Strongly Enhanced Recombination via Two-Center Electronic Correlations

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In the presence of a neighboring atom, electron-ion recombination can proceed resonantly via excitation of an electron in the atom, with subsequent relaxation through radiative decay. It is shown that this two-center dielectronic process can largely dominate over single-center radiative recombination at internuclear distances as large as several nanometers. The relevance of the predicted process is demonstrated by using examples of water-dissolved alkali cations and warm dense matter.

Recombination of free electrons with atomic or molecular ions is a fundamental process of general interest and relevance to various scientific disciplines [1,2]. Recombination into single atomic centers may proceed in three ways. First, the electron can be captured into a bound state upon photoemission, referred to as radiative recombination (RR), the time inverse of photoionization. Second, for certain energies of the incident electron, the recombination can proceed resonantly via formation of an autoionizing state (time-reversed Auger decay); afterwards, the system stabilizes through radiative deexcitation. This dielectronic recombination (DR) process is particularly important for low-charged ions. Finally, three-body recombination, in which an electron is captured by an ion transferring excess energy to another free electron, dominates in high-density plasmas.

When an atom is not isolated in space but close to another atom, the electronic structures at the two centers can be coupled by long-range electromagnetic interactions leading to a variety of interesting phenomena. For example, interatomic electron-electron correlations are responsible for various deexcitation processes in slow atomic collisions [3], including Penning ionization, the population inversion in a He-Ne laser, and the energy transfer in quantum optical ensembles [4] or cold Rydberg gases [5]. They also play an important role in biological systems as Förster resonances between chromophores [6]. 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. Stimulated by detailed theoretical predictions [7], this interatomic decay process has been observed in recent years in various systems such as van der Waals clusters [8], rare gas dimers [9], and water molecules [10].

Recently, a process has been calculated [11] in which the capture of an incident electron by an ion (or atom) proceeds via the Coulomb interaction of this electron with a neighboring atom leading to ionization of the latter.

Keeping the total charge of the two centers unchanged, such a process effectively results in an interatomic electron exchange.

In this Letter, we introduce a process in which an incident electron can be captured due to resonant electronic correlations involving two neighboring atomic centers. The centers may be (but are not limited to) atoms, ions, or molecules. In this process, which may be termed two-center dielectronic recombination (2CDR), the electron is captured by one of the centers with simultaneous resonant excitation of the other center which subsequently deexcites via spontaneous radiative decay (see Fig. 1). In contrast to the process considered in [11], 2CDR is a genuine capture process in which the total charge of the centers is changed. Using examples from various fields of science, we will show that 2CDR can very significantly contribute to recombination exceeding the usual single-center RR by orders of magnitude.

In order to emphasize the basic physics of 2CDR, let us consider recombination in a simple system consisting of an incident electron, a bare nucleus (the nucleus A), an atom with one "active" electron (the atom B), and the radiation field. Both the bare and atomic nuclei are supposed to be at rest. We take the position of the bare nucleus as the origin
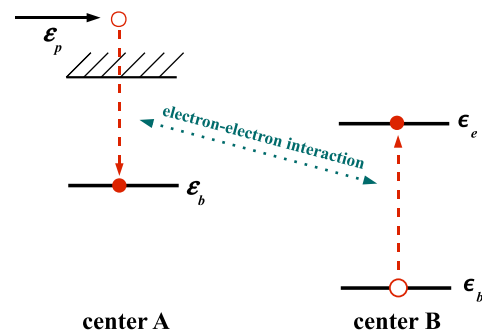

FIG. 1 (color online). Scheme of two-center dielectronic recombination (2CDR). Depicted is the first step, where an electron is captured at center A with simultaneous excitation of an atom at center B. Afterwards, atom B deexcites via photoemission.

and denote the coordinates of the atomic nucleus, the incident, and atomic electrons by $\mathbf{R}$, $\mathbf{r}_1$, and $\mathbf{r}_2 = \mathbf{R} + \boldsymbol{\xi}$, respectively, where $\boldsymbol{\xi}$ is the position of the atomic electron with respect to the atomic nucleus.

We shall assume that the distance R is not too large, $R \ll c/\omega_0$, where c is the speed of light and ω_0 is the difference between the initial and final energies of the incident electron (its transition frequency). Then one can neglect the retardation effects and treat the interaction between the charged particles as instantaneous Coulombic. Additionally, we shall also suppose that the distance R is not too small either, so that one can still speak about the individual subsystems: "the incident electron plus the nucleus A" and the atom B. Under such conditions the energy exchange between the electrons is most efficient for dipole-allowed transitions, and, restricting our attention only to the latter ones, the interaction between these subsystems can be reduced to that of two electric dipoles

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

where δ_{ij} is 1 for $i = j$ and 0 otherwise, and a summation over the repeated indices is implied. Atomic units (a.u.) are used throughout unless otherwise stated.

In the process under consideration one has essentially three different basic two-electron configurations: (I) $\psi_{\mathbf{p}}$, the incident electron is in the continuum, while the atomic electron is in the ground state; (II) ψ_a, the incident electron is in a bound (ground) state and the atomic electron is excited; (III) ψ_c, both electrons are in the corresponding ground states.

In addition to the electrons, the quantum degrees of freedom in the process are also represented by the radiation field. The latter is initially in its vacuum state $|0\rangle$ and then undergoes a transition into a state $|\mathbf{k}, \lambda\rangle$ corresponding to the emission of a photon with momentum $\mathbf{k}$ and polarization vector $\mathbf{e}_\lambda$ (with $\mathbf{e}_\lambda \cdot \mathbf{k} = 0$, $\lambda = 1, 2$).

Taking all this into account, the state vector of the system—consisting of the radiation field and the two electrons, interacting with the nuclei, each other, and the radiation field—can be written as

$$|\Psi\rangle = \left(\int d^3\mathbf{p} \, b_{\mathbf{p}} \psi_{\mathbf{p}} + a \psi_a \right) |0\rangle + \sum_{\mathbf{k}, \lambda} c_{\mathbf{k}, \lambda} \psi_c |\mathbf{k}, \lambda\rangle, \tag{2}$$

where the unknown time-dependent coefficients $b_{\mathbf{p}}$, a, and $c_{\mathbf{k}, \lambda}$ satisfy the initial conditions $a(t \to -\infty) = 0$, $c_{\mathbf{k}, \lambda}(t \to -\infty) = 0$, and $b_{\mathbf{p}}(t \to -\infty) = \delta(\mathbf{p} - \mathbf{p}_i)$, where $\mathbf{p}_i$ is the asymptotic momentum of the incident electron.

The total (effective) Hamiltonian reads

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{\text{ph}} + V_{AB} + \hat{W}. \tag{3}$$

Here, $\hat{H}_A$, $\hat{H}_B$, and $\hat{H}_{\text{ph}}$ are the Hamiltonians for the subsystems A, B, and the radiation field, respectively, and the interaction V_{AB} is given by Eq. (1). Further, $\hat{W} = \frac{1}{c}\hat{\mathbf{A}}(\mathbf{r}_1) \cdot \hat{\mathbf{p}}_1 + \frac{1}{c}\hat{\mathbf{A}}(\mathbf{r}_2) \cdot \hat{\mathbf{p}}_2$ is the interaction of the electrons with the

radiation field, where $\hat{\mathbf{p}}_1$ and $\hat{\mathbf{p}}_2$ are the electron momenta and $\hat{\mathbf{A}}(\mathbf{r})$ is the vector potential for the quantized radiation field.

Taking into account Eqs. (1)–(3) one can show that the recombination cross section reads

$$\sigma = \frac{4\pi^2 \omega_0}{c^3 v_i} \sum_{\lambda=1}^{2} \int d\Omega_{\mathbf{k}} \left| \langle \phi_b | \mathbf{e}_\lambda \cdot \hat{\mathbf{p}}_1 | \phi_{\mathbf{p}_i} \rangle \right.$$
$$+ \frac{V_{a,\mathbf{p}_i}}{E_{p_i} - E_a + i\Gamma/2} \left(\langle \varphi_b | \mathbf{e}_\lambda \cdot \hat{\mathbf{p}}_2 | \varphi_e \rangle \right.$$
$$\left. \left. + \int d^3\mathbf{p} \frac{V_{\mathbf{p},a} \langle \phi_b | \mathbf{e}_\lambda \cdot \hat{\mathbf{p}}_1 | \phi_{\mathbf{p}} \rangle}{\varepsilon_{p_i} - \varepsilon_p + i0} \right) \right|^2. \tag{4}$$

Here, $\Omega_{\mathbf{k}}$ is the solid angle of the emitted photon, v_i is the incident electron velocity, $\phi_{\mathbf{p}}$ and ϕ_b are the continuum and bound states of this electron in the field of the nucleus A, and φ_b and φ_e are the ground and excited states of the electron in the atom B. The energies of these states are denoted by ε_p, ε_b, ϵ_b, and ϵ_e, respectively, and $E_p = \varepsilon_p + \epsilon_b$ and $E_a = \varepsilon_b + \epsilon_e$. Further,

$$V_{a,\mathbf{p}} = \langle \psi_a | V_{AB} | \psi_{\mathbf{p}} \rangle$$
$$= \frac{\langle \phi_b | r_i | \phi_{\mathbf{p}} \rangle \langle \varphi_e | \xi_j | \varphi_b \rangle}{R^3} \left(\delta_{ij} - 3 \frac{R_i R_j}{R^2} \right), \tag{5}$$

and $\Gamma = \Gamma_a + \Gamma_{\text{rad}}^{(B)}$ denotes the total width of the resonant two-electron state, where $\Gamma_a = 2\pi |\mathbf{p}_i| \int d\Omega_{\mathbf{p}_i} |V_{a,\mathbf{p}_i}|^2$ and $\Gamma_{\text{rad}}^{(B)}$ are the respective contributions due to two-center Auger decay and spontaneous radiative decay of the excited state of the atom B.

According to Eq. (4) there are three qualitatively different quantum pathways for capturing the incident electron. (i) The transition $\phi_{\mathbf{p}_i} \to \phi_b$ occurs without the participation of the atom B via direct photon emission. (ii) The electron is captured from the state $\phi_{\mathbf{p}_i}$ into the state ϕ_b by inducing the transition $\varphi_b \to \varphi_e$ in the atom B; the latter afterwards deexcites by photon emission. (iii) The incident electron undergoes the transitions $\phi_{\mathbf{p}_i} \to \phi_b \to \phi_{\mathbf{p}} \to \phi_b$ in which the first two steps are accompanied by the (radiationless) transitions $\varphi_b \to \varphi_e \to \varphi_b$ in the atom B while the last one proceeds via photon emission. The pathways (ii) and (iii) are resonant and become efficient only if the energies E_{p_i} and E_a are very close.

When considering solely the pathway (ii) in Eq. (4), we obtain the partial cross section for 2CDR. Averaged over incoming electron angles, it reads

$$\sigma_{\text{2CDR}} = \frac{\pi}{p_i^2} \frac{\Gamma_a \Gamma_{\text{rad}}^{(B)}}{(E_{p_i} - E_a)^2 + \Gamma^2/4}. \tag{6}$$

We note that, when more than one intermediate state of the same energy exists in atom B (reachable by a dipole transition), the cross sections (4) and (6) involve an appropriate sum over these states.

Let us now consider two illustrative examples. First we discuss a very simple and basic situation which can be

treated easily in detail. Assume that an electron recombines with a proton into the $1s$ state while a He^+ ion is located nearby which may be excited to a $2p$ level with magnetic quantum number m: $e^- + H^+ + He^+(1s) \rightarrow H(1s) + He^+(2p_m) \rightarrow H(1s) + He^+(1s) + \gamma$. In this case the electron wave functions are known analytically and we obtain

$$\Gamma_a(2p_m) = \frac{2^{21}\pi}{3^{11}} \frac{C_m}{R^6} \frac{Z_A^6}{Z_B^2 \omega_0^5} \frac{e^{-(4Z_A/p_i)\arctan(p_i/Z_A)}}{1 - e^{-2\pi Z_A/p_i}}, \quad (7)$$

with $C_0 = 1$ and $C_{\pm 1} = 1/4$ for the intermediate $2p_m$ states in He^+ with $m = 0$ and $m = \pm 1$, respectively. The quantization axis is chosen along the internuclear separation vector $\mathbf{R}$. For the nuclear charges $Z_A = 1$ and $Z_B = 2$ of the example, we obtain $\Gamma_a(2p_0) = 4\Gamma_a(2p_{\pm 1}) \approx 0.08/R^6$. The radiative decay width $\Gamma_{\text{rad}}^{(B)} = 2^{17}\omega_0^3/(3^{11}c^3 Z_B^2) \approx 2.4 \times 10^{-7}$ a.u. surpasses the Auger widths for $R \gtrsim 8$ a.u. Assuming a resonant electron energy $\varepsilon_{p_i} = 1$ a.u., the 2CDR cross section (6) largely exceeds single-center RR up to $R \approx 100$ a.u. (see Fig. 2). Therefore, even taking into account that only a small fraction of the electrons might be able to participate in 2CDR because of its resonant character, it is obvious that this process can compete with and even strongly dominate over single-center RR.

In a complete picture of the recombination process, all the channels and their interference must be accounted for since they lead to the same final state [see Eq. (4)]. As a result, we obtain

$$\sigma = \frac{\sigma_{\text{RR}}^{(A)}}{3} \sum_{m=-1}^{1} \frac{[E_{p_i} - E_a + q_m \Gamma_a(2p_m)]^2 + (\Gamma_{\text{rad}}^{(B)}/2)^2}{(E_{p_i} - E_a)^2 + \Gamma^2/4}. \quad (8)$$

Here, $q_0 = -2|\langle\varphi_b|\boldsymbol{\xi}\cdot\mathbf{R}|\varphi_e\rangle|^2/(R^5\Gamma_a(2p_0))$ and $q_{\pm 1} = -2q_0$ can be termed as two-center Fano parameters. Similarly to the usual Fano parameters in the case of single-center DR [2,12], they describe the relative strength
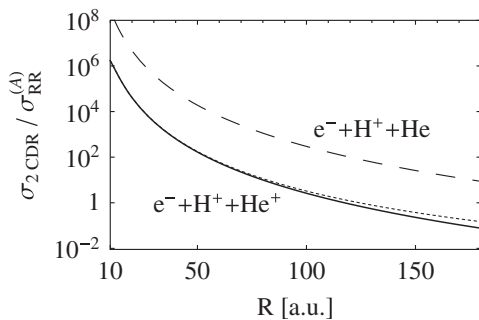

FIG. 2. Ratio of $\sigma_{2\text{CDR}}$ to $\sigma_{\text{RR}}^{(A)}$ as a function of internuclear distance. The solid line and the dotted line refer to the system "$e^- + H^+ + He^+(1s)$," with the dotted line including retardation effects. For comparison, the system "$e^- + H^+ + He(1s^2)$" is described by the dashed line. In both cases, the change of the incident electron energy is assumed to be resonant with the corresponding first dipole-allowed transition energy for the center B ($\varepsilon_{p_i} = 1$ and 0.28 a.u., respectively).

of the indirect (2CDR) versus the direct (RR) capture channels as a function of the incident electron energy. However, in contrast to single-center DR, in our case the Fano parameters depend on the internuclear distance, implying that the shape of the recombination cross section varies with R (see Fig. 3 for an illustration).

2CDR in systems similar to the previous example is of relevance in plasmalike environments such as warm dense matter [13] where typical densities ~ 0.1 g/cm^3 and temperatures T corresponding to $kT \sim 1$ eV prevail. This state of matter is found, e.g., in astrophysical objects or thermonuclear fusion plasmas and can be produced in the laboratory by intense laser-solid interaction [14]. 2CDR can clearly affect the time evolution and charge balance of warm dense matter systems. Indeed, at $\omega_0 \sim 1$ a.u. and $R \sim 10$ a.u., it dominates over RR by ≈ 7 orders of magnitude at the resonance. For $\Gamma \sim 10^{-7}$ a.u., a fraction of $\Gamma/kT \sim 10^{-6}$ of all electrons contributes to 2CDR, implying that it greatly exceeds RR also in the total number of recombination events.

Within a more general (but less detailed) approach, 2CDR can also be treated to a good approximation in much more complex systems. To this end, we note that the two-center Auger width can be expressed in terms of $\Gamma_{\text{rad}}^{(B)}$ and the photoionization cross section $\sigma_{\text{PI}}^{(A)}$ of atom A as $\Gamma_a \sim (1/R^6)(c/\omega_0)^4 \sigma_{\text{PI}}^{(A)} \Gamma_{\text{rad}}^{(B)}$ up to a numerical prefactor of order unity [15]. The photoionization cross section is related to the RR cross section $\sigma_{\text{RR}}^{(A)}$ via the principle of detailed balance: $p_i^2 \sigma_{\text{RR}}^{(A)} \propto (\omega_0/c)^2 \sigma_{\text{PI}}^{(A)}$. Exactly on the resonance, the ratio between the cross sections for 2CDR and single-center RR thus becomes

$$\sigma_{2\text{CDR}}/\sigma_{\text{RR}}^{(A)} \sim (c/R\omega_0)^6, \quad (9)$$

assuming that $\Gamma_a \lesssim \Gamma_{\text{rad}}^{(B)}$ holds, which will be the case at sufficiently large values of R.

The next example illustrates that 2CDR can be of relevance in (bio)chemical environments as well, where free electrons are always present due to photoionization by ultraviolet radiation [16]. When an alkali salt such as NaCl is dissolved in water, the molecule dissociates into an alkali cation (Na^+) and a remaining anion (Cl^-) which are both surrounded by water molecules forming hydration shells. We consider the $Na^+(H_2O)_n$ complex where on average $n = 6$ water molecules shield the cation at a mean distance of about $R \approx 6$ a.u. [17]. The ionization energy of neutral Na is 5.14 eV, and the first (photo) absorption band in water begins at ≈ 6.7 eV, reaching its maximum at ≈ 7.5 eV. According to Eq. (9), the assistance by a single water molecule at $R = 10$ a.u. and resonant electron energies $\varepsilon_{p_i} \approx 1.5$–4 eV would enhance the recombination with the Na^+ ion by ≈ 10 orders of magnitude. This number can serve as a lower estimate for the enhancement effect at the real value of $R \approx 6$ a.u. (where the dipole approximation might not be very reliable). The dramatic enhancement is further amplified by the fact that
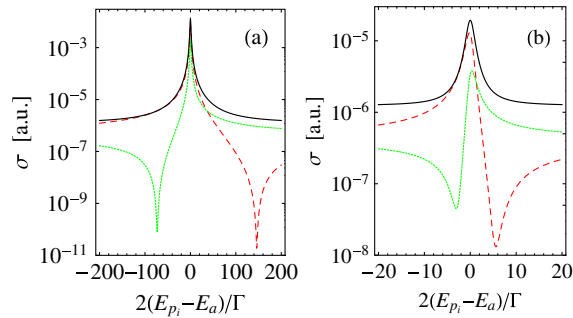
FIG. 3 (color online). Fano profiles for the $2p_0$ (red dashed curves) and $2p_1$ (green dotted curves) intermediate states and for the whole process $e^- + H^+ + He^+(1s) \rightarrow H(1s) + He^+(1s) + \gamma$ (black solid curves). The internuclear distances are (a) $R = 25$ a.u. and (b) $R = 75$ a.u.

more than one water molecule surrounds the cation, which can be taken into account approximately by multiplication with the coordination number $n = 6$ [11]. Since the absorption band in water is relatively broad, we may conclude that there is also an enormous effect for the total number of recombination events (integrated over the incident electron energies).

This example clearly demonstrates that 2CDR can be important in chemical systems. It may be generalized to solvated biomolecules where the enhanced recombination can lead to accelerated bond breaking and dissociation, which may initiate a subsequent reaction chain producing chemically active fragments and radicals [16,18].

Let us very briefly compare 2CDR with single-center DR. The latter is described by a formula analogous to Eq. (6) but occurs, in general, at different resonance energies. Single-center Auger rates $\Gamma_a^{(A)}$ are typically orders of magnitude larger than the radiative ones. As a result, at comparable resonance energies, the ratio $\sigma_{2CDR}/\sigma_{DR}^{(A)} \propto \Gamma_a \Gamma_a^{(A)}/(\Gamma_{rad}^{(A)} \Gamma_{rad}^{(B)})$ can largely exceed unity. One can also show that the ratio of the energy-integrated cross sections (i.e., of the resonance strengths) varies in a broad range depending on the system parameters and can be both smaller and larger than unity. The latter is the case, for instance, in the example of Na^+ in water considered above. Such competitiveness of 2CDR with single-center DR (despite $\Gamma_a^{(A)} \gg \Gamma_a$) is due to the fact that here the majority of initially captured electrons remains bound because $\Gamma_a \lesssim \Gamma_{rad}^{(B)}$.

Finally, we would like to mention that 2CDR (as well as the process considered in [11]) can be viewed as a kind of three-body recombination in which—in contrast to its standard case—the role of the free assisting electron is played by an (initially) bound electron.

In conclusion, we have shown that the presence of neighboring atomic centers at nanometer distances can resonantly enhance the recombination (or attachment) probability by orders of magnitude. The resonance effect is so strong that it can largely outperform RR even after averaging over incident electron energy distributions much broader than the resonance width. Representing a hitherto unexplored and efficient recombination mechanism, this two-center process is of general interest by itself and deserves further study. Additionally, it may play a significant role in chemical and dense plasma environments where it can substantially affect the quantum dynamics and time evolution of the system.

Concerning experimental verification of the predicted effects, 2CDR with water molecules seems to be most feasible. Indeed, electron recombination with $Na^+(D_2O)$ was already explored in a storage ring, but at lower energies ($\varepsilon_{p_i} \lesssim 0.1$ eV) [19]. Moreover, dedicated experiments on hydrated atoms and molecules have become possible just recently, utilizing liquid jets of aqueous solution injected into vacuum chambers. Atomic collision studies [18] and ultrafast photoelectron spectroscopy [20] on solvated substances are carried out this way, for example. Similar methods could be applied to study the 2CDR.

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