mathbf{p},e}|\hat{V}_{AB}|\psi_g\rangle\widetilde{g}_{\mathbf{k},\lambda}}{\omega - E_{p,e}^k + i0},
\end{aligned}
\tag{10}
$$

where the choice $+i0$ for handling the singularities corresponds to looking for a state which asymptotically is the superposition of an incident wave and an outgoing scattered wave. Neglecting the last term on the right-hand side of each of these two formulas [14] we substitute the resulting expressions for $\widetilde{g}_{\mathbf{k},\lambda}$ and $\widetilde{\beta}_{\mathbf{p}}^{\mathbf{k},\lambda}$ into the first two equations of (8). This yields

$$
\begin{aligned}
&\left(\omega - E_a - \sum_{\mathbf{k},\lambda}\frac{|\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle|^2}{\omega - E_g^k + i0}\right.\\
&\left. - \sum_{\mathbf{k},\lambda}\int d^3\mathbf{p}\frac{|\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}}\rangle|^2}{\omega - E_{p,e}^k + i0}\right)\widetilde{a} = \int d^3\mathbf{p}\,\widetilde{V}_{a,\mathbf{p}}\,\widetilde{\alpha}_{\mathbf{p}},\\
&(\omega - \overline{E}_{p,g})\widetilde{\alpha}_{\mathbf{p}} = \widetilde{V}_{\mathbf{p},a}\,\widetilde{a}\\
&\quad + \sum_{\mathbf{k},\lambda}\int d^3\mathbf{p}'\frac{\langle u_{\mathbf{p}};\mathbf{k},\lambda|\hat{W}_A|0;u_0\rangle\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}'}\rangle}{\omega - E_g^k + i0}\widetilde{\alpha}_{\mathbf{p}'},
\end{aligned}
\tag{11}
$$

where

$$
\begin{aligned}
\widetilde{V}_{a,\mathbf{p}} &= \langle\psi_a|\hat{V}_{AB}|\psi_{\mathbf{p},g}\rangle\\
&\quad + \sum_{\mathbf{k},\lambda}\frac{\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}}\rangle}{\omega - E_g^k + i0}\\
&\quad + \sum_{\mathbf{k},\lambda}\frac{\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}}\rangle}{\omega - E_{p,e}^k + i0},
\end{aligned}
$$

$$
\begin{aligned}
\widetilde{V}_{\mathbf{p},a} &= \langle\psi_{\mathbf{p},g}|\hat{V}_{AB}|\psi_a\rangle\\
&\quad + \sum_{\mathbf{k},\lambda}\frac{\langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle\langle u_{\mathbf{p}};\mathbf{k},\lambda|\hat{W}_A|0;u_0\rangle}{\omega - E_g^k + i0}\\
&\quad + \sum_{\mathbf{k},\lambda}\frac{\langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle\langle u_{\mathbf{p}};\mathbf{k},\lambda|\hat{W}_A|0;u_0\rangle}{\omega - E_{p,e}^k + i0}
\end{aligned}
\tag{12}
$$

are the matrix elements of the full electron-electron interaction and

$$
\begin{aligned}
\overline{E}_{\mathbf{p},g} &= E_{\mathbf{p},g} + \sum_{\mathbf{k},\lambda}\frac{|\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle|^2}{\omega - E_{p,e}^k + i0}\\
&\equiv E_{\mathbf{p},g} + \sum_{\mathbf{k},\lambda}\frac{|\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle|^2}{\omega - E_{p,e}^k}
\end{aligned}
\tag{13}
$$

is a real quantity describing the shift of the electron continuum energy caused by the coupling to the radiation field [15].

On the right-hand side of the second equation in Eqs. (11) we shall neglect the second term, which corresponds to virtual continuum-bound-continuum electron transitions via the exchange of two photons. Then, by taking into account that an equation of the type $(x - x_0)f(x) = g(x)$ has a general solution of the form $f(x) = \mu\delta(x - x_0) + g(x)/(x - x_0 \pm i0)$, where in our case μ is determined using the initial conditions, it is not difficult to show that the solution of

Eq. (11) reads

$$\widetilde{a}(\omega) = \frac{\sqrt{2\pi}\,\delta(\omega-\overline{E}_{p_0,g})\widetilde{V}_{a,\mathbf{p}_0}}{\omega-E_a-\sum_{\mathbf{k},\lambda}\frac{|\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle|^2}{\omega-E_g^k+i0}-\sum_{\mathbf{k},\lambda}\int d^3\mathbf{p}\frac{|\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_\mathbf{p}\rangle|^2}{\omega-E_{p,e}^k+i0}-\int d^3\mathbf{p}\frac{\widetilde{V}_{a,\mathbf{p}}\widetilde{V}_{\mathbf{p},a}}{\omega-E_{p,g}+i0}},$$

$$\widetilde{\alpha}_\mathbf{p}(\omega) = \sqrt{2\pi}\,\delta^{(3)}(\mathbf{p}-\mathbf{p}_0)\delta(\omega-\overline{E}_{p_0,g}) + \frac{\sqrt{2\pi}\,\delta(\omega-\overline{E}_{p_0,g})\,\widetilde{V}_{\mathbf{p},a}}{\omega-\widetilde{E}_{\mathbf{p},g}+i0} \times \frac{\widetilde{V}_{a,\mathbf{p}_0}}{\omega-E_a-\sum_{\mathbf{k},\lambda}\frac{|\langle\chi_e;0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle|^2}{\omega-E_g^k+i0}-\sum_{\mathbf{k},\lambda}\int d^3\mathbf{p}\frac{|\langle u_0;0|\hat{W}_A|\mathbf{k},\lambda;u_\mathbf{p}\rangle|^2}{\omega-E_{p,e}^k+i0}-\int d^3\mathbf{p}\frac{\widetilde{V}_{a,\mathbf{p}}\widetilde{V}_{\mathbf{p},a}}{\omega-E_{p,g}+i0}}. \tag{14}$$

Using expressions (14) we now can determine from the third line of Eqs. (8) the coefficient $\widetilde{g}_{\mathbf{k},\lambda}$,

$$\widetilde{g}_{\mathbf{k},\lambda} = \frac{\sqrt{2\pi}\,\delta(\omega-\overline{E}_{p_0,g})}{\omega-E_g-\omega_k+i0}\Bigg[\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_\mathbf{p}\rangle + \frac{\widetilde{V}_{a,\mathbf{p}_0}}{\omega-E_a-\sum_{\mathbf{k}',\lambda'}\frac{|\langle\chi_e;0|\hat{W}_B|\mathbf{k}',\lambda';\chi_0\rangle|^2}{\omega-E_g^{k'}+i0}-\sum_{\mathbf{k}',\lambda'}\int d^3\mathbf{p}\frac{|\langle u_0;0|\hat{W}_A|\mathbf{k}',\lambda';u_\mathbf{p}\rangle|^2}{\omega-E_{p,e}^{k'}+i0}-\int d^3\mathbf{p}\frac{\widetilde{V}_{\mathbf{p},a}\widetilde{V}_{a,\mathbf{p}}}{\omega-\overline{E}_{p,g}+i0}} \times\left(\langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle+\int d^3\mathbf{p}\frac{\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_\mathbf{p}\rangle\widetilde{V}_{\mathbf{p},a}}{\omega-\overline{E}_{p,g}+i0}\right)\Bigg], \tag{15}$$

and obtain its (inverse) Fourier transform

$$g_{\mathbf{k},\lambda}(t) = \frac{\exp(-i\overline{E}_{p_0,g}t)}{\overline{E}_{p_0,g}-E_g-\omega_k+i0}\Bigg[\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_\mathbf{p}\rangle + \frac{\widetilde{V}_{a,\mathbf{p}_0}}{\overline{E}_{p_0,g}-E_a-\sum_{\mathbf{k}',\lambda'}\frac{|\langle\chi_e;0|\hat{W}_B|\mathbf{k}',\lambda';\chi_0\rangle|^2}{\overline{E}_{p_0,g}-E_g^{k'}+i0}-\sum_{\mathbf{k}',\lambda'}\int d^3\mathbf{p}\frac{|\langle u_0;0|\hat{W}_A|\mathbf{k}',\lambda';u_\mathbf{p}\rangle|^2}{\overline{E}_{p_0,g}-E_{p,e}^{k'}+i0}-\int d^3\mathbf{p}\frac{\widetilde{V}_{a,\mathbf{p}}\widetilde{V}_{\mathbf{p},a}}{\overline{E}_{p_0,g}-\overline{E}_{p,g}+i0}} \times\left(\langle\chi_0;\mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle+\int d^3\mathbf{p}\frac{\langle u_0;\mathbf{k},\lambda|\hat{W}_A|0;u_\mathbf{p}\rangle\,\widetilde{V}_{\mathbf{p},a}}{\overline{E}_{p_0,g}-\overline{E}_{p,g}+i0}\right)\Bigg]. \tag{16}$$

1. *Electron-electron interaction and the retardation effect*

The solution of Eqs. (7) also yields the interaction between the electrons [see Eqs. (12)]. With the help of Eqs. (12) we find that for electrons undergoing electric dipole transitions, this interaction can be cast into the following form:

$$\widetilde{\hat{V}}_{AB} = r_{1i}\xi_j\Theta_{ij}, \tag{17}$$

where r_{1i} and ξ_j $(i,j=x,y,z)$ are the components of the coordinates of the electrons, a summation over the repeated indices is implied, and the real and imaginary parts of the complex tensor Θ_{ij} are given by

$$\mathrm{Re}(\Theta_{ij}) = \frac{\cos(k_0R)+k_0R\,\sin(k_0R)}{R^3}\left(\delta_{ij}-\frac{3R_iR_j}{R^2}\right) - \frac{k_0^2\,\cos(k_0R)}{R}\left(\delta_{ij}-\frac{R_iR_j}{R^2}\right),$$

$$\mathrm{Im}(\Theta_{ij}) = \frac{\sin(k_0R)-k_0R\,\cos(k_0R)}{R^3}\left(\delta_{ij}-\frac{3R_iR_j}{R^2}\right) - \frac{k_0^2\,\sin(k_0R)}{R}\left(\delta_{ij}-\frac{R_iR_j}{R^2}\right). \tag{18}$$

In contrast to the instantaneous form of the interaction between two electric dipoles, given by Eq. (1), the interaction given by Eqs. (17) and (18) takes into account the fact that in order to propagate between the centers A and B, the electromagnetic field needs a finite time (the retardation effect). This effect becomes of great importance when the time $\tau \sim R/c$ which the light needs for traversing the distance between the electrons compares with the effective time $\tau_e \sim 1/\omega_0$ of the electron transitions: At $k_0R \gtrsim 1$ the use of the instantaneous and retarded forms of the electron-electron interaction leads to substantial differences in the calculated results. On the other hand, if the distance R is relatively small ($k_0R \ll 1$), it follows from Eq. (18) that, as expected, the interaction (17) practically reduces to its instantaneous form (1).

It worth noting that the form of the interaction given by Eqs. (17) and (18) is gauge independent. In particular, it also follows when one considers the coupling $\sum_{\mu=0}^{3} j_{\mu}^{(1)} A_{(2)}^{\mu}$ between the transition four-current $j_{\mu}^{(1)}$ of one of the electrons and the four-potential $A_{(2)}^{\mu}$ of the electromagnetic field, created by the other electron, without using the second quantization for the field.

2. The shift and width of the "autoionizing" state ψ_a

According to, e.g., Eq. (16), the interaction between the electrons and the interaction of the electrons with the radiation field cause the two-electron level ψ_a to acquire a new (and complex) energy which is given by

$$\begin{aligned} Z_a &= E_a + \sum_{\mathbf{k},\lambda} \frac{|\langle \chi_e; 0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle|^2}{\overline{E}_{p_0,g} - E_g^k + i0} \\ &\quad + \int d^3\mathbf{p} \frac{\widetilde{V}_{a,\mathbf{p}} \widetilde{V}_{\mathbf{p},a}}{\overline{E}_{p_0,g} - \overline{E}_{p,g} + i0} \\ &\quad + \sum_{\mathbf{k},\lambda} \int d^3\mathbf{p} \frac{|\langle u_0; 0|\hat{W}_A|\mathbf{k},\lambda;u_{\mathbf{p}}\rangle|^2}{\overline{E}_{p_0,g} - E_{p,e}^k + i0} \\ &= \overline{E}_a - i\frac{\overline{\Gamma}_a}{2}, \end{aligned} \tag{19}$$

where in the second line of Eq. (19) $\overline{E}_a$ and $\overline{\Gamma}_a$ denote the new position and the width of the level ψ_a [16]. The second, the third, and the last term on the right-hand side of the first line of Eq. (19) appear due to, respectively, the spontaneous radiative decay of the excited state of B, the two-center autoionizing decay, and the (nonresonant) coupling of the ground and continuum states of A embedded in the radiation field. The first two of these terms are complex, which results in both the shifting and broadening of the level ψ_a, while the latter one is real and, thus, contributes to the level shift only. Therefore, the total width $\overline{\Gamma}_a$ of the level ψ_a can be written as the sum of the width Γ_r, which is due to the spontaneous radiative decay, and the autoionizing width Γ_a, which appears because of the coupling of the level ψ_a to the electron continuum states caused by the two-center electron-electron interaction.

It follows from Eq. (19) that the radiative width is simply given by

$$\Gamma_r = 2\pi \sum_{\mathbf{k},\lambda} |\langle \chi_e; 0|\hat{W}_B|\mathbf{k},\lambda;\chi_0\rangle|^2 \, \delta(\omega_k + \epsilon_0 - \epsilon_e).$$

Obtaining the autoionizing width Γ_a from Eq. (19) is slightly more complicated and is worthy of a few comments. Indeed, one has to note that because the tensor (18) is not a real quantity, the matrix elements of the electron-electron interaction $\widetilde{V}_{a,\mathbf{p}}$ and $\widetilde{V}_{\mathbf{p},a}$ are not complex conjugate. However, when calculating Γ_a one may, in fact, approximate the electron-electron interaction by its instantaneous form, which makes the product $\widetilde{V}_{a,\mathbf{p}} \widetilde{V}_{\mathbf{p},a}$ real. This approximation is quite sufficient since at large distances R, where the difference between the retarded and instantaneous forms of this interaction becomes of importance, the autoionizing width is already so small that the total width of the state ψ_a is determined practically solely by the radiative width Γ_r.

3. The phase shift between the radiative transitions on the centers A and B

The explicit form of the transition matrix elements $\langle \chi_0; \mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle$ and $\langle u_0; \mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle$ is given by

$$\begin{aligned} &\langle \chi_0; \mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle \\ &\quad = \sqrt{\frac{2\pi}{V\omega_k}} \int d^3\mathbf{r}_2 \, \chi_0^*(\boldsymbol{\xi}) \exp(-i\mathbf{k}\cdot\mathbf{r}_2) \mathbf{e}_{\mathbf{k},\lambda} \cdot \hat{\mathbf{p}}_2 \chi_e(\boldsymbol{\xi}) \\ &\quad \approx \sqrt{\frac{2\pi}{V\omega_k}} \exp(-i\mathbf{k}\cdot\mathbf{R}) \int d^3\boldsymbol{\xi} \, \chi_0^*(\boldsymbol{\xi}) \mathbf{e}_{\mathbf{k},\lambda} \cdot \hat{\mathbf{p}}_{\boldsymbol{\xi}} \chi_e(\boldsymbol{\xi}) \end{aligned} \tag{20}$$

and

$$\begin{aligned} &\langle u_0; \mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle \\ &\quad = \sqrt{\frac{2\pi}{V\omega_k}} \int d^3\mathbf{r}_1 \, u_0^*(\mathbf{r}_1) \exp(-i\mathbf{k}\cdot\mathbf{r}_1) \mathbf{e}_{\mathbf{k},\lambda} \cdot \hat{\mathbf{p}}_1 u_{\mathbf{p}}(\mathbf{r}_1) \\ &\quad \approx \sqrt{\frac{2\pi}{V\omega_k}} \int d^3\mathbf{r}_1 \, u_0^*(\mathbf{r}_1) \mathbf{e}_{\mathbf{k},\lambda} \cdot \hat{\mathbf{p}}_1 u_{\mathbf{p}}(\mathbf{r}_1). \end{aligned} \tag{21}$$

Note that in obtaining Eqs. (20) and (21) we used the dipole approximation within each of the centers. Comparing these equations we see that there arises a phase shift $\mathbf{k}\cdot\mathbf{R}$ between the radiative transitions on the centers A and B caused by their different positions in space. In particular, in the case of recombination this shift can lead to an interference effect in the emitted light when, depending on the direction of the light propagation, the coherent emission of the photon by the centers A and B either increases or decreases, or it leaves unchanged the light intensity compared to the case of light emission by the noninteracting centers A and B.

III. CROSS SECTIONS

In what follows we shall assume that the energy shifts are already included in the definition of the corresponding initial energies of the levels; i.e., we set $\overline{E}_{p,g} = E_{p,g}$, $\overline{E}_a = E_a$, and so on.

A. Cross sections for recombination

Using Eq. (16) one can calculate cross sections for two-center dielectronic recombination. In particular, one can show that the differential cross section for recombination in the solid angle $\Omega_{\mathbf{k}}$ of the emitted photon reads

$$\begin{aligned} \frac{d\sigma^{\mathrm{2CDR}}}{d\Omega_{\mathbf{k}}} &= \frac{(2\pi)^4 V_{\mathrm{ph}} V_{\mathrm{el}} \omega_0^2}{c^3 v_i} \sum_{\lambda=1}^{2} \Bigg| \langle u_0; \mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle \\ &\quad + \frac{\widetilde{V}_{a,\mathbf{p}_0}}{\varepsilon_{p_0} + \epsilon_0 - \varepsilon_0 - \epsilon_e + i\overline{\Gamma}_a/2} \\ &\quad \times \Bigg(\langle \chi_0; \mathbf{k},\lambda|\hat{W}_B|0;\chi_e\rangle \\ &\quad + \int d^3\mathbf{p} \frac{\langle u_0; \mathbf{k},\lambda|\hat{W}_A|0;u_{\mathbf{p}}\rangle \, \widetilde{V}_{\mathbf{p},a}}{\varepsilon - \varepsilon_p + i0} \Bigg)_{p_0} \Bigg|^2, \end{aligned} \tag{22}$$

where $\omega_0 = \varepsilon_{p_i} - \varepsilon_0$ is the energy of the emitted photon, and v_i and $V_{\rm el}$ are, respectively, the velocity of and the normalization volume for the incident electron. The total cross section for recombination can be obtained by integrating Eq. (22) over the emission angles of the photon.

According to Eqs. (16) and (22) there are three different pathways for recombination of the incident electron and the subsystem A^+: (i) They can recombine directly via the emission of a photon without any participation of the subsystem B. (ii) The incident electron undergoes a transition $u_{\mathbf{p}_0} \to u_0$ by inducing the transition $\chi_0 \to \chi_e$ in the subsystem B; the latter afterward deexcites by photon emission. (iii) The incident electron undergoes transitions $\phi_{\mathbf{p}_0} \to \phi_b \to \phi_{\mathbf{p}} \to \phi_b$ in which the first two steps are accompanied by the (radiationless) transitions $\chi_0 \to \chi_e \to \chi_0$ in the subsystem B and the last one proceeds via photon emission. Pathways (ii) and (iii) are resonant and become efficient only if the energy ε_{p_0} of the incident electron lies in the interval $\varepsilon_0 + \epsilon_e - \epsilon_0 - \overline{\Gamma}_a \lesssim \varepsilon_{p_0} \lesssim \varepsilon_0 + \epsilon_e - \epsilon_0 + \overline{\Gamma}_a$.

B. Total cross section for photoionization

The cross sections for photoionization can be obtained using either a consideration similar to that discussed earlier for radiative recombination or the principle of detailed balance. In particular, for the total photoionization cross section one can obtain

$$\sigma^{\rm 2CPI} = \frac{2\pi p_f V_{\rm ph}}{c} \sum_{\lambda=1}^{2} \int d\Omega_{\mathbf{p}} \left| \langle u_{\mathbf{p}}; 0|\hat{W}_A|\mathbf{k}_i,\lambda_i; u_0\rangle + \frac{\widetilde{V}_{\mathbf{p},a}}{\epsilon_0 + \omega_0 - \epsilon_e + i\overline{\Gamma}_a/2} \left(\langle \chi_e; 0|\hat{W}_B|\mathbf{k}_i,\lambda_i; \chi_0\rangle + \int d^3\mathbf{p} \frac{\widetilde{V}_{a,\mathbf{p}}\, \langle u_{\mathbf{p}}; 0|\hat{W}_A|\mathbf{k}_i,\lambda_i; u_0\rangle}{\varepsilon_0 + \omega_0 - \varepsilon_p + i0} \right) \right|^2, \quad (23)$$

where $p_f = \sqrt{2(\varepsilon_0 + \omega_0)}$ is the absolute value of the momentum of the ejected photoelectron and $\Omega_{\mathbf{p}}$ is the solid angle of the ejection.

Similarly to the case of recombination, Eq. (23) shows that there are also three qualitatively different pathways for ionization of the atom: (i) The atom A is directly ionized by the electromagnetic field without any participation of the atom B. (ii) The field excites the atom B into the state χ_e; the latter subsequently deexcites by transferring the excess of energy to the electron of atom A, which leads to its ionization. (iii) The electromagnetic field drives the electron of atom A into the continuum but the electron returns to the ground state u_0 due to the two-center electron-electron interaction and, only afterward, the same interaction transfers the electron into the final continuum state $u_{\mathbf{p}_0}$. As in the case with recombination, pathways (ii) and (iii) are resonant and become effective only if the energy ε_{p_0} of the field frequency lies in the interval $\epsilon_e - \epsilon_0 - \overline{\Gamma}_a \lesssim \omega_0 \lesssim \epsilon_e - \epsilon_0 + \overline{\Gamma}_a$.

IV. SOME NUMERICAL RESULTS AND DISCUSSION

In Fig. 3 we show the ratio between the cross section $\sigma^{\rm 2CPI}$ for photoionization of Li in a Li-He system and the cross section for photoionization of an isolated Li atom. This ratio

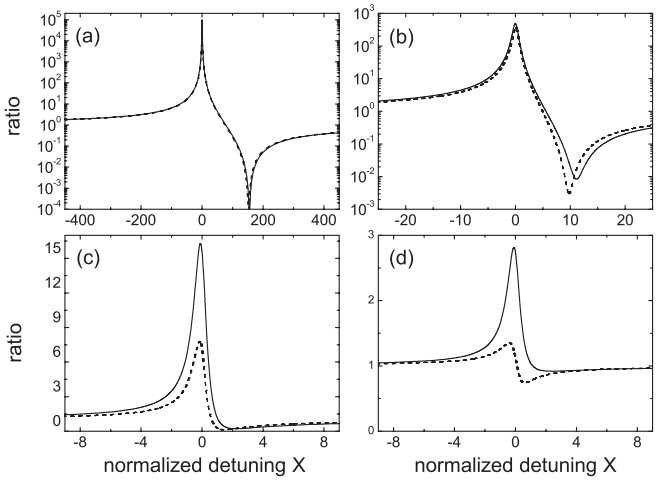

FIG. 3. The ratio between the cross sections for ionization of Li in a Li-He system and for ionization of a separated Li atom. The electromagnetic field is assumed to be linearly polarized along the internuclear vector **R**. The ratio was calculated for four different internuclear distances R [(a) $R = 20$ Å, (b) $R = 50$ Å, (c) $R = 100$ Å, and (d) $R = 200$ Å] and is given as a function of the normalized detuning $X = (\omega_0 - \omega_{\rm res})/\overline{\Gamma}_a$ from the resonant frequency $\omega_{\rm res} = \epsilon_e - \epsilon_0 \approx 21$ eV corresponding to the $1s^2\,{}^1S$–$1s2p\,{}^1P$ transition in He. Solid and dashed curves display results obtained with the electron-electron interaction in the form (17) and (1), respectively.

is given for four internuclear distances ($R = 20$ Å, $R = 50$ Å, $R = 100$ Å, and $R = 200$ Å) as a function of the normalized detuning $X = (\omega_0 - \omega_{\rm res})/\overline{\Gamma}_a$ from the resonant frequency $\omega_{\rm res} = \epsilon_e - \epsilon_0 \approx 21$ eV corresponding to the $1s^2\,{}^1S$–$1s2p\,{}^1P$ transition in He. The electromagnetic field is assumed to be linearly polarized along the internuclear vector **R**.

There are a few points in Fig. 3 that are worth mentioning. First, the figure demonstrates that the presence of a neighboring He atom can lead to a huge increase in the ionization cross section of Li in the vicinity of the resonant frequency $\omega_{\rm res}$ provided the interatomic distance R is not very large. The range of the vicinity of the resonance is itself very small. However, the enhancement of ionization in this range may be so large that a substantial increase in the number of ionization events can be quite visible even if the system is irradiated by the electromagnetic field, which is not monochromatic.

Indeed, assuming that $k_0 R \ll 1$ and, simultaneously, $\Gamma_a \ll \Gamma_r$, one can show [12] that the ratio of the partial contributions to the cross section yielded by the resonance and direct channels, respectively, integrated over the spectral width $\Delta\omega_0$ ($\Delta\omega_0 \ll \omega_0$) of the electromagnetic field, is given by

$$\eta \approx \left(\frac{c/\omega_0}{R}\right)^3 \left(\frac{a_0}{R}\right)^3 \frac{1/a_0}{Z_B^2 \Delta\omega_0}, \quad (24)$$

where a_0 is the Bohr radius [17]. Although the resonance channel is effective only in the vicinity of the resonance, whereas the direct channel may act for the whole width $\Delta\omega_0 \gg \overline{\Gamma}_a$, using Eq. (24) one can convince oneself that the ratio η can reach quite large values. For example, for a Li-He system if $R \approx 10$ Å [18], $\omega_0 \approx 21$ eV, and $\Delta\omega_0 \sim 0.1$ eV, the photoionization of Li is enhanced by $\eta \sim 10$.

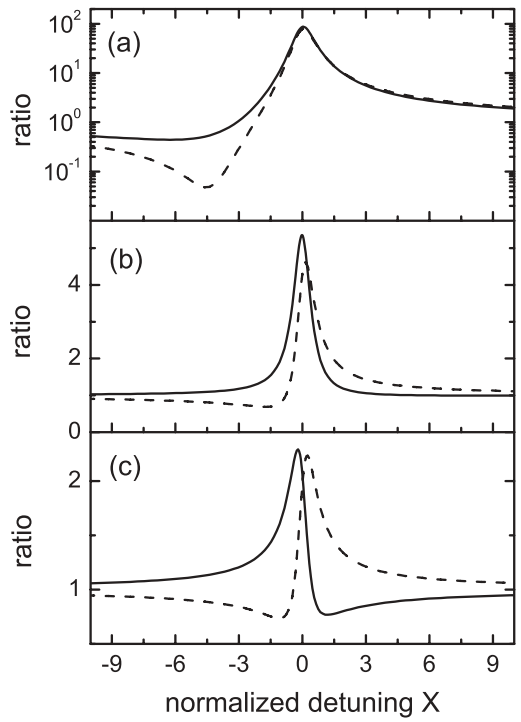

FIG. 4. The ratio between the cross sections for ionization of Li in a Li-He system and for ionization of a separated Li atom. The electromagnetic field is assumed to be linearly polarized and propagate parallel to the internuclear vector **R**. The ratio was calculated for three different internuclear distances R [(a) $R = 50$ Å, (b) $R = 100$ Å, and (c) $R = 200$ Å] and is given as a function of the normalized detuning $X = (\omega_0 - \omega_{\rm res})/\overline{\Gamma}_a$ from the resonant frequency $\omega_{\rm res} = \epsilon_e - \epsilon_0 \approx 21$ eV corresponding to the $1s^2\,{}^1S$–$1s2p\,{}^1P$ transition in He. Solid and dashed curves display results obtained with and without taking into account the phase difference $\exp(-i\mathbf{k}\cdot\mathbf{R})$ between the electromagnetic transitions on the two centers.

Second, the shape of the plots, presented in Fig. 3, clearly display the so-called Fano profile [19] caused by the interference between the direct and resonant ionization pathways. Thus, the figure shows how the interference manifests itself in the photoionization process. At relatively small values of R, the interference becomes important only at very large values of the detuning X because at small X the resonance channel turns out to be much stronger than the direct one. With the increase of the internuclear distance, the resonance channel rapidly weakens and the interference becomes important at small values of X.

Third, at large R the retardation effect becomes of importance, influencing both the magnitude and the shape of the calculated results.

In Fig. 4 we display the ratio between the ionization cross sections obtained for the same atomic system Li-He, but now with the assumption that the photon momentum **k** is parallel to the vector **R**. The ratio was calculated with and without taking into account the term $\exp(-i\mathbf{k}\cdot\mathbf{R})$ [see Eqs. (20) and (21)], which contains the phase shift accumulated between the electromagnetic transitions occurring on the two centers due to their different positions in space. It follows from this figure that the phase shift may have a substantial effect on the shape and absolute value of the ionization cross section.

V. CONCLUSIONS

We have discussed in some detail a theoretical description of two-center radiative recombination and two-center resonant photoionization by a weak electromagnetic field. Such processes are possible in an atomic system composed of two well separated in space subsystems A and B, if the ionization potential of one of them (A) is smaller than the excitation energy ΔE_B of a dipole-allowed transition in the other subsystem (B).

Under such conditions if a free electron is incident on an ion A^+ in the presence of the subsystem B, then recombination of the electron with A^+ can be strongly influenced by B provided the difference between the initial and final energies of the $(e^- + A^+)$ subsystem is close to ΔE_B. One encounters a similar situation if the system $A + B$ is irradiated by an electromagnetic field with frequency close to the excitation energy of B. Then, ionization of A can be very substantially modified compared to the case of ionization of A in the absence of B.

Our treatment of these processes was based on the use of the noncovariant QED approach. Within it the interaction between charged particles is regarded as occurring both via instantaneous Coulomb potentials and the coupling of these particles to the radiation field, which is described by a vector potential. By expanding the state vector for the total quantum system, which consists of A, B, and the radiation field, into a complete set of states, differential equations for the unknown time-dependent coefficients of this expansion were obtained. They were solved using the Fourier transformation. Besides obtaining the coefficients necessary to compute cross sections, this solution also yielded the full form of the two-center electron-electron interaction, which takes into account the finiteness of the speed of light, thus describing the retardation effect.

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[14] One can show that keeping these terms does not have any substantial impact on the final result.

[15] Because the set of states used in the expansion (5) is not complete, its use does not enable one to properly describe the shifts of the energy levels. Therefore, in what follows $\overline{E}_{\mathbf{p},g}$ should be regarded as a parameter.

[16] While the complete set of states used in the expansion (5) is quite sufficient for obtaining the widths, as was already mentioned, it cannot fully describe the shifts of energy levels. Therefore, within the present description $\overline{E}_a$ (and similarly $\overline{E}_{\mathbf{p},g}$) should be regarded merely as a parameter.

[17] Note that when R decreases, η becomes less dependent on R and eventually independent of R at distances where $\Gamma_a > \Gamma_r$.

[18] The value 10 Å is of the order of the distance between Li and nearby He atoms in a system consisting of a Li atom attached to a helium nanodroplet.

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