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## Resonantly enhanced photoionization in correlated three-atomic systems

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## Resonantly enhanced photoionization in correlated three-atomic systems

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**Abstract.** Modifications of photoionization arising from resonant electron–electron correlations between neighbouring atoms in an atomic sample are studied. The sample contains atomic species *A* and *B*, with the ionization potential of *A* being smaller than the energy of a dipole-allowed transition in *B*. The atoms are subject to an external radiation field which is near resonant with the dipole transition in *B*. Photoionization of an atom *A* may thus proceed via a two-step mechanism: photoexcitation in the subsystem of species *B*, followed by interatomic Coulombic decay. As a basic atomic configuration, we investigate resonant photoionization in a three-atomic system *A–B–B* consisting of an atom *A* and two neighbouring atoms *B*. It is found that, under suitable conditions, the presence of neighbouring atoms can strongly affect the photoionization process, including its total probability, time development and photoelectron spectra. In particular, comparing our results with those for photoionization of an isolated atom *A* and a two-atomic system *A–B*, respectively, we reveal the characteristic impact made by the third atom.



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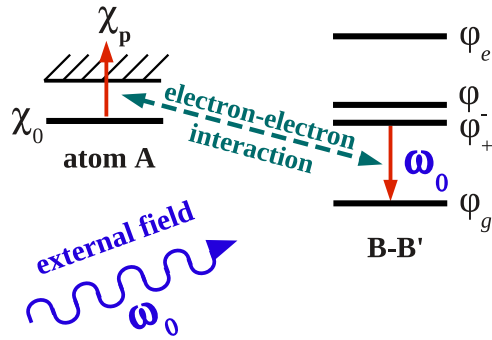
## 1. Introduction

Photoionization of atoms and molecules is one of the most fundamental quantum processes. It played a key role in the early days of quantum mechanics and has ever since been paving the way for a better understanding of the structure and dynamics of matter on a microscopic scale. Today, kinematically complete photoionization experiments allow for accurate tests of the most sophisticated *ab initio* calculations. Besides, photoionization studies in a new frequency domain are currently becoming feasible because of the availability of novel extreme ultraviolet and x-ray radiation sources [1–3], giving rise to corresponding theoretical developments (see, e.g., [4–6]).

Various photoionization mechanisms rely crucially on electron–electron correlations. Prominent examples are single-photon double ionization as well as resonant photoionization. The latter proceeds through resonant photoexcitation of an autoionizing state with subsequent Auger decay. In recent years, a similar kind of ionization process has been studied in systems consisting of two (or more) atoms. Here, a resonantly excited atom transfers its excitation energy radiationlessly via interatomic electron–electron correlations to a neighbouring atom, leading to its ionization. This Auger-like decay involving two atomic centres is nowadays commonly known as interatomic Coulombic decay (ICD) [7, 8]. It has been observed, for instance, in noble gas dimers and water molecules [9]. In metal oxides, the closely related process called multi-atom resonant photoemission was also observed [10].

We have recently studied resonant two-centre photoionization in heteroatomic systems and shown that this ionization channel can be remarkably strong [11–13]. In particular, it can dominate over the usual single-centre photoionization by orders of magnitude. Besides, the characteristic effects resulting from a strong coupling of the ground and autoionizing states by a relatively intense photon field were identified. Also, resonant two-photon ionization in a system of two identical atoms was investigated in [14]. We note that photoionization in two-atomic systems was also studied in [15–18]. The inverse of two-centre photoionization (in weak external fields) is two-centre dielectronic recombination [19].

In this paper, we extend our investigations on electron correlation-driven interatomic processes by considering the photoionization of an atom *A* in the presence of *two* neighbouring atoms *B* (see figure 1). All atoms are assumed to interact with each other and with an external radiation field. We show that the photoionization of atom *A* via photoexcitation of the system of two neighbouring atoms *B* and subsequent ICD can be, by far, the dominant ionization channel. Moreover, we reveal the characteristic properties of the process with regard to its



**Figure 1.** Schematic illustration of photoionization of an atom  $A$  in the presence of an external laser field and two neighbouring atoms  $B$  and  $B'$ . Apart from the direct photoionization of  $A$ , there are interatomic channels via resonant photoexcitation of the ‘molecular’ system  $B-B'$  and subsequent ICD.

temporal dependence and photoelectron spectra. In particular, comparing our results with those for photoionization in a system composed of two atoms  $A$  and  $B$ , we demonstrate the influence that the presence of the second atom  $B$  may have.

Atomic units (au) are used throughout the paper unless otherwise stated.

## 2. Theoretical framework

Let us consider a system consisting of three atoms,  $A$ ,  $B$  and  $B'$ , where  $B$  and  $B'$  are atoms of the same element and  $A$  is different. We shall assume that all these atoms are separated by sufficiently large distances such that free atomic states represent a reasonable initial basis set to start with.

Let the ionization potential  $I_A$  of atom  $A$  be smaller than the excitation energy  $\Delta E_B$  of a dipole-allowed transition in atoms  $B$  and  $B'$ . Under such conditions, if our system is irradiated by an electromagnetic field with frequency  $\omega_0 \approx \Delta E_B$ , the ionization process of this system (i.e. essentially of the atom  $A$ ) can be qualitatively different compared to the case when a single, isolated atom  $A$  is ionized. Indeed, in such a case,  $A$  can be ionized not only directly but also via resonant photoexcitation of the subsystem of  $B$  and  $B'$ , with its consequent deexcitation through energy transfer to  $A$ , resulting in ionization of the latter.

In the following, we consider photoionization in the system of atoms  $A$ ,  $B$  and  $B'$  in more detail. For simplicity, we suppose that the nuclei of all atoms are at rest during photoionization. Denoting the origin of our coordinate system by  $O$ , we assume that the nuclei of the atoms  $B$  and  $B'$  are located on the  $Z$ -axis:  $\mathbf{R}_B = (0, 0, Z_B)$  and  $\mathbf{R}_{B'} = (0, 0, Z_{B'})$ . The coordinates of the nucleus of the atom  $A$  are given by  $\mathbf{R}_A = (X_A, Y_A, Z_A)$ . The coordinates of the (active) electron of atom  $\lambda$  with respect to its nucleus are denoted by  $\mathbf{r}_\lambda$ , where  $\lambda \in \{A, B, B'\}$ .

The total Hamiltonian describing the three atoms embedded in an external electromagnetic field reads

$$H = \hat{H}_0 + \hat{V}_{AB} + \hat{V}_{AB'} + \hat{V}_{BB'} + \hat{W}_A + \hat{W}_B + \hat{W}_{B'}, \quad (1)$$

where  $\hat{H}_0$  is the sum of the Hamiltonians for the noninteracting atoms  $A$ ,  $B$  and  $B'$ .

We shall assume that the (typical) distances  $\Delta R$  between the atoms are not too large,  $\Delta R \ll c/\Delta E_B$ , where  $c$  is the speed of light, such that retardation effects in the electromagnetic

interactions can be ignored. If transitions of electrons between bound states in atoms  $B$  and  $B'$  are of dipole character, then the interaction between each pair of atoms  $(\lambda, \gamma)$  (with  $\lambda, \gamma \in \{A, B, B'\}$ ) can be written as

$$\hat{V}_{\lambda,\gamma} = \frac{(\mathbf{r}_\lambda)_i (\mathbf{r}_\gamma)_j}{R_{\lambda,\gamma}^3} \left( \delta_{ij} - \frac{3 (\mathbf{R}_{\lambda,\gamma})_i (\mathbf{R}_{\lambda,\gamma})_j}{R_{\lambda,\gamma}^2} \right), \quad (2)$$

where  $\mathbf{R}_{\lambda,\gamma} = \mathbf{R}_\lambda - \mathbf{R}_\gamma$  and  $\delta_{ij}$  is the Kronecker symbol. Note that in (2) a summation over the repeated indices  $i$  and  $j$  is implied.

In (2),  $\hat{W}_\lambda$  denotes the interaction of the atom  $\lambda$  with the laser electromagnetic field. The latter will be treated as a classical, linearly polarized field, described by the vector potential  $\mathbf{A}(t) = \mathbf{A}_0 \cos(\omega_0 t)$ , where  $\mathbf{A}_0 = c\mathbf{F}_0/\omega_0$ ,  $\omega_0 = ck_0$  is the angular frequency and  $\mathbf{F}_0$  is the field strength. The interaction  $\hat{W}_\lambda$  then reads

$$\hat{W}_\lambda = \frac{1}{c} \mathbf{A}(t) \cdot \hat{\mathbf{p}}_\lambda, \quad (3)$$

where  $\hat{\mathbf{p}}_\lambda$  is the momentum operator for the electron in atom  $\lambda$ .

Our treatment of photoionization will be based on the following points.

Oscillator strengths for dipole-allowed bound-bound transitions can be very strong. This means that, provided that the distances between all the atoms in our system are of the same order of magnitude, the interaction between atoms  $B$  and  $B'$  is much more effective than the interaction between atoms  $A$  and  $B$  (or  $A$  and  $B'$ ). Besides, atoms  $B$  and  $B'$  will, in general, couple much more strongly to a resonant laser field than atom  $A$ . In what follows, we shall assume that the intensity of the laser field is relatively low such that the interaction between atoms  $B$  and  $B'$  changes the states of the system more substantially than the coupling of these atoms to the laser field. Therefore, we shall begin with building states of the  $B$ - $B'$  subsystem in the absence of the field. The second step of our treatment will be to include the interaction of the  $B$ - $B'$  subsystem with the laser field and, in the third step, we complete the treatment of ionization by considering the interaction of atom  $A$  with both the laser field and the field-dressed subsystem of atoms  $B$  and  $B'$ .

- I. We denote the ground and excited states of the undistorted atoms  $B$  and  $B'$  by  $\phi_0$ ,  $\phi_e$  and  $\phi'_0$ ,  $\phi'_e$ , respectively. Let the corresponding energies of these states be  $\varepsilon_0$  and  $\varepsilon_e$ . The state  $\psi_{BB'}$  of the  $B$ - $B'$  subsystem can be expanded into the 'complete' set of undistorted atomic states represented by the configurations (i)  $\phi_0\phi'_0$ , (ii)  $\phi_0\phi'_e$ , (iii)  $\phi_e\phi'_0$  and (iv)  $\phi_e\phi'_e$ . In the approximation, which neglects the interatomic interaction, the configurations  $\phi_0\phi'_e$  and  $\phi_e\phi'_0$  are characterized by exactly the same value of the (undistorted) energy  $E_{0e} = \varepsilon_0 + \varepsilon_e$ . The latter, in turn, strongly differs from the energies  $E_{00} = 2\varepsilon_0$  and  $E_{ee} = 2\varepsilon_e$  which are characteristic of the configurations  $\phi_0\phi'_0$  and  $\phi_e\phi'_e$ , respectively. Therefore, provided that the distance between the atoms is not too small, the interaction  $V_{BB'}$  will strongly mix the configurations (ii) and (iii) only, while the other configurations (i) and (iv) will be affected only very weakly. Taking this into account, it is not difficult to find the states of the subsystem of interacting atoms  $B$  and  $B'$  which read

$$\begin{aligned} \varphi_g &= \phi_0\phi'_0, \\ \varphi_+ &= \frac{1}{\sqrt{2}} (\phi_e\phi'_0 + \phi_0\phi'_e), \end{aligned}$$

$$\begin{aligned}\varphi_- &= \frac{1}{\sqrt{2}} (\phi_e \phi'_0 - \phi_0 \phi'_e), \\ \varphi_e &= \phi_e \phi'_e.\end{aligned}\quad (4)$$

These two-atomic states are normalized and mutually orthogonal. They possess energies given by  $E_g = 2\varepsilon_0$ ,  $E_+ = \varepsilon_0 + \varepsilon_e + v_{BB'}$ ,  $E_- = \varepsilon_0 + \varepsilon_e - v_{BB'}$  and  $E_e = 2\varepsilon_e$ , respectively, where  $v_{BB'} = \langle \phi_e \phi'_0 | \hat{V}_{BB'} | \phi_0 \phi'_e \rangle$ . Note that, for definiteness,  $v_{BB'}$  has been assumed to be real and negative here, as will always be the case in our examples below (see section 3).

- II. Let us now consider two interacting atoms  $B$  and  $B'$  embedded in a resonant laser field. One can look for a state of such a system by expanding it into the new set of states given by equation (4),

$$\psi(t) = g(t)\varphi_g + a_+(t)\varphi_+ + a_-(t)\varphi_- + b(t)\varphi_e. \quad (5)$$

Inserting the expansion (5) into the corresponding wave equation, we obtain a set of coupled equations for the unknown time-dependent coefficients  $g(t)$ ,  $a_+(t)$ ,  $a_-(t)$  and  $b(t)$ :

$$\begin{aligned}i\frac{dg}{dt} - E_g g &= \langle \varphi_g | \hat{W}_B + \hat{W}_{B'} | \varphi_+ \rangle a_+ + \langle \varphi_g | \hat{W}_B + \hat{W}_{B'} | \varphi_- \rangle a_- \\ &\quad + \langle \varphi_g | \hat{W}_B + \hat{W}_{B'} | \varphi_e \rangle b, \\ i\frac{da_+}{dt} - E_+ a_+ &= \langle \varphi_+ | \hat{W}_B + \hat{W}_{B'} | \varphi_g \rangle g + \langle \varphi_+ | \hat{W}_B + \hat{W}_{B'} | \varphi_- \rangle a_- \\ &\quad + \langle \varphi_+ | \hat{W}_B + \hat{W}_{B'} | \varphi_e \rangle b, \\ i\frac{da_-}{dt} - E_- a_- &= \langle \varphi_- | \hat{W}_B + \hat{W}_{B'} | \varphi_g \rangle g + \langle \varphi_- | \hat{W}_B + \hat{W}_{B'} | \varphi_+ \rangle a_+ \\ &\quad + \langle \varphi_- | \hat{W}_B + \hat{W}_{B'} | \varphi_e \rangle b, \\ i\frac{db}{dt} - E_e b &= \langle \varphi_e | \hat{W}_B + \hat{W}_{B'} | \varphi_g \rangle g + \langle \varphi_e | \hat{W}_B + \hat{W}_{B'} | \varphi_+ \rangle a_+ \\ &\quad + \langle \varphi_e | \hat{W}_B + \hat{W}_{B'} | \varphi_- \rangle a_-.\end{aligned}\quad (6)$$

The system of equations (6) can be greatly simplified by noting the following. Firstly, all transition matrix elements of the interaction with the laser field, which involve the asymmetric state  $\varphi_-$ , are equal to zero and, thus, only the remaining three states can be coupled by the field. Secondly, if we suppose that the frequency of the laser field is resonant with the transitions  $\varphi_g \leftrightarrow \varphi_+$  and that the field is relatively weak such that the nonresonant transitions  $\varphi_+ \leftrightarrow \varphi_e$  are much less effective than the above resonant ones, system (6) effectively reduces to

$$\begin{aligned}i\frac{dg}{dt} - E_g g &= \langle \varphi_g | \hat{W}_B + \hat{W}_{B'} | \varphi_+ \rangle a_+, \\ i\frac{da_+}{dt} - E_+ a_+ &= \langle \varphi_+ | \hat{W}_B + \hat{W}_{B'} | \varphi_g \rangle g,\end{aligned}\quad (7)$$

which can be readily solved by using the rotating wave approximation. Assuming that the field is switched on suddenly at  $t = 0$ , we obtain two solutions

$$\begin{aligned} \psi_1(t) = & \frac{1}{z_2 - z_1} \left[ (z_2 + \omega_0 - E_+) e^{-iz_2 t} - (z_1 + \omega_0 - E_+) e^{-iz_1 t} \right] \varphi_g \\ & + \frac{W_{+,g}}{z_2 - z_1} (e^{-iz_2 t} - e^{-iz_1 t}) e^{-i\omega_0 t} \varphi_+ \end{aligned} \quad (8)$$

and

$$\begin{aligned} \psi_2(t) = & \frac{W_{g,+}}{z_2 - z_1} (e^{-iz_2 t} - e^{-iz_1 t}) \varphi_g \\ & + \frac{1}{z_2 - z_1} \left[ (z_2 - E_g) e^{-iz_2 t} - (z_1 - E_g) e^{-iz_1 t} \right] e^{-i\omega_0 t} \varphi_+. \end{aligned} \quad (9)$$

In the above equations, we have introduced

$$\begin{aligned} z_1 = & \frac{1}{2} (E_g + E_+ - \omega_0 - \Omega_R), \\ z_2 = & \frac{1}{2} (E_g + E_+ - \omega_0 + \Omega_R), \end{aligned} \quad (10)$$

where  $\Omega_R = \sqrt{(E_+ - E_g - \omega_0)^2 + 4 |W_{g,+}|^2}$  is the Rabi frequency,  $W_{g,+} = \langle \varphi_g | \mathbf{F}_0 \cdot (\hat{\mathbf{p}}_B + \hat{\mathbf{p}}_{B'}) / (2\omega_0) | \varphi_+ \rangle$  and  $W_{+,g} = (W_{g,+})^*$ .

The two solutions in (8) and (9) correspond to two different initial conditions: at  $t = 0$  the system is either in the state  $\varphi_g$  or in  $\varphi_+$ . They are orthogonal to each other and form a ‘complete’ set of field-dressed states of the subsystem  $B-B'$ . Note also that we have neglected the spontaneous radiative decay of the excited state  $\varphi_+$  which, in our case, is justified as long as  $|W_{g,+}| \gg \Gamma_r$ , where  $\Gamma_r$  is the radiative width of  $\varphi_+$ .

- III. Now, as the last step, we shall add atom  $A$  to our consideration. Let  $\chi_0$  and  $\chi_{\mathbf{p}}$ , where  $\mathbf{p}$  is the electron momentum, be the ground and a continuum state of a single, isolated atom  $A$ . The wavefunction of the total system  $A-B-B'$  can be expanded into the following ‘complete’ set of states:

$$\Psi(t) = \alpha_0(t) \psi_1 \chi_0 + \beta_0(t) \psi_2 \chi_0 + \int d^3 \mathbf{p} \alpha_{\mathbf{p}}(t) \psi_1 \chi_{\mathbf{p}} + \int d^3 \mathbf{p} \beta_{\mathbf{p}}(t) \psi_2 \chi_{\mathbf{p}}. \quad (11)$$

Here, the initial conditions are given by  $\alpha_0(0) = 1$ ,  $\beta_0(0) = 0$  and  $\alpha_{\mathbf{p}}(0) = \beta_{\mathbf{p}}(0) = 0$ . The coupling of atom  $A$  to both the subsystem  $B-B'$  and the laser field involves bound–continuum transitions which are normally much less effective than the (resonant) bound–bound ones. For this reason, we may assume that the interactions of  $A$  with the laser field and the  $B-B'$  subsystem are weak and consider ionization of atom  $A$  in the lowest order of perturbation theory in these two interactions. As a result, inserting expansion (11) into the corresponding Schrödinger equation, we obtain

$$\begin{aligned} i \frac{d\alpha_{\mathbf{p}}}{dt} - \epsilon_{\mathbf{p}}^A \alpha_{\mathbf{p}} = & \exp(-i\epsilon_g^A t) \langle \psi_1 \chi_{\mathbf{p}} | \hat{W}_A + \hat{V}_{AB} + \hat{V}_{AB'} | \psi_1 \chi_0 \rangle, \\ i \frac{d\beta_{\mathbf{p}}}{dt} - \epsilon_{\mathbf{p}}^A \beta_{\mathbf{p}} = & \exp(-i\epsilon_g^A t) \langle \psi_2 \chi_{\mathbf{p}} | \hat{V}_{AB} + \hat{V}_{AB'} | \psi_1 \chi_0 \rangle, \end{aligned} \quad (12)$$

where  $\epsilon_g^A$  is the energy of the electron in the initial state  $\chi_0$  of atom  $A$  and  $\epsilon_p^A$  is the electron energy after the emission. The energy spectrum of emitted electrons, as a function of time, is thus given by

$$\sigma(\epsilon_p^A, t) = \int d\Omega_p p (|\alpha_p(t)|^2 + |\beta_p(t)|^2), \quad (13)$$

where  $\Omega_p$  is the solid angle of emission. The time-dependent probability for ionization of the three-atomic system accordingly reads

$$P(t) = \int d^3\mathbf{p} (|\alpha_p(t)|^2 + |\beta_p(t)|^2) = \int_0^\infty d\epsilon_p^A \sigma(\epsilon_p^A, t). \quad (14)$$

Equations (12) are readily solved analytically. With the redefinitions  $\tilde{\alpha}_p(t) = \exp(-i\epsilon_p^A t)\alpha_p(t)$  and  $\tilde{\beta}_p(t) = \exp(-i\epsilon_p^A t)\beta_p(t)$ , which do not change the moduli of the complex amplitudes, we obtain

$$\begin{aligned} \tilde{\alpha}_p(t) = & - \left[ \frac{1}{2\omega_0} \langle \chi_p | \mathbf{F}_0 \cdot \hat{\mathbf{p}}_A | \chi_0 \rangle + \frac{W_{+,g}(U_{AB} + U_{AB'})}{\sqrt{2}(z_2 - z_1)} \right] \frac{e^{i(\epsilon_p^A - \epsilon_g^A - \omega_0)t} - 1}{\epsilon_p^A - \epsilon_g^A - \omega_0} \\ & + (z_2 + \omega_0 - E_+) \frac{W_{+,g}(U_{AB} + U_{AB'})}{\sqrt{2}(z_2 - z_1)^2} \frac{e^{i(z_2 - z_1 + \epsilon_p^A - \epsilon_g^A - \omega_0)t} - 1}{z_2 - z_1 + \epsilon_p^A - \epsilon_g^A - \omega_0} \\ & + (z_1 + \omega_0 - E_+) \frac{W_{+,g}(U_{AB} + U_{AB'})}{\sqrt{2}(z_2 - z_1)^2} \frac{e^{i(z_1 - z_2 + \epsilon_p^A - \epsilon_g^A - \omega_0)t} - 1}{z_1 - z_2 + \epsilon_p^A - \epsilon_g^A - \omega_0} \end{aligned} \quad (15)$$

and

$$\begin{aligned} \tilde{\beta}_p(t) = & - \frac{W_{+,g}^2(U_{AB} + U_{AB'})}{\sqrt{2}(z_2 - z_1)^2} \left( 2 \frac{e^{i(\epsilon_p^A - \epsilon_g^A - \omega_0)t} - 1}{\epsilon_p^A - \epsilon_g^A - \omega_0} \right. \\ & \left. - \frac{e^{i(z_2 - z_1 + \epsilon_p^A - \epsilon_g^A - \omega_0)t} - 1}{z_2 - z_1 + \epsilon_p^A - \epsilon_g^A - \omega_0} - \frac{e^{i(z_1 - z_2 + \epsilon_p^A - \epsilon_g^A - \omega_0)t} - 1}{z_1 - z_2 + \epsilon_p^A - \epsilon_g^A - \omega_0} \right). \end{aligned} \quad (16)$$

Here, we introduced the abbreviation

$$U_{AB} = \frac{\langle \chi_p | (\mathbf{r}_A)_i | \chi_0 \rangle \langle \phi_0 | (\mathbf{r}_B)_j | \phi_e \rangle}{R_{A,B}^3} \left( \delta_{ij} - \frac{3(\mathbf{R}_{A,B})_i (\mathbf{R}_{A,B})_j}{\mathbf{R}_{A,B}^2} \right) \quad (17)$$

and correspondingly for  $U_{AB'}$ . The time integration in equations (12) was performed from 0 to  $t$ . Note that the calculation of the amplitudes only requires the knowledge of the dipole matrix elements between the ground and continuum states in atom  $A$  and the ground and excited states in atoms  $B$ .

### 3. Results and discussion

Based on the results obtained in the previous section, let us now turn to the discussion of some aspects of photoionization in a system consisting of one lithium and two helium atoms. We suppose that in our three-atomic system the positions of the lithium and helium atoms are given by the vectors  $\mathbf{R}_{\text{Li}} = (0, 0, 0)$ ,  $\mathbf{R}_{\text{He}} = (0, 0, Z)$  and  $\mathbf{R}_{\text{He}'} = (0, 0, -Z)$ , respectively. Note that an



equidistant partition of atoms guarantees that the influence of each of the He atoms on the Li atom is equally strong. The effects of the simultaneous presence of two neighbouring atoms, as compared to just one neighbouring atom, are thus most distinguished in this case. Our system is initially (at time  $t = 0$ ) in its ground configuration and is irradiated by a monochromatic laser field. The field is linearly polarized along the  $Z$ -axis and its frequency is resonant with the  $\varphi_g - \varphi_+$  transition in the He–He subsystem, i.e.  $E_+ - E_g - \omega_0 = 0$ .

In our numerical calculations, we describe each of the helium and lithium atoms as an effective one-electron system. In such a system, the electron moves in an effective potential whose parameters are chosen in such a way as to match the energy eigenvalues of all bound states of relevance. The continuum states of lithium are obtained by using the same effective potential as for its ground state.

### 3.1. Ionization probabilities

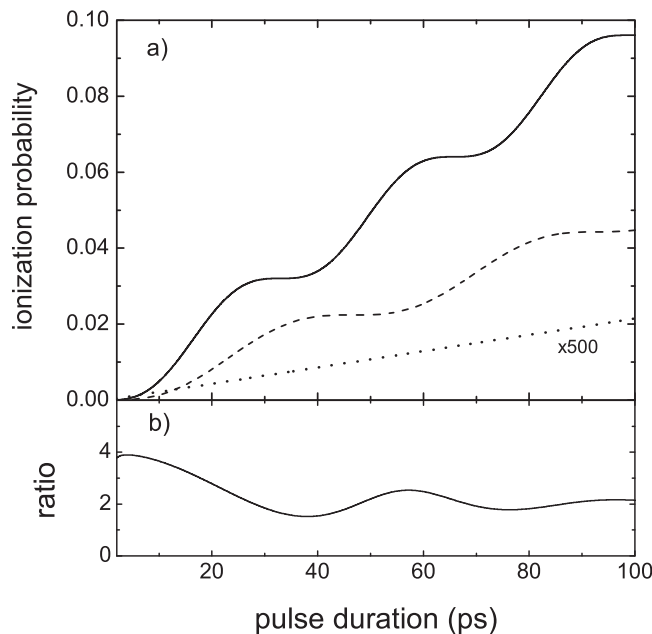
We start our discussion by considering the ionization probability of the Li–He–He system as given by equation (14). First, by choosing  $Z = 14$  au, we obtain that the energy splitting  $\Delta E_{\pm} = |E_+ - E_-|$  between the states  $\varphi_+$  and  $\varphi_-$  of the He–He subsystem is  $5.4 \times 10^{-4}$  eV. Assuming a field strength of  $F_0 = 10^{-5}$  au, the corresponding Rabi frequency amounts to  $\Omega_{R_{\text{He-He}}} = 2 |W_{g,+}| = 1.3 \times 10^{-4}$  eV which is substantially less than  $\Delta E_{\pm}$ . The radiative width of the  $\varphi_+$  state is much smaller, being of the order of  $\Gamma_r \sim 10^{-7}$  eV. With respect to the Li–He distance chosen, we note that in a system consisting of a Li atom attached to a He nanodroplet, the mean distance between the Li atom and the droplet surface is about 5–7 Å, which corresponds to 10–14 au.

In figure 2(a), we present the probability for ionization of our system as a function of time. The probability shows a nonmonotonic behaviour in which time intervals, when the ionization probability rapidly increases, are separated by intervals, when the probability remains practically constant, reflecting oscillations of the electron populations with the Rabi frequency  $\Omega_{R_{\text{He-He}}}$  between the ground and excited states of the He–He subsystem in a resonant electromagnetic field.

For comparison, we also show in figure 2(a) the results for ionization of a single (separated) Li atom and for ionization in a two-atomic Li–He system. In the latter case, the lithium atom is located at the origin ( $\mathbf{R}_{\text{Li}} = (0, 0, 0)$ ) and the coordinates of the helium atom are  $\mathbf{R}_{\text{He}} = (0, 0, 14 \text{ au})$ . The frequency of the laser field is assumed to be resonant with the  $1s^2\ ^1\text{S} - 1s2p\ ^1\text{P}$  transition frequency of the corresponding bound states of a single He atom.

In contrast to the single-atom ionization, in both the two- and three-atomic cases the ionization probability demonstrates a step-wise temporal development in which time intervals of rapid probability growth are followed by intervals of almost constant probability. We point out that in the three-atomic case, however, the size of these time intervals is shorter by a factor of  $\sqrt{2}$ .

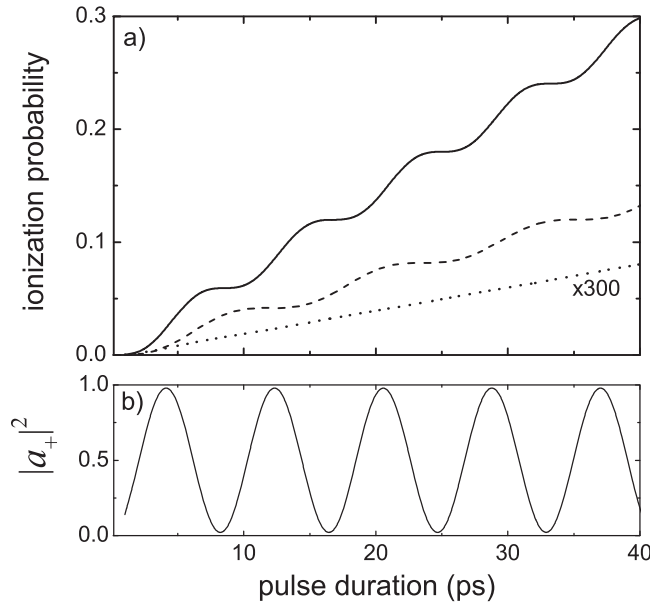
Compared to the ionization of a single Li atom, ionization in the two-atomic system is very strongly enhanced [11–13]. When the three-atomic system is irradiated, the enhancement increases even further. In the range of small values of  $t$ , where all ionization probabilities still increase monotonically, this additional enhancement is equal to a factor of 4 (see figure 2(b)). At larger  $t$ , however, when the two ionization probabilities exhibit step-wise behaviours, this additional enhancement due to the presence of the second He atom is reduced to a factor close to 2 on average, as can also be seen in figure 2(b).



**Figure 2.** (a) Photoionization probability for Li, Li-He and Li-He-He systems in an external electromagnetic field, given as a function of time. The field strength is  $F_0 = 10^{-5}$  au (corresponding to a field intensity of  $3.5 \times 10^6$  W cm $^{-2}$ ), the field is linearly polarized and its frequency is resonant with the corresponding transition in the He or He-He subsystem. The distances between Li and each of the He atoms is always 14 au. The atomic positions are aligned along the field polarization with the Li atom in the middle of the three-atomic system. The solid, dash and dot curves display the results for Li-He-He, Li-He and Li systems, respectively. Note that the ionization probability for an isolated Li atom has been multiplied by a factor of 500. For more explanation see the text. (b) Ratio of the ionization probability of the Li-He-He system to the ionization probability of the Li-He system.

All the above features can be understood by noting the following.

- (i) For the chosen set of parameters of our two- and three-centre systems, the indirect channels of ionization, which involve two- or three-atomic correlations, are substantially stronger than the direct one. Therefore, these correlations have a dominating effect on the ionization.
- (ii) At small times (i.e. at  $t < \Omega_{R_{\text{He-He}}}^{-1} \approx 5$  ps), ionization in the two- and three-atomic systems is basically a two-step process: the first step is photoexcitation in the He or He-He subsystem and the second step is a consequent energy transfer to Li. In each case, both these steps are described by basically the same dipole transition matrix element of the subsystem. Since, compared to a single He atom, this dipole element in He-He is by  $\sqrt{2}$  larger than in He, one obtains a factor of 2 for the enhancement in the ionization amplitude, leading to a factor of 4 in the ionization probability. (It is interesting to note that an enhancement by a factor of 4 would also follow from an analysis which treats the neighbouring atoms as independent of each other [20].)
- (iii) At larger  $t$ , when Rabi oscillations show up, the second step ‘saturates’ in the sense that the averaged probability to find the corresponding subsystem in the excited state becomes



**Figure 3.** (a) The same as figure 2(a) but for a Li–He interatomic distance of  $Z = 10$  au and an external field strength of  $F_0 = 4 \times 10^{-5}$  au (corresponding to a field intensity of  $5.6 \times 10^7$  W cm $^{-2}$ ). The ionization probability for an isolated Li atom (dot curve) has been multiplied by a factor of 300. (b) Time evolution of the population probability of the  $\varphi_+$  state.

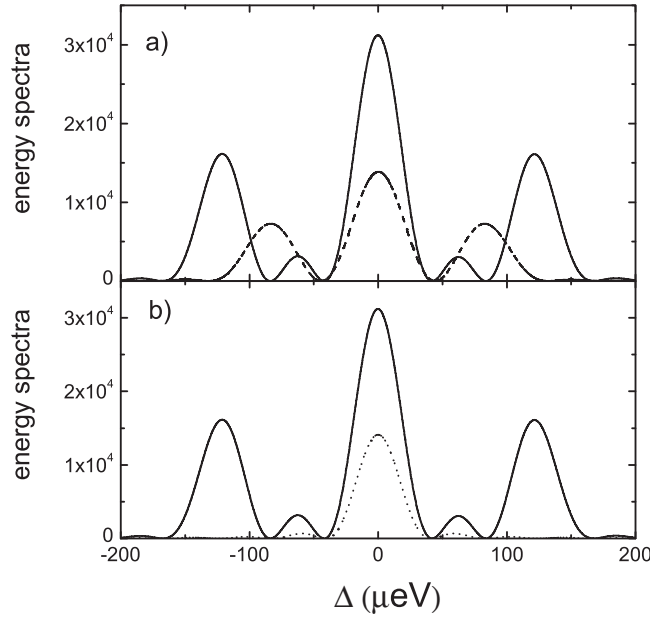
equal to 50%. Therefore, the ionization probability in the three-atomic system is now larger (on average) by a factor of 2 only.

- (iv) The origin of the step-wise behaviours of the ionization probabilities for the two- and three-atomic systems lies in the oscillations of the population between the ground and excited states in the He atom (for the two-atomic case) or in the He–He subsystem (for the three-atomic case). The scale of these oscillations is set by the Rabi frequency and, because in the He–He subsystem the latter is larger by a factor of  $\sqrt{2}$ , the corresponding time intervals are shorter by the same factor.

In order to obtain further insights into the ionization process and to illustrate its scaling properties, we present in figure 3(a) the ionization probability for another set of parameters. The distance between the Li atom and each of the He atoms has been reduced to  $Z = 10$  au, whereas the applied field strength was increased to  $F_0 = 4 \times 10^{-5}$  au. The energy splitting in the He–He subsystem thus amounts to  $\Delta E_{\pm} = 1.5 \times 10^{-3}$  eV, and the Rabi frequency is  $\Omega_{R_{\text{He-He}}} = 5 \times 10^{-4}$  eV.

As before, the shape of the curves in figure 3(a) can be traced back to points (i)–(iv), which are also valid here. In comparison with figure 2(a), however, one can see that the step duration is shortened in figure 3(a) for both the Li–He–He and the Li–He system. The reason is the enhanced Rabi frequency which is proportional to the applied field strength and, thus, four times larger. Figure 3(b), moreover, illustrates that the steps in the time dependence of the ionization probabilities directly correspond to the oscillating population dynamics of the  $\varphi_+$  state.

Besides, the ionization probabilities in the two- and three-atomic systems have grown substantially. This is because the indirect ionization channels due to correlation, which dominate



**Figure 4.** Energy spectra of the emitted electrons, as a function of  $\Delta = \epsilon_p^A - \epsilon_g^A - \omega_0$ , for the same parameters as in figure 2. The pulse duration is 100 ps. (a) Solid and dash curves show the results for ionization of the Li–He–He and Li–He systems, respectively. (b) Solid and dot curves display the results for ionization of the Li–He–He and Li systems, respectively. The results for the Li system have been multiplied by a factor of 500.

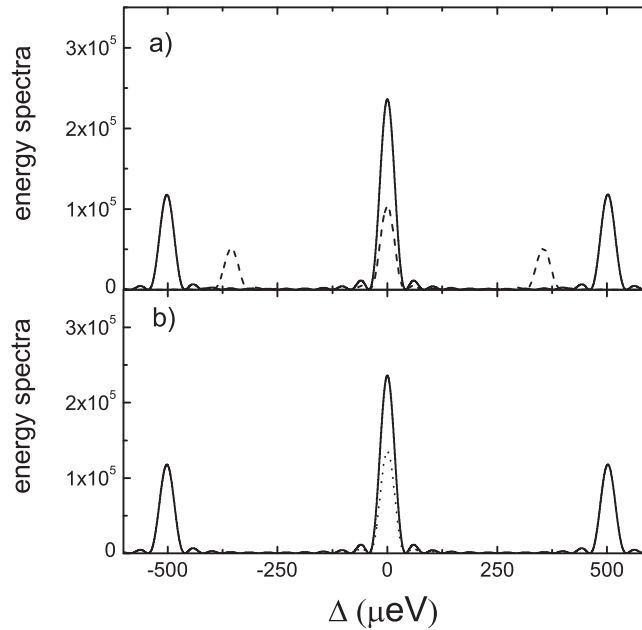
the ionization process, scale inversely with the interatomic distance to the sixth power,  $P \propto Z^{-6}$ . This scaling results from the unretarded dipole–dipole interaction between the Li and He atom(s) as given in equation (2). Hence, as compared with figure 2(a), the ionization probability has increased by a factor of  $\approx 8$  (on average).

Also, the ionization probability of the single Li atom has strongly increased due to the larger field strength applied. Within the first order of perturbation theory with respect to  $\hat{W}_A$ , as employed in equation (12), the ionization probability scales with  $F_0^2$  and has thus been enhanced by a factor of 16. As a consequence, the ratio of the ionization probability of the Li–He–He system (as well as the Li–He system) to the ionization probability of the single Li atom has roughly halved. Note that the indirect ionization channel via interatomic correlations is independent of the intensity of the applied electromagnetic field, provided that the frequency of the latter is exactly on the resonance (see also equations (15) and (16)).

### 3.2. Photoelectron spectra

Additional information about the ionization process can be obtained by considering the energy spectrum of emitted electrons. Such a spectrum is shown in figure 4 for the same systems and parameters as in figure 2 and for a pulse duration of  $T = 100$  ps.

In panel (a), we compare the energy spectra of electrons emitted in the process of photoionization of the Li–He–He and Li–He systems. In both cases, the main feature is the presence of three pronounced maxima. The origin of these peaks is similar to the splitting into



**Figure 5.** The same as figure 4 but for a Li–He interatomic distance of  $Z = 10$  au and an external field strength of  $F_0 = 4 \times 10^{-5}$  au (corresponding to a field intensity of  $5.6 \times 10^7$  W cm $^{-2}$ ). The results for an isolated Li atom shown by the dot curve in panel (b) have been multiplied by a factor of 300.

three lines of the energy spectrum of photons emitted during atomic fluorescence in a resonant electromagnetic field [21]. In such a field, the ground and excited levels of the He and He–He subsystems split into two sub-levels, which differ by the corresponding Rabi frequency  $\Omega_R$ . As a result, the resonant electronic correlations between these subsystems and the Li atom lead to an energy transfer to the Li which peaks at  $\omega_0$  and  $\omega_0 \pm \Omega_R/2$ . Since, as already mentioned, the Rabi frequencies of these subsystems differ by a factor of  $\sqrt{2}$ , the magnitude of the separation between the corresponding maxima in panel (a) of figure 4 also differs by this factor. Note also that the widths of these main maxima as well as the appearance of additional multiple maxima, seen in the figure, are related to the finiteness of the pulse duration; the distance between the latter is roughly given by  $2\pi/T \approx 40$   $\mu$ eV. We point out that a sufficiently long pulse duration is required in order to prevent overlapping of the three main peaks, i.e.  $T$  should be substantially larger than  $2\pi/\Omega_R$ . For the present parameters, this condition reads  $T \gg 10$ –20 ps.

The distinct influence which the interatomic electron–electron correlations exert on the shape of the photoelectron spectra is further highlighted in panel (b) of figure 4. It compares the energy spectra of photoelectrons emitted from our Li–He–He system and an isolated Li atom. In the latter case, there is only one main maximum, while the two main side peaks are missing, as one would expect (the additional multiple maxima are related again to the finiteness of the pulse duration).

Finally, the corresponding electron spectra for the parameters of figure 3 at  $T = 100$  ps are shown in figure 5. As compared with figure 4, the distance between the central peak and each of the two side peaks is now larger by a factor of 4. The reason is the four times enhanced field strength, which leads to a correspondingly enhanced Rabi frequency. The peak widths have not changed as compared with figure 4, since the pulse duration has been kept fixed.

#### 4. Conclusion and outlook

We have studied resonant photoionization in a system  $A-B-B'$  consisting of three atoms, with two atoms  $B$  of the same element and one different atom  $A$ . We have shown that the mutual correlations among the atoms can largely enhance the ionization probability and distinctly modify also other properties of the process in a characteristic manner. In particular, as compared to the case of resonant photoionization in a two-atom system  $A-B$ , it has been demonstrated that the presence of a second atom  $B$  can (i) further enhance the photoionization process, (ii) change the time dependence of the ionization probability and (iii) move the side peaks in the photoelectron spectrum further apart.

The present study significantly extends our previous investigations of resonant photoionization in two-atomic systems [11–14]. We have seen that the presence of a third atom is capable of changing the ionization process both qualitatively (leading, e.g., to a ‘molecular’ level splitting) and quantitatively (e.g. increasing the Rabi frequency and enhancing the ionization). A detailed understanding of these three-atom correlation effects is a necessary prerequisite before one can move on to examine the general case of resonant photoionization in a system of  $N$  mutually correlated atoms. The latter could be realized by attaching, for example, a Li atom to a He cluster or nanodroplet. The peculiar features of the correlation-driven photoionization process, including the enormous enhancement of the ionization probability, may be expected to become evident also in such more complex systems. Due to the spatial distribution of the He atoms, both with respect to angles and distances to the Li atom, the strength of the enhancement is expected to scale here with the coordination number of the Li atom.

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