Two-Center Resonant Photoionization

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(Received 8 July 2010; revised manuscript received 30 August 2010; published 5 October 2010)

Photoionization of an atom A, in the presence of a neighboring atom B, can proceed both directly and via resonant excitation of B with subsequent energy transfer to A through two-center electron-electron correlation. We show that in such a case the photoionization process can be very strongly enhanced and acquire interesting characteristic features, both in its time development and the electron spectrum.

DOI: 10.1103/PhysRevLett.105.153002 PACS numbers: 32.80.Hd, 33.60.+q, 82.50.Hp

Ever since Einstein proposed his interpretation of the photoelectric effect [1], photoionization (PI) studies on atoms and molecules have played a key role in our understanding of the basic laws of quantum physics. Modern PI experiments providing complete information on all quantum degrees of freedom allow for stringent tests of the most advanced calculations [2]. A new era of PI studies is presently being opened by the worldwide emergence of advanced light sources such as x-ray free-electron laser (XFEL) facilities (see [3] and references therein).

The structure and time evolution of matter on a microscopic scale crucially depends on electron-electron correlations. Their influence ranges from atoms and small molecules to organic macromolecules and solids. Electron correlations are responsible for deexcitation reactions in slow atomic collisions [4] and quantum gases [5]. They play a prominent role in energy transfer between chromophores [6] and lattice dynamics in polymers [7]. They also represent the origin of magnetism and superconductivity [8]. Another effect caused by electron correlations is interatomic Coulombic decay (ICD) of inner-valence vacancies [9]. ICD was observed in rare gas dimers, clusters and water molecules [10–13]. Interatomic decays were also studied in metallic compounds [14–16]. Electron-ion recombination can be strongly influenced by the presence of a neighboring atom as well [17].

PI may reveal particularly clean manifestations of electronic correlations. Prominent examples are single-photon double ionization [18], laser-induced autoionization [19], and nonsequential double ionization in strong laser fields [20].

Against this background we study in this Letter photoionization, which involves resonant electronic correlations between two neighboring atomic centers (atoms, ions or molecules). In this process, which may be termed two-center resonant photo ionization (2CPI), one of the reaction pathways for ionization of an atom is radiationless transfer of excitation from a neighboring atom, whose bound states are resonantly coupled by the external electromagnetic (EM) field (see Fig. 1). Characteristic properties of 2CPI are revealed both in quite weak and more intense EM fields. In case of weak fields PI can be enhanced by orders of magnitude in the presence of a neighboring atom. The case of more intense fields is characterized by a stepwise development of the ionization in time and multiple peaks in the energy spectrum of photoelectrons. Corresponding experiments may be feasible at synchrotron or XFEL beam lines. Our study thus connects the currently very active research areas of interatomic phenomena [9–17] and field-induced PI dynamics [3]. Another example of this topical combination are decay mechanisms in multiply ionized clusters [21] after XFEL irradiation.

In order to understand the basics of 2CPI, we consider PI in a very simple atomic system consisting of two one-electron atoms (A and B). Both are initially in their ground states and separated by a distance R large enough, such that one can still speak about individual atoms. Let, for definiteness, the ionization potential $I_A = -\varepsilon_0$ of the atom A be smaller than the excitation energy $\Delta E_B = \epsilon_e - \epsilon_0$ of a dipole allowed $1s$-np transition in the atom B. If such a system is irradiated by an EM field with frequency $\omega_0 \approx \Delta E_B$, the presence of the atom B may have a substantial influence on the ionization process. Indeed, in such a case the atom A can be ionized not only directly but also via resonance photoexcitation of the atom B into the nl state with its consequent deexcitation through ICD [22].

Let us suppose that the atomic nuclei having charge numbers Z_A and Z_B, respectively, are at rest. We 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.

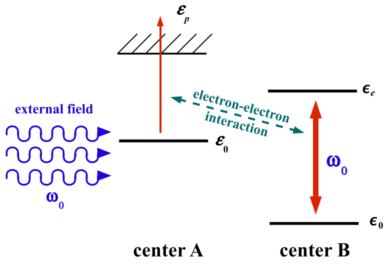

FIG. 1 (color online). Scheme of two-center resonant photoionization (2CPI).

Our consideration of the photoionization process is based on the equation [23]

$$i\partial_t|\Psi\rangle = (\hat{H}_0 + \hat{W} + \hat{V}_{\text{rad}})|\Psi\rangle. \tag{1}$$

Here $|\Psi\rangle$ is the state vector of the system consisting of the atoms A, B and the radiation field, $\hat{H}_0$ is the sum of the Hamiltonians for the noninteracting atoms A and B and the free radiation field, $\hat{V}_{\text{rad}}$ the interaction of the electrons with the radiation field and $\hat{W}$ is the interaction of the electrons with the external EM field. The latter will be taken as a classical, linearly polarized field, described by the vector potential $\mathbf{A} = c\mathbf{F}_0/\omega_0 \cos(\omega_0 t - \mathbf{k}_0 \cdot \mathbf{r})$, where $\omega_0 = ck_0$ and $\mathbf{k}_0$ are the angular frequency and wave vector, c is the speed of light and $\mathbf{F}_0$ is the field strength. The interaction $\hat{W}$ then reads

$$\begin{gathered}\hat{W} = \hat{W}_0^+ \exp(-i\omega_0 t) + \hat{W}_0^- \exp(i\omega_0 t),\\ \hat{W}_0^\pm = \sum_{j=1,2} \exp(\pm i\mathbf{k}_0 \cdot \mathbf{r}_j) \frac{\mathbf{F}_0}{2\omega_0} \cdot \hat{\mathbf{p}}_j,\end{gathered} \tag{2}$$

where $\hat{\mathbf{p}}_j$ is the momentum operator for the jth electron.

In order to treat the interaction of the electrons with the radiation field we adopt the covariant approach in which this field is described by four potentials in a Lorentz gauge and the interaction between the electrons is mediated by the exchange of transverse, longitudinal and scalar photons [24].

In the process under consideration we have essentially four different basic two-electron configurations: (i) $\psi_g = u_0(\mathbf{r}_1)\chi_0(\boldsymbol{\xi})$—both electrons are in the corresponding ground states u_0 and χ_0; (ii) $\psi_a = u_0(\mathbf{r}_1)\chi_e(\boldsymbol{\xi})$, in which the electron of the atom A is in the ground state while the electron of the atom B is in the excited state χ_e; (iii) $\psi_{\mathbf{p},g} = u_\mathbf{p}(\mathbf{r}_1)\chi_0(\boldsymbol{\xi})$—the electron of the atom A is in a continuum state $u_\mathbf{p}$ and the electron of the atom B in the ground state; and (iv) $\psi_{\mathbf{p},e} = u_\mathbf{p}(\mathbf{r}_1)\chi_e(\boldsymbol{\xi})$—the electron of the atom A is in a state $u_\mathbf{p}$ while the electron of the atom B is in the state χ_e.

The radiation field is initially in its vacuum state $|0\rangle$ and then undergoes a transition into a state $|\mathbf{k}, \lambda\rangle$ in which one transverse ($\lambda = 1, 2$), longitudinal ($\lambda = 3$) or scalar ($\lambda = 0$) photon with momentum $\mathbf{k}$ is present.

Taking all this into account, one can look for the solution for $|\Psi\rangle$ by expanding it into the "complete" set of quantum states according to

$$\begin{aligned}|\Psi\rangle = \bigg(&g\psi_g + a\psi_a + \int d^3\mathbf{p}\,\alpha_\mathbf{p}\psi_{\mathbf{p},g}\\ &+ \int d^3\mathbf{p}\,\beta_\mathbf{p}\psi_{\mathbf{p},e}\bigg)|0\rangle + \sum_{\mathbf{k},\lambda}\bigg(g_{\mathbf{k},\lambda}\psi_g + a_{\mathbf{k},\lambda}\psi_a\\ &+ \int d^3\mathbf{p}\,\alpha_\mathbf{p}^{\mathbf{k},\lambda}\psi_{\mathbf{p},g} + \int d^3\mathbf{p}\,\beta_\mathbf{p}^{\mathbf{k},\lambda}\psi_{\mathbf{p},e}\bigg)|\mathbf{k}, \lambda\rangle.\end{aligned} \tag{3}$$

By inserting (3) into (1) one obtains a set 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 $\{\beta_\mathbf{p}^{\mathbf{k},\lambda}\}$. These equations can be solved analytically if one uses the first order perturbation theory or the rotating-wave approximation with respect to the interaction $\hat{W}$.

Solving these equations also yields the interaction $\hat{V}^{ee}$ between the electrons. Although the electron motion is nonrelativistic, this interaction nevertheless has, in general, to account for the retardation effect. It becomes of great importance when the time $\sim R/c$, which the light needs for traversing the distance between the electrons, compares with or exceeds the effective time $\sim 1/\omega_0$ of the electron transitions. For electrons undergoing electric dipole transitions the interaction V^{ee} reads

$$\hat{V}^{ee} = \frac{\alpha}{R^3}(e^{ik_0R} - ik_0Re^{-ik_0R}) - \frac{k_0^2\beta}{R}e^{ik_0R}, \tag{4}$$

where $\alpha = r_{1i}\xi_j(\delta_{ij} - 3R_iR_j/R^2)$, $\beta = r_{1i}\xi_j(\delta_{ij} - R_iR_j/R^2)$, r_{1i} and ξ_j ($i, j = x, y, z$) are the components of the coordinates of the electrons and a summation over the repeated indices is implied. It follows from (4) that at distances $R \ll k_0^{-1}$ the interaction practically reduces to the instantaneous interaction of two electric dipoles while at $k_0R \gtrsim 1$ the use of the instantaneous and retarded forms for this interaction leads to large differences.

We first examine the case of a weak EM field, where relatively simple formulas can be obtained for the ionization probability p_A^{ion}. The weak-field case is described by the first order perturbation theory with respect to the interaction $\hat{W}$ that is valid when $\max\{W_{e,0}^B, \Gamma_i\}T \ll 1$, where $W_{e,0}^B = \langle\chi_e|\hat{W}_0^+|\chi_0\rangle$, $\Gamma_i = 2\pi\int d\Omega_\mathbf{p}p_0|W_{\mathbf{p}_0,0}^A|^2$ ($W_{\mathbf{p},0}^A = \langle u_\mathbf{p}|\hat{W}_0^+|u_0\rangle$) is the width of the ground state of the atom A caused by its (direct) photo decay and T is the pulse duration of the EM field. Assuming for definiteness that the field is instantaneously switched on at $t = 0$, when both atoms are in the ground states, we obtain that the probability to find the atom A in its continuum states is, for sufficiently long pulses ($\bar{\Gamma}_aT > 1$), given by

$$p^{2\text{CPI}} = \int d\Omega_\mathbf{p}\left|W_{\mathbf{p}_0,0}^A + \frac{V_{\mathbf{p}_0,a}^{ee}\tilde{W}_{e,0}^B}{\epsilon_0 + \omega_0 - \epsilon_e + i\bar{\Gamma}_a/2}\right|^2T. \tag{5}$$

Here, $\Omega_\mathbf{p}$ and $|\mathbf{p}_0| = \sqrt{2(\varepsilon_0 + \omega_0)}$ are the solid angle and the absolute value of the momentum of the emitted electron, respectively, $V_{\mathbf{p},a}^{ee} = \langle u_\mathbf{p}, \chi_0|\hat{V}^{ee}|u_0, \chi_e\rangle$, $\bar{\Gamma}_a = \Gamma_a + \Gamma_r$ is the total width of the state ψ_a, where Γ_a and Γ_r are the contributions due to ICD and spontaneous radiative decay of the state χ_e, respectively, and

$$\tilde{W}_{e,0}^B = W_{e,0}^B + \int d^3\mathbf{p}\frac{V_{a,\mathbf{p}}^{ee}W_{\mathbf{p},0}^A}{\varepsilon_0 + \omega_0 - \varepsilon_p + i0}. \tag{6}$$

Equations (5) and (6) show that there are three qualitatively different pathways for ionization of the atom A. (i) The atom A is directly ionized by the EM 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 EM field drives the electron of atom A into the continuum but the electron returns back into the ground state u_0 due to the two-center electron-electron interaction and only afterwards the same interaction transfers the electron into the final continuum state $u_{\mathbf{p}_0}$. The pathways (ii) and (iii) are resonant and become efficient only if the frequency ω_0 lies in the interval $\Delta E_B - \bar{\Gamma}_a \lesssim \omega_0 \lesssim \Delta E_B + \bar{\Gamma}_a$.

For illustration in Fig. 2 we show the ratio $p^{2\mathrm{CPI}}/p^{(i)}$, where $p^{2\mathrm{CPI}}$ is the ionization probability for Li in a Li-He system and $p^{(i)} = \frac{T}{2\pi}\Gamma_i$ is the ionization probability for an isolated Li atom. This ratio is given for $R = 10$ Å as a function of the normalized detuning $X = (\omega_0 - \omega_{\mathrm{res}})/\bar{\Gamma}_a$ from the resonant frequency $\omega_{\mathrm{res}} = \epsilon_e - \epsilon_0 \approx 21$ eV corresponding to the $1s^{2\,1}S - 1s2p\,^1P$ transition in He. Figure 2 demonstrates a huge increase in ionization at small X and the importance of interference between the different reaction pathways at large X.

Assuming that $k_0 R \ll 1$, the partial contribution of the pathway (ii) reads

$$p^{(ii)} = \frac{T}{2\pi}\frac{\Gamma_a |W^B_{e,0}|^2}{(\epsilon_0 + \omega_0 - \epsilon_e)^2 + \bar{\Gamma}_a^2/4}. \tag{7}$$

According to Fig. 2 the $p^{(ii)}/p^{(i)}$ ratio can reach enormous values at the resonance frequency $\omega_{\mathrm{res}} = \epsilon_e - \epsilon_0$. At distances R, where $\Gamma_a < \Gamma_r$, the ratio of the integral contributions of these two channels is given by

$$\eta \sim \frac{p^{(ii)} \times \bar{\Gamma}_a}{p^{(i)} \times \Delta\omega_0} \approx \left(\frac{c/\omega_0}{R}\right)^3 \left(\frac{a_0}{R}\right)^3 \frac{1/a_0}{Z_B^2 \Delta\omega_0}, \tag{8}$$

where a_0 is the Bohr radius and $\Delta\omega_0$ is the spectral width of the EM field. When R decreases, η becomes less steeply dependent on R and eventually R independent at distances, where $\Gamma_a > \Gamma_r$. Although the pathway (ii) is effective only in the vicinity of the resonance while the direct channel may act for the whole width $\Delta\omega_0 \gg \bar{\Gamma}_a$, the ratio η can be quite large.

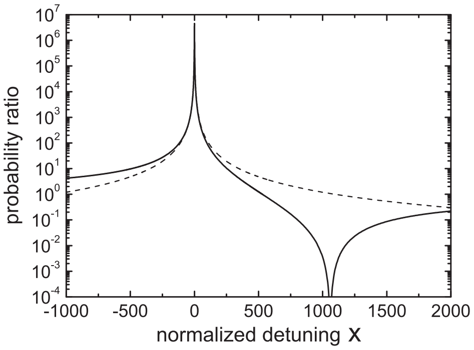

FIG. 2. The ratios $p^{2\mathrm{CPI}}/p^{(i)}$ (solid curve) and $p^{(ii)}/p^{(i)}$ (dashed curve) for a Li-He system at $R = 10$ Å.

Let us consider van der Waals heterodimer NaKr [25] in the electronic ground state. For $R \approx 10$ Å, $\omega_0 \approx 10$ eV, corresponding to the $4p - 5s$ transition in Kr, and assuming $\Delta\omega_0 \sim 1$ meV, the PI of Na ($I_A = 5.14$ eV) is enhanced by $\eta \sim 10^4$ due to 2CPI. This number may be considered a lower bound of the enhancement effect at the real equilibrium distance $R \approx 5$ Å, where the assumption $\Gamma_a < \Gamma_r$ underlying Eq. (8) might not hold.

Another suitable van der Waals dimer is ^{7}Li^{4}He. It is a very weakly bound and largely extended molecule. The mean internuclear separation is predicted to be $R \approx$ 30–40 Å [26]. Remarkably, even at distances that large, 2CPI triples the ionization yield from Li at $\omega_0 \approx 21$ eV (and assuming again $\Delta\omega_0 \sim 1$ meV), which corresponds to the $1s^{2\,1}S - 1s2p\,^1P$ transition in He. An alternative way of observing 2CPI in the Li-He system might employ Li atoms attached to helium nanodroplets.

2CPI may also occur in biological tissue after absorption of light or UV radiation. In fact, the process resembles the energy transfer between organic molecules via Förster resonances and related bystander effects [6]. The main difference is that 2CPI involves a resonant coupling to the continuum.

To conclude our discussion of weak-field 2CPI we note that it is closely related to multiatom resonant photoemission (MARPE) via photoexcitation of core electrons [15]. MARPE relies on basically similar physical mechanisms as weak-field 2CPI but was found much less efficient because the large transition frequencies involved strongly decrease the role of the interatomic coupling compared to that of the intra-atomic decay channels.

Let us now turn to ionization in stronger EM fields, when $\max\{W^B_{e,0}, \Gamma_i\}T \gtrsim 1$, which can be considered using the rotating-wave approximation. Compared to the weak-field case, ionization of the atom A due to the presence of the atom B is now enhanced less dramatically, but acquires interesting new features. In Fig. 3 we show the probability of ionization of a Li atom in the EM field with $F_0 = 10^{-4}$ a.u. ($I = 3.5 \times 10^8$ W/cm^2) when a He atom is located nearby (at $R = 5$, 7.5 and 10 Å). The frequency $\omega_0 \approx 21$ eV is chosen to be resonant to the $1s^{2\,1}S - 1s2p\,^1P$ transition in He. For simplicity it is assumed that $\mathbf{F}_0 \parallel \mathbf{R}$ [27]. For comparison the ionization probability of an isolated Li is also displayed.

For the parameters chosen one has $\Gamma_i = 2.7 \times 10^{-8}$ eV, $|W^B_{e,0}| = 4.3 \times 10^{-4}$ eV, $\Gamma_r = 4 \times 10^{-7}$ eV and $\Gamma_a = 4.9 \times 10^{-6}$, 4.2×10^{-7} and 7.6×10^{-8} eV for $R = 5$, 7.5 and 10 Å, respectively. It is seen in the figure that compared to the ionization probability of an isolated Li atom, which simply monotonically increases with time, ionization in the presence of a He atom shows a stepwise behavior in which time intervals, where the ionization probability rapidly increases, are separated by intervals, where the probability remains almost constant.

The origin of this is rather simple. In the resonant EM field the population of He oscillates between its ground and

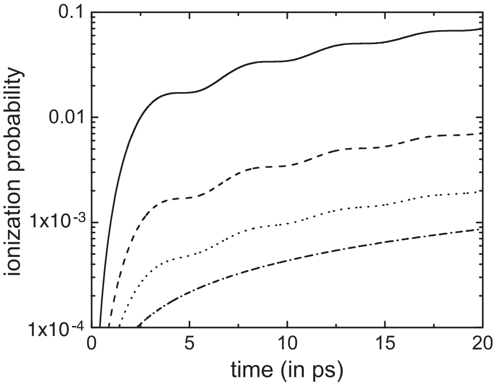

FIG. 3. Ionization probability for Li in the presence of He as a function of time. $F_0 = 10^{-4}$ a.u., the field frequency is resonant to the $1s^{21}S - 1s2p^1P$ transition in He. The solid, dash and dot curves display results for $R = 5$, 7.5, and 10 Å, respectively. For comparison, the ionization probability for an isolated Li atom in the same EM field is shown by the dash-dotted curve.

excited states with the frequency $\Omega = 2|W^B_{e,0}|$. Once the population of the excited state becomes noticeable, ICD comes into play opening the additional pathway for ionization of the Li atom. When most of the population has returned back into the ground state of He, ICD effectively switches off and the ionization process weakens. Since Γ_a exceeds Γ_i for all the three distances, for all of them the ICD channel has a strong effect on the ionization of Li.

Additional insight into 2CPI can be obtained by considering the energy spectrum of emitted electrons. At sufficiently large T it consists of three pronounced peaks (see Fig. 4). Their origin is similar to the splitting into three lines of the energy spectrum of photons emitted during atomic fluorescence in a resonant EM field [28]. In such a field the ground and excited levels of the center B split into two sublevels, which in the case $\omega_0 = \omega_{\rm res}$ differ by Ω: $\epsilon_0 \rightarrow \epsilon_0 \pm \Omega/2$ and $\epsilon_e \rightarrow \epsilon_e \pm \Omega/2$. As a result, when undergoing autoionizing transitions the energy transfer to the center A peaks at ω_0 and $\omega_0 \pm \Omega/2$.

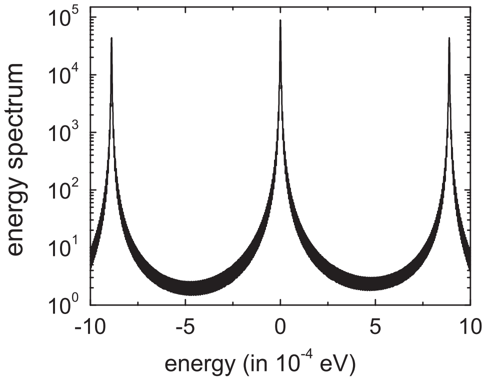

FIG. 4. Energy spectrum of the emitted electrons, as a function of $\Delta = \varepsilon_p - \varepsilon_0 - \omega_0$, for the same atomic system and field as in Fig. 3, $R = 5$ Å and $T = 920$ ps.

In conclusion, PI of an atomic center A can change dramatically in the presence of a neighboring center B at nanometer distances provided one of the transition frequencies of the latter is close to the field frequency. This resonance effect is especially strong in the case of weak EM fields when it may enhance photoionization by orders of magnitude. In stronger EM fields photoionization acquires new interesting features. In particular, a stepwise increase in the ionization probability with time and a splitting of the photoelectron spectrum into three prominent lines, similar to resonance fluorescence, arise. This efficient two-center ionization mechanism may also play a significant role in chemical and biological systems.

B. N. acknowledges the support from the DFG under the project VO 1278/2-1.

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