Long-time joint spectra and entanglement of two photoelectrons originating in interacting auto-ionization systems

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Abstract
Two auto-ionization systems in a stationary optical field that are mutually interacting via the dipole–dipole interaction are considered. Their evolution is found analytically. Joint spectra of two ionized electrons are analyzed in detail in the long-time limit for comparable strengths of direct and indirect ionization paths as well as the dominating indirect ionization path. Entanglement in the state of two ionized electrons is quantified using the density of quadratic negativity. Suitable conditions for obtaining highly entangled states are discussed.

Keywords: two-electron ionization spectra, auto-ionization, dipole-dipole interaction, Fano model, bipartite entanglement, quadratic negativity

1. Introduction
Ionization is one of the most interesting physical processes arising from the interaction of atoms or molecules with electromagnetic fields. Ionized electrons are characterized by their ionization spectra that contain information about the electronic structure of the ionized atoms or molecules. For this reason, ionization processes have been used as a strong tool for the investigation of electronic structures [1, 2]. The ionization spectra are very sensitive to individual bound excited electronic states through which the ionization can efficiently proceed (for an extended list of references, see e.g [3–6]).

The mechanism of auto-ionization occurring with the contribution of a bound excited state has been extensively studied for He atoms containing only two electrons. Quantum mechanical calculations have shown that there is a large probability of exciting both electrons together [7] due to the strong electron–electron correlations present in the electronic ground state [8]. The energy of one of the excited electrons given to the other excited electron then allows ionization of this electron. The first electron then returns to its ground state.

This process, modelled in [9–11] with the inclusion of an additional probe field, has recently been observed using attosecond pump-probe spectroscopic techniques [12, 13].

The presence of an auto-ionizing state in atoms manifests itself in the ionization spectra by the so-called Fano zero [14]. It denotes an electron energy missing in the ionization spectrum. This occurs because of the completely destructive interference between the different paths of ionization, including the interference between direct and indirect (through an auto-ionizing state) ionization processes [15]. This interference also results in sharp peaks in the ionization spectra caused by intense laser pulses [16, 17]. As predicted by Fano [14], n zeroes will be present for n auto-ionizing levels for an atom as long as only a single ionization channel is available. They are replaced by local minima when more ionization channels are present, and they may even disappear in molecules because of the presence of nuclear motion [18].

The presence of auto-ionizing states considerably influences many physical effects. For example, auto-ionization systems have been investigated as media exhibiting electromagnetically-induced transparency [19–21]. They have also
been applied for slowing down the light propagating through the medium with auto-ionizing states [20]. Moreover, special attention has been devoted to the problem of near-threshold ionization [22] including quantum anti-Zeno effect [23]. The role of elastic collisions and finite laser spectral width has been analyzed for such systems in [24]. Auto-ionization has even been considered for weak quantum fields [25], in particular, for squeezed light [26]. Interestingly, Fano profiles and Fano resonances can appear not only in typical atomic/optical models. They have been found, for instance, in plasmonic systems [27, 28], various nanoscale structures [29] including quantum dots [30] or in a broad range of superconducting systems [31–33]. We note that states of the continuum and bound states participate together in the effect called the Feshbach resonance [34]. In this effect, a quasi-bound molecular state is formed from the state of two free atoms. This results in considerable enhancement of inelastic collision processes [35].

Ionization can also be observed due to the electronic Coulomb interaction between two excited electrons being at two neighbor atoms. In this case, energy of one excited electron is given to the excited electron on the neighbor atom at which ionization occurs [36]. If two excited electrons emerge from the interaction with the strong electromagnetic field, we have two-center resonant photo-ionization [37, 38]. Also, two-center dielectronic recombination [38, 39] which is just the inverse process in which a free electron is captured by a positively charged system of two neighbor atoms, has been suggested. These effects are important in atomic and molecular clusters in which the exponential character of these processes can be modified by additional interactions, e.g by capturing the ionized electron [40].

In an intense external field, double ionization may occur leaving two free ionized electrons [7]. It has been extensively studied in isolated atoms or molecules [41]. The dynamics of double ionization is predominantly governed by the strong Coulomb interaction among the electrons and the core of an atom. As a consequence, strong correlations in momenta of two ionized electrons occur [42, 43]. Considering He atoms, rotational and bending modes of the two-excited-electron motion preceded the ionization have been identified [44]. Double ionization of Ne atoms has been experimentally studied in [45].

Here, we consider another process in which two electrons are ionized in such a way that their energies are highly correlated. Contrary to the double ionization model of a single atom, we consider a system of two neighbor atoms or molecules under the interaction with a strong cw external field. Each atom or molecule provides one ionized electron. We assume here that each atom or molecule can be ionized through an auto-ionizing level or by the process of direct ionization. We show that, as a result of the dipole–dipole interaction between two atoms or molecules, the state of two ionized electrons can be strongly entangled and both electrons can exhibit strong spectral correlations.

The model considered here is analyzed using the algebraic method applied already by Fano [14]. Our model represents a generalization of the previously developed models in which ionization spectra and correlations between an ionized electron and a bound electron found at a neighbor atom have been studied. It has been shown that the so-called dynamical Fano zeroes occurring once per the Rabi period can be observed in conditional ionization spectra, independently on the presence [46] or absence [47] of an auto-ionizing level. Moreover, for the previously discussed systems, the dipole–dipole interaction leads to the generation of entangled states encompassing both the ionized and the bound electrons [48, 49]. The observed spectral correlations have been conveniently quantified by the density of quadratic negativity [50] defined in terms of partially transposed statistical operators [51, 52]. Moreover, it has been shown that the dipole–dipole interaction does not suppress the occurrence of the Fano zero in general, but its existence is restricted to only rather special conditions [53, 54]. Also a quantized field has been considered for the two-atom auto-ionizing model showing that many sharp peaks in the ionization spectra originating in discrete field energies can occur [49].

It will be shown that the exact Fano zeroes typical for ionization spectra of individual atoms cannot occur in the analyzed model of two auto-ionizing systems. On the other hand, many spectral features found in the Fano model of an auto-ionization system [14] are present in the analyzed system including sharp peaks and dips. The applied algebraic approach provides analytical formulas that allow to get a deep insight into the behavior of two interacting auto-ionization subsystems analyzing spectral correlations and entanglement [55] of the state of two ionized electrons. Similarly as in [48] the density of quadratic negativity is applied to quantify quantum spectral correlations. Although the model is discussed in general using the values of parameters emphasizing its main features, the values of parameters suitable for molecular condensates (including molecular crystals) [56] are also considered.

The paper is organized as follows. The Hamiltonian of two coupled auto-ionization systems in a stationary optical field is given in section 2, together with the corresponding dynamical equations and their solution. Quadratic negativity and its density as quantifiers of entanglement between two ionized electrons is introduced in section 3. Long-time photoelectron ionization spectra for the cases of comparable direct and indirect ionization paths (subsection 4.1) and dominating indirect ionization path (subsection 4.2) are analyzed in section 4. Entanglement in the long-time photoelectron spectra is discussed in section 5. Section 6 is devoted to the process of ionization in molecular condensates. Section 7 contains our conclusions. Analytical solution of the model without the mutual interaction is provided in appendix A. Appendix B is devoted to the competition of the dipole–dipole interactions between discrete auto-ionizing levels and with the continua.

2. Hamiltonian, dynamical equations and their solution

We consider two auto-ionization systems describing, e.g, two atoms or molecules that mutually interact by the dipole–dipole interaction (for the scheme, see figure 1). Both the ionization systems denoted as $a$ and $b$ are assumed to have one auto-ionizing level. They interact with a stationary optical
field with amplitude $\alpha_L$ and frequency $E_L$ through the corresponding dipole moments. Hamiltonian $\hat{H}_j$ describing the auto-ionization system $j$, $j = a, b$, can be written as ($\hbar = 1$ is assumed, [57]):

$$\hat{H}_j = \hat{H}_j^0 + \hat{H}_j^L, \quad j = a, b,$$  (1)

$$\hat{H}_j^0 = E_j^0 |1\rangle_j \langle 1| + \int dE_j E_j |E_j\rangle \langle E_j|$$

$$+ \int dE_j \left( V_j |E_j\rangle \langle E_j| + \text{H.c.} \right).$$  (2)

$$\hat{H}_j^L = \left[ \mu_j \alpha_L \exp(-iE_j t) |1\rangle_j \langle 0|$$

$$+ \int dE_j \beta_j \alpha_L \exp(-iE_j t) |E_j\rangle \langle 0| + \text{H.c.} \right].$$  (3)

In equations (1)–(3), Hamiltonian $\hat{H}_j^0$ describes the inner structure of auto-ionization system $j$ whereas Hamiltonian $\hat{H}_j^L$ arises from the interaction of the system with the optical field. Symbol $E_j^0$ denotes the excitation energy from the ground state $|0\rangle_j$ into the excited bound state $|1\rangle_j$ of atom $j$. The continuum of atom $j$ is formed by states $|E_j\rangle$ having energies $E_j$. The Coulomb configuration interaction between states $|1\rangle_j$ and $|E_j\rangle$ inside the continuum is described by coupling constant $V_j$. Dipole moments $\mu_j$ and $\beta_j$ characterize an optical excitation of the corresponding states. Symbol H.c. stands for the Hermitian conjugated term.

The dipole–dipole interaction between atoms $a$ and $b$ leads to energy transfer [56]. It can be described by the following Hamiltonian $\hat{H}_{\text{trans}}$:

$$\hat{H}_{\text{trans}} = |J_{ab}| \langle 0|_a 1|_b \langle 0|_b 1|_a \rangle$$

$$+ \int dE_a J_{ab} |E_a\rangle \langle 1|_b \langle 0|_b$$

$$+ \int dE_b J_{ab} |0|_a \langle E_b|_b \langle 1|_a \langle 0|_a \rangle + \text{H.c.}. \quad (4)$$

In this interaction, one electron loses its energy and returns into its ground state, whereas the other electron takes this energy and moves into its own excited/ionized state. Constant $J_{ab}$ describes the interaction between excited states $|1\rangle_b$ and $|1\rangle_b$ whereas constant $J_{ab}$ characterizes the interaction between excited state $|1\rangle_b [1\rangle_a]$ and ionized states $|E_a\rangle [E_b\rangle]$. We assume that the electrons in ionized states do not mutually interact.

A general quantum state of two electrons at atoms $a$ and $b$ written in the frame rotating with frequency $E_L$ can be expressed as:

$$|\psi\rangle(t) = c_{00}(t) |0\rangle_a |0\rangle_b + c_{10}(t) |1\rangle_a |0\rangle_b$$

$$+ c_{01}(t) |0\rangle_a |1\rangle_b + c_{11}(t) |1\rangle_a |1\rangle_b + \int dE_a \left[ d_{a,0}(E_a, t) |E_a\rangle \langle 0|_b$$

$$+ d_{a,1}(E_a, t) |E_a\rangle \langle 1|_b \right] + \int dE_b \left[ d_{b,0}(E_b, t) |0\rangle_b |E_b\rangle$$

$$+ d_{b,1}(E_b, t) |1\rangle_b |E_b\rangle \right] + \int dE_a \int dE_b d(E_a, E_b, t) |E_a\rangle |E_b\rangle. \quad (5)$$

Time-dependent coefficients $c_{00}$, $c_{01}$, $c_{10}$, $c_{11}$, $d_{a,0}(E_a)$, $d_{a,1}(E_a)$, $d_{b,0}(E_b)$, $d_{b,1}(E_b)$, and $d(E_a, E_b)$ characterize the state $|\psi\rangle$ at an arbitrary time $t$. They can be conveniently grouped into the vectors $\mathbf{c}(t) = [c_{00}(t), c_{01}(t), c_{10}(t), c_{11}(t)]$ and $\mathbf{d}(E_i, t) = [d_{i,0}(E_i, t), d_{i,1}(E_i, t)]$ for $i = a, b$. Symbol $\mathbf{T}$ denotes transposition. Normalization of the state $|\psi\rangle(t)$ in equation (5) provides the relation $\mathbf{c}(t)\mathbf{c}(t)^t + \sum_{j=a,b} \int dE_i d(E_i, t) \mathbf{d}(E_i, t)\mathbf{d}(E_i, t)^t + \int dE_a \int dE_b |d(E_a, E_b, t)|^2 = 1$.

The Schrödinger equation with the overall Hamiltonian $\hat{H}_L + \hat{H}_B + \hat{H}_{\text{trans}}$ provides the following dynamical equations for the coefficients characterizing state $|\psi\rangle(t)$ written in equation (5):

$$\frac{d}{dt} \left[ \begin{array}{c} \mathbf{c}(t) \\ d_{a,0}(E_a, t) \\ d_{a,1}(E_a, t) \\ d_{b,0}(E_b, t) \\ d_{b,1}(E_b, t) \\ \int dE_a B_a \\ 0 \\ 0 \\ \int dE_b B_b \\ 0 \\ 0 \end{array} \right] = \left[ \begin{array}{c} \mathbf{0} \\ \mathbf{K}_a \\ \mathbf{I}_a \\ \mathbf{0} \\ \mathbf{K}_b \\ \mathbf{I}_b \\ \mathbf{0} \end{array} \right],$$  (6)

In equation (6), symbol $\mathbf{I}$ (0) stands for the unity (zero) matrix of appropriate dimension(s).
Matrices $A$, $B_a$, $B_b$, $K_a$, $K_b$, $I_a$, and $I_b$ introduced in equation (6) are defined as follows:

$$
A = \begin{bmatrix}
0 & \mu_0^a \alpha_0^a \mu_0^b \alpha_0^b & 0 \\
\mu_0^a \alpha_0^a & \Delta E_0^a & J_{ab} \mu_0^b \alpha_0^b \\
\mu_0^a \alpha_0^a & J_{ab} \mu_0^b \alpha_0^b & 0 \\
0 & \mu_0^a \alpha_0^a & \Delta E_0^a + \Delta E_0^b
\end{bmatrix},
$$

(7)

$$
B_a = \begin{bmatrix}
\bar{\rho}_a^a \alpha_a^a & 0 & 0 \\
0 & V_{h}^a & 0 \\
0 & 0 & V_{h}^a
\end{bmatrix},
$$

and

$$
B_b = \begin{bmatrix}
\bar{\rho}_b^a \alpha_b^a & 0 & 0 \\
0 & V_{h}^b & 0 \\
0 & 0 & V_{h}^b
\end{bmatrix},
$$

$$
K_a = \begin{bmatrix}
0 & \mu_0^a \alpha_0^a & \mu_0^b \alpha_0^b \\
\mu_0^a \alpha_0^a & 0 & 0 \\
\mu_0^a \alpha_0^a & 0 & 0
\end{bmatrix},
$$

$$
I_a = \begin{bmatrix}
\rho_0^a \alpha_0^a & 0 & 0 \\
0 & V_{l}^a & 0 \\
0 & 0 & V_{l}^a
\end{bmatrix},
$$

$$
I_b = \begin{bmatrix}
\rho_0^a \alpha_0^a & 0 & 0 \\
0 & V_{l}^b & 0 \\
0 & 0 & V_{l}^b
\end{bmatrix}.
$$

The Laplace transform $\Delta \hat{\epsilon}(\epsilon)$ of the following form:

$$
\hat{\epsilon}(\epsilon) = \int f(t) \exp(-\epsilon t) \, dt.
$$

In the next step, we neglect the terms in equations (13) and (14) containing the integrations over $E_a$ and $E_b$. As shown in appendix A these terms equal zero for independent atoms $a$ and $b$. Weakness of the dipole–dipole interaction compared to the Coulomb one then justifies this approximation that leaves us the following decoupled equations:

$$
[(\epsilon - E_a + E_L) \mathbf{1} + K_b] \hat{d}_a(E_a, \epsilon) = B_a^i \hat{\epsilon}(\epsilon),
$$

(16)

$$
[(\epsilon - E_b + E_L) \mathbf{1} + K_a] \hat{d}_b(E_b, \epsilon) = B_b^i \hat{\epsilon}(\epsilon).
$$

(17)

These equations can be solved using the decomposition of matrices $L_a$ and $L_b$ [47],

$$
L_j = \sum_{k=1,2} \lambda_j^k L_j^k, \quad j = a, b,
$$

(18)

in which $\lambda_j^k$ are eigenvalues of the matrix $L_j$ and matrices $L_j^k$ and $L_j^b$ fulfill the relation $L_j^k + L_j^b = \mathbf{1}$. Formulas for eigenvalues $\lambda_j^k$ are derived as follows:

$$
\lambda_j^k = a_j^k \pm \sqrt{a_j^k a_j^k - a_j^k}, \quad j = a, b;
$$

$$
a_j^k = \left[ \sqrt{\left| \mu_j \alpha_j \right|^2 + \left| V_j \right|^2} - \Delta E_0^k \right] / 2,
$$

$$
a_j^k = -i \sqrt{\left| \mu_j \alpha_j \right|^2 \Delta E_0^k - \left| \mu_j \alpha_j \right|^2} + i \left| \mu_j \alpha_j \right| V_j + \text{c.c.},
$$

(19)

where c.c. denotes the complex conjugated term. Using eigenvalues $\lambda_j^k$, the matrices $L_j^k$ are expressed as:

$$
L_j^k = \frac{1}{\lambda_j^k - \lambda_j^l} (L_j - \lambda_j^k \mathbf{1}).
$$

(20)

Substitution of the decomposition (18) into equation (16) allows to obtain the solution of equation (16) in the simple form:

$$
\hat{d}_a(E_a, \epsilon) = \sum_{k=1,2} \frac{L_a^k B_b^i \hat{\epsilon}(\epsilon)}{\epsilon - E_a + E_b + \lambda_k^b}.
$$

(21)

The solution of equation (17) is derived from that written in equation (21) by the formal substitution $a \leftrightarrow b$.

Substitution of the solutions $\hat{d}_a(E_a, \epsilon)$ and $\hat{d}_b(E_b, \epsilon)$ into equation (8) and subsequent integration over energies $E_a$ and $E_b$ provides the equation:

$$
(\epsilon \mathbf{1} - \lambda^0) \hat{\epsilon}(\epsilon) = i \epsilon \mathbf{0}.
$$

(22)
In equation (22), matrix $\tilde{A}$ is defined as
\[
\tilde{A} = A - i\pi \sum_{j=a,b} B_j B_j^T.
\] (23)

The solution of equation (22) can be conveniently written in terms of eigenvalues $\Lambda_k$ and eigenvectors $p_k$ and $p_k^*$ of the matrix $\tilde{A}$ decomposed as $\tilde{A} = \mathbf{PAP}^{-1}$,
\[
\tilde{c}(\epsilon) = \sum_{k=1}^{4} p_k \left[ p_k^{-1} c(0) \right] \frac{1}{\epsilon - \Lambda_k}.
\] (24)

Whereas eigenvectors $p_k$ form columns of the matrix $\mathbf{P}$, eigenvectors $p_k^*$ occur as rows of the inverse matrix $\mathbf{P}^{-1}$.

Substituting equation (24) into equation (21), coefficients $d_{ab}(E_a, \epsilon)$ are obtained in the form:
\[
d_{ab}(E_a, \epsilon) = \sum_{j=1}^{4} \sum_{k=1}^{4} \left[ \mathbf{L}_j^T \mathbf{B}_j^{ab} p_k \right] \left[ p_k^{-1} c(0) \right] \frac{1}{\epsilon - \Lambda_k} + \{a \leftrightarrow b\}.
\] (25)

It can be shown by direct calculation that the integration over $E_a$ in equation (14) using the solution (25) gives zero. Similarly, the solution for $d_{ab}(E_b, \epsilon)$ obtained from the symmetry $a \leftrightarrow b$ results in zero after the integration in equation (13). This confirms consistency of the approximation leading to equations (16) and (17).

Finally, using equation (25) the expression (12) for coefficients $d(E_a, E_b, \epsilon)$ is expressed as:
\[
d(E_a, E_b, \epsilon) = \frac{i}{\epsilon - E_a + E_b - 2E_L} \sum_{j=1}^{4} \sum_{k=1}^{4} \left[ \mathbf{L}_j^T \mathbf{B}_j^{ab} p_k \right] \left[ p_k^{-1} c(0) \right] \frac{1}{\epsilon - \Lambda_k} + \{a \leftrightarrow b\}.
\] (26)

Symbol $\{a \leftrightarrow b\}$ in equation (26) replaces the term obtained by the exchange of the indicated indices.

The inverse Laplace transform of the above formulas then provides the coefficients in the time domain. Equation (24) attains the following form:
\[
c(t) = \sum_{k=1}^{4} p_k \left[ p_k^{-1} c(0) \right] \exp(-i\Lambda_k t).
\] (27)

Decomposition of rational functions into partial fractions followed by the Laplace transform leaves formula (25) as follows:
\[
d_{ab}(E_a, t) = \sum_{j=1}^{4} \sum_{k=1}^{4} \left[ \mathbf{L}_j^T \mathbf{B}_j^{ab} p_k \right] \left[ p_k^{-1} c(0) \right] \frac{1}{\epsilon - E_a - E_b - 2E_L} \times \left[ \exp(-i(E_a - E_b - \lambda_j^L) t) - \exp(-i\Lambda_k t) \right].
\] (28)

Similarly, equation (26) takes the following form in the time domain:
\[
d(E_a, E_b, t) = \sum_{j=1}^{4} \sum_{k=1}^{4} \left[ \mathbf{L}_j^T \mathbf{B}_j^{ab} p_k \right] \left[ p_k^{-1} c(0) \right] \frac{1}{E_a + E_b - 2E_L - \Lambda_k} \times \left[ \exp(-i(E_a - E_b - \lambda_j^L) t) - \exp(-iE_a E_b - \lambda_j^L) t) \right] + \{a \leftrightarrow b\}.
\] (29)

As eigenvalues $\lambda_j^a$ and $\lambda_j^b$ ($\Lambda_k$) have positive (negative) imaginary parts, the above formulas considerably simplify in the long-time limit $t \to \infty$.
\[
c^\infty(t) = [0, 0, 0, 0]^T,
\]
\[
d^\infty(E_j, t) = [0, 0]^T, j = a, b
\]
\[
d^\infty(E_a, E_b, t) = \sum_{j=1}^{4} \sum_{k=1}^{4} \left[ \mathbf{L}_j^T \mathbf{B}_j^{ab} p_k \right] \left[ p_k^{-1} c(0) \right] \frac{1}{E_a + E_b - 2E_L - \Lambda_k} \times \left[ \exp(-i(E_a - E_b - \lambda_j^L) t) - \exp(-iE_a E_b - \lambda_j^L) t) \right] + \{a \leftrightarrow b\}.
\] (30)

Both atoms are thus completely ionized in the long-time limit. In this limit, also the norm of the long-time joint photoelectron ionization spectrum $|d^\infty(E_a, E_b)|^2$ is determined analytically.
\[
\int dE_a \int dE_b \left| d^\infty(E_a, E_b) \right|^2 = 4\pi^2 \sum_{j=1}^{4} \sum_{k=1}^{4} \left[ \mathbf{L}_j^T \mathbf{B}_j^{ab} p_k \right] \left[ p_k^{-1} c(0) \right] \frac{1}{E_a + E_b - 2E_L - \Lambda_k} + \{a \leftrightarrow b\}.
\] (31)

As both atoms interact through the dipole–dipole interaction, energies $E_a$ and $E_b$ of the ionized electrons are correlated to some extent. This correlation is quantified by covariance $C$ defined as:
\[
C = \frac{\langle E_a E_b \rangle}{\langle E_a^2 \rangle^{1/2} \langle E_b^2 \rangle^{1/2}}.
\] (32)

In equation (32), the mean values $\langle E_a^k E_b^l \rangle$ for $k, l \in N$ are defined as:
\[
\langle E_a^k E_b^l \rangle = \int dE_a \int dE_b E_a^k E_b^l \left| d^\infty(E_a, E_b) \right|^2
\] (33)
using the long-time joint photoelectron ionization spectrum \(|d^n(E_a, E_b)|^2\) determined in equation (30). As these correlations have quantum origin, they can alternatively be described by quadratic negativity as it is done in the following section.

3. Quadratic negativity for the composite system

We first consider a simplified model analyzed in [46, 47]. In this model, atom \(a\) has only two discrete states \([0]_a\) and \([1]_a\) whereas atom \(b\) contains the whole continuum \([E_b]\) of states with energies \(E_b\). A general state \(|\psi_q\rangle\) of this system described by coefficients \(d_0(E_b)\) and \(d_1(E_b)\) takes the following form:

\[
|\psi_q\rangle = \int dE_b\left[d_0(E_b)|0\rangle_a + d_1(E_b)|1\rangle_a\right]|E_b\rangle.
\]

(34)

Quadratic negativity \(N_q\) quantifies the amount of non-separability of a state [50] as visible in negativity of the corresponding partially transposed statistical operator [51, 52]. It is determined by negative eigenvalues of the partially transposed statistical operator. The quadratic negativity of the state \(|\psi_q\rangle\) written in equation (34) has been derived in [48] in the form:

\[
N_q = 2\sum_{j,k=0}^1 \int dE_b \int dE_b' \left[d_j^*(E_b)d_k(E_b)d_j'(E_b')d_k(E_b') - d_j'(E_b)d_k(E_b)d_j(E_b')d_k(E_b')\right].
\]

(35)

Formula (35) can be recast as follows:

\[
N_q = 2\int dE_b\varrho_q(E_b)^1 \int dE_b'\varrho_q(E_b')n_q(E_b, E_b'),
\]

(36)

where \(\varrho_q\) gives the density of states \(|E_b\rangle\) in the continuum of atom \(b\):

\[
\varrho_q(E_b) = \sum_{j=0}^1 |d_j(E_b)|^2.
\]

(37)

Joint density of quadratic negativity \(n_q\) introduced in equation (36) is obtained in the form:

\[
n_q(E_b, E_b') = 1 - \frac{\sum_{j,k=0}^1 d_j^*(E_b)d_k(E_b)d_j'(E_b')d_k(E_b')}{\varrho_q(E_b)\varrho_q(E_b')}.
\]

(38)

The joint density of quadratic negativity \(n_q\) gives quadratic negativity of the bipartite system formed by the states \(|0\rangle_a, |1\rangle_a\) and \(|E_b\rangle\). According to equation (36), quadratic negativity \(N_q\) is given as a weighted sum of quadratic negativities between the two-level atom \(a\) and all possible pairs of states inside the continuum of atom \(b\).

This interpretation suggests a straightforward generalization to the case of two continua substituting \([0]_a \rightarrow |E_a\rangle\) and \([1]_a \rightarrow |E_a'\rangle\) and integrating over frequencies \(E_a\) and \(E_a'\):

\[
N = \int dE_a \int dE_a' \int dE_b \int dE_b' \left[\delta^n(E_a, E_b)d(E_a, E_b)d^n(E_a', E_b')d(E_a', E_b') - \delta^n(E_a, E_b)d(E_a', E_b)d^n(E_a', E_b)\right].
\]

(39)

3.1. Coefficients \(d(E_a, E_b)\) determine a state \(|\psi\rangle\) common to both continua at atoms \(a\) and \(b\):

\[
|\psi\rangle = \int dE_a \int dE_b \left[d(E_a, E_b)|E_a\rangle|E_b\rangle\right]|E_a\rangle|E_b\rangle.
\]

(40)

They also give densities \(q_a\) and \(q\) describing an ionized electron at atom \(a\) and both ionized electrons, respectively:

\[
q_a(E_a) = |d(E_a, E_b)|^2, \quad q_a(E_a, E_b) = \int dE_b q(E_b, E_b).
\]

(41)

Following the same argumentation as that applied earlier for the simplified model considered in [48], the joint density of quadratic negativity \(n\) can be introduced:

\[
n(E_a, E_a', E_b, E_b') = 2q_{ab}(E_a, E_b)q_{ab}(E_a', E_b') - \delta^n(E_a, E_b)d(E_a, E_b)d^n(E_a', E_b') \times \delta^n(E_a', E_b)d(E_a', E_b')d(E_a', E_b') - \delta^n(E_a, E_b)d(E_a', E_b)d^n(E_a', E_b).
\]

(42)

Quadratic negativity \(N\) can then be expressed using the densities \(q_a\) and \(q\) introduced in equation (41):

\[
N = \int dE_a q_a(E_a) \int dE_a' q_a(E_a') \times \int dE_b q(E_b, E_b) + q(E_b', E_b') \times \int dE_b' q(E_b', E_b') + q(E_b', E_b') \times n(E_a, E_a', E_b, E_b').
\]

(43)

Formula (43) can be recast into a simple form using the reduced statistical operator \(\tilde{\rho}_b\) of the continuum of atom \(b\):

\[
N = 2\left[1 - \int dE_b \int dE_b' \left|\tilde{\rho}_b(E_b, E_b')\right|^2\right].
\]

(44)

\[
\tilde{\rho}_b(E_b, E_b') = \int dE_a d(E_a, E_b)d^n(E_a, E_b).
\]

(45)

An analogous formula based on the reduced statistical operator of atom \(a\) can also be derived.

Another expression for quadratic negativity \(N\) can be reached using the Schmidt decomposition of state \(|\psi\rangle\) given in equation (40):

\[
d(E_a, E_b) = \sum_n \lambda_n(E_a)\delta_{a,n}\delta_n(E_b).
\]

(46)
\( \lambda_n \) being coefficients of the decomposition. Functions \( f_n \) and \( g_n \) introduced in equation (46) form the dual orthonormal bases. Quadratic negativity \( N \) can then be determined according to the formula:

\[
N = 2 \left[ 1 - \sum_n \lambda_n^2 \right]. \quad (47)
\]

Any separable state gives \( N = 0 \), whereas we have \( N = 2(N_0 - 1)/N_0 \) for the maximally entangled state in \( N_0 \times N_0 \) dimensions. We note that the formula in equation (47) can be rewritten as \( N = 2(1 - 1/K) \) where \( K \) denotes the Schmidt number of independent modes.

We note that if atoms \( a \) and \( b \) contain also discrete levels the consideration of amplitude spectra with \( \delta \)-functions allows for easy incorporation of such levels into the above developed description (for details, see [48]).

Entanglement of two ionized electrons can easily be modified by filtering the energies of electrons. Quadratic negativity \( N_a \) characterizing a state with energies \( E_a \) of electron \( a \) in interval \( (E_a - \Delta E, E_a + \Delta E) \) is obtained along the formula:

\[
N_a(\hat{E}_a^0) = \frac{2}{\pi} \int_{E_a^0-\Delta E}^{E_a^0+\Delta E} dE_a q_a(E_a) \int_{E_a^0-\Delta E}^{E_a^0+\Delta E} dE'_a \times q_a(E'_a) \int dE_b \left[ q_{ab}(E_a, E_b) + q_{ab}(E'_a, E_b) \right] \times \int dE_b \left[ q_{ab}(E_a, E_b) + q_{ab}(E'_a, E_b) \right] \times n(E_a, E_b, E_b),
\]

\[
N_a = \int_{E_a^0-\Delta E}^{E_a^0+\Delta E} dE_a \int dE_b \left| d(E_a, E_b) \right|^2. \quad (48)
\]

If also energies \( E_b \) of electron \( b \) are limited to interval \( (E_b^0 - \Delta E, E_b^0 + \Delta E) \), quadratic negativity \( N_{ab} \) of the resultant state is determined as follows:

\[
N_{ab}(\hat{E}_a^0, \hat{E}_b^0) = \frac{2}{\pi} \int_{E_a^0-\Delta E}^{E_a^0+\Delta E} dE_a q_a(E_a) \int_{E_b^0-\Delta E}^{E_b^0+\Delta E} dE_b q_b(E_b) \times q_{ab}(E_a, E_b) \times q_{ab}(E_b, E_a) \times \int dE_b \left[ q_{ab}(E_a, E_b) + q_{ab}(E_b, E_a) \right] \times n(E_a, E_b, E_b),
\]

\[
N_{ab} = \int_{E_a^0-\Delta E}^{E_a^0+\Delta E} dE_a \int_{E_b^0-\Delta E}^{E_b^0+\Delta E} dE_b \left| d(E_a, E_b) \right|^2. \quad (49)
\]

4. Long-time photoelectron ionization spectra

In the following, we restrict ourselves to the most common case of two identical atoms. The discussion of photoelectron ionization spectra is divided into two parts according to the relative strength of direct and indirect ionization paths. For the discussion, we introduce a useful parametrization that generalizes the parametrization introduced by Fano [14, 54].

\[
\gamma_j = \pi \left| V_{ij} \right|^2, \quad \gamma_j = \pi \left| J_{ij} \right|^2,
\]

\[
q_j = \frac{\mu_j}{\pi \mu_j V_{ij}}, \quad \bar{q}_b = \frac{\mu_b}{\pi \mu_b J_{ij}},
\]

\[
\Gamma_j = \gamma_j + \bar{q}_j, \quad \Omega_j = \sqrt{4 \pi \bar{J}_j} (Q_{ij} + i \tilde{\mu}_{j} \alpha_j), \quad j = a, b. \quad (50)
\]

In equation (50), \( \gamma_j, \bar{q}_j \) gives damping of the continuum at atom \( j \) caused by the Coulomb (dipole–dipole) interaction and \( \Gamma_j \) is the overall damping. Parameter \( q_j, \bar{q}_j \) gives the ratio of indirect and direct ionization strengths related to the Coulomb (dipole–dipole) interaction. Parameter \( \Omega_j \) is linearly proportional to the pumping strength of ionization at atom \( j \). As both atoms interact with the same laser field of amplitude \( \alpha_j \), the introduction of two additional parameters is convenient:

\[
m = \frac{\mu_a}{\mu_b}, \quad \Omega = \frac{\Omega_a + \Omega_b}{2}. \quad (51)
\]

Whereas parameter \( m \) gives the ratio of dipole moments for the auto-ionizing states at both atoms, parameter \( \Omega \) describes average pumping strength. A suitable parametrization is based upon common parameters \( m \) and \( \Omega \) and parameters \( \gamma_j, \bar{q}_j \) and \( q_j \) of individual atoms defined in equation (50). We note that \( m = 1 \) for two identical atoms and parameters \( \gamma_j, \bar{q}_j \) and \( \Omega_j \), \( j = a, b \), coincide with the usual ones defined by Fano [14].

4.1. Spectra for comparable direct and indirect ionization paths

If the values of the Fano parameters \( q_a \) and \( q_b \) are close to the unity they characterize the case in which both ionization paths compete each other. This results in the creation of the Fano zeroes at energies \( E_a^0 - \gamma_a q_a \) and \( E_b^0 - \gamma_b q_b \) of electrons at atoms \( a \) and \( b \), respectively. Individual spectra are formed by peaks that move down to lower energies with the increasing values of pumping parameter \( \Omega \). Whereas the peaks are above the Fano energy for lower values of pumping parameter \( \Omega \), they occur below the Fano energy for greater values of parameter \( \Omega \). As shown in figure 2(a) for ionization spectrum \( I_a \) of atom \( a \), the dipole–dipole interaction with continuum (described by parameters \( J_{ab} \) and \( J_b \)) moves the peaks towards energies \( E_a^0 \) and \( E_b^0 \) of the auto-ionizing levels. This behavior reflects the fact that the dipole–dipole interaction with continuum itself ionizes atoms \( a \) and \( b \) and thus diminishes the contributions of direct and indirect ionization paths whose interference is responsible for energy shifts of the peaks. On the other hand, the dipole–dipole interaction between the discrete auto-ionizing levels (described by parameter \( J_{ab} \)) tends to form a peak close to energy \( E_a^0 \) (or \( E_b^0 \)) in individual ionization spectra, as documented in figure 2(b). Two peaks coexist together in the spectra for intermediate values of parameter \( J_{ab} \). If the dipole–dipole interaction between discrete auto-ionizing levels is
sufficiently strong, there occurs one large peak in the photoelectron ionization spectrum $I_a$ of atom $a$ (or atom $b$). It is separated by two minima from the tails built by the direct and indirect ionization paths. The presence of two minima in the spectrum reflects nontrivial mutual influence between the dipole–dipole interaction on one side and the direct and indirect ionization paths on the other side.

The dipole–dipole interaction mutually correlates energies of the ionized electrons at atoms $a$ and $b$ (see figure 3). This results in pure states of two ionized electrons entangled in energies $E_a$ and $E_b$. Correlations increase with the increasing strength of both dipole–dipole interactions with the continua and between the discrete auto-ionizing levels. In fact, ‘anti-correlation’ occurs between energies $E_a$ and $E_b$ of the electrons that expresses the conservation law of energy in the stationary system ($E_a + E_b \approx 2E_L$). Comparison of the joint photoelectron ionization spectra $I$ plotted in figure 3(b) and (c) reveals that the stronger the dipole–dipole interaction the tighter the energy correlations.

If the dipole–dipole interactions with the continuum and between the discrete auto-ionizing levels have comparable strengths, a well-formed minimum occurs in the

**Figure 2.** Long-time intensity photoelectron ionization spectrum $I_a$ of atom $a$ $\left[ I_a(E_a) = \int dE_b \left| d^{\text{int}}(E_a, E_b) \right|^2 \right]$ as a function of normalized energy $(E_a - E_a^0)/\Gamma_a$ for (a) $\gamma_a = \gamma_b = 0$ (independent atoms, curve without symbols), 0.1 (curve with *), 1 (curve with $\circ$), $J_c = 0$ and (b) $J_a = 0$ (independent atoms, curve without symbols), 0.56 (curve with *), 1 (curve with $\circ$), 1.68 (curve with $\triangle$), $\gamma_a = \gamma_b = 0$; $E_a = E_b = E_L = 1$, $q_a = q_b = 1$, $\gamma_a = \gamma_b = 1$, $\Omega = 1$, $m = 1$.

**Figure 3.** Topo graphs of long-time joint photoelectron ionization spectra $I$ plotted as a function of normalized energies $(E_a - E_a^0)/\Gamma_a$ and $(E_b - E_b^0)/\Gamma_b$ of atoms $a$ and $b$, respectively, for (a) $\gamma_a = \gamma_b = 0$, $J_c = 0$ (independent atoms), (b) $\gamma_a = \gamma_b = 1$, $J_c = 0$ and (c) $\gamma_a = \gamma_b = 0$, $J_c = 1.68$. Values of the other parameters are written in the caption to figure 2; log stands for decimal logarithm.
photopoint electron ionization spectrum \( I_a \) (\( I_b \)) of atom \( a \) (\( b \)) (see figure 4). If the original spectra without the dipole–dipole interactions lie above the Fano zeros, the intensity of this minimum is close to zero [see figure 4(a)]. If the original spectra are below the Fano zeros, the minimum intensity does not reach zero but the intensity profile exhibits a sharp minimum accompanied by a neighbor sharp peak [see figure 4(b)]. Both cases give clear evidence about the strong mutual influence of ionization channels based on the continuum and the discrete levels. Conditions for the balance of two ionization channels based on the dipole–dipole interaction have been found in appendix B using the Fano diagonalization approach.

4.2. Spectra for the dominating indirect ionization path

High values of the Fano parameters \( q_a \) and \( q_b \) occur in this region, in which the ionized states are reached nearly exclusively from discrete auto-ionizing levels with energies \( E_{a}^{0} \) and \( E_{b}^{0} \). The individual photopoint electron ionization spectra of both atoms thus consist of peaks centered around energy \( E_{a}^{0} \) (\( E_{b}^{0} \)) for atom \( a \) (\( b \)). There occurs the Autler-Townes splitting of these peaks [58] for intense pumping. It occurs whenever the speed of populating an auto-ionizing level is faster than its depletion due to the Coulomb configuration interaction \([\mathcal{H}_{ab}] > |V_{ab}|\). As shown in figure 5 comparing the cases of independent and interacting atoms, the dipole–dipole interaction with the continuum weakens the Autler-Townes splitting. This is a consequence of the fact that the dipole–dipole interaction makes the transfer of electrons from discrete excited auto-ionizing levels into their continua faster and so partly suppresses the effect of ‘population reversion’ at the discrete auto-ionizing levels responsible for the splitting. On the other hand, the dipole–dipole interaction between the discrete auto-ionizing levels only slightly modifies the ionization spectra, as documented in figure 5. This follows from the considered symmetric configuration of atoms \( a \) and \( b \) that minimizes the influence of parameter \( J_{ab} \) to the populations of discrete levels \( E_{a}^{0} \) and \( E_{b}^{0} \).

The dipole–dipole interaction with the continuum strongly modifies the joint photopoint electron ionization spectra \( I \) that belong to the states entangled in energies. Dramatic change of the joint photopoint electron ionization spectrum \( I \) caused by this interaction is illustrated in figure 6 in which the dipole–dipole interaction nearly completely suppresses the Autler-Townes splitting.

5. Entanglement in long-time photopoint electron ionization spectra

The joint photopoint electron ionization spectra \( I \) plotted in figures 3(b) and (c) and 6(b) reflect strong correlations in energies \( E_{a} \) and \( E_{b} \) of the ionized electrons created due to the dipole–dipole interaction. These correlations emerging during the quantum evolution are non-classical. They reflect the bipartite entanglement that can be quantified by quadratic
negativity $N$ introduced in section 3. Alternatively, they can be described by the von Neumann entropy $S$ of the reduced statistical operators of individual electrons $a$ and $b$. We note that entropy $S$ is a monotonous function of negativity $N$. Contrary to entropy, quadratic negativity $N$ can be expressed via its joint density $\rho$ introduced in equation (41). This represents an important advantage as it allows to connect entanglement with spectral properties of the ionized electrons.

Assuming other parameters fixed, the increasing values of parameters $J_a$ ($\gamma_a$) and $J_b$ ($\gamma_b$) describing the dipole–dipole interactions with the continua result in greater values of negativity $N$ (see figure 7(a)). Similarly, the greater the values of parameter $J_{ab}$ characterizing the dipole–dipole interaction between the discrete auto-ionizing levels, the greater the values of negativity $N$ (see figure 7(b)). In figure 7, the comparison of curves giving negativity $N$ and covariance $C$ of energies reveals that even the classical covariance $C$ can be used as a good indicator of mutual coupling of two ionized electrons.

Whereas the dipole–dipole interactions with the continua and between the discrete auto-ionizing levels influence the ionization spectra in general in a complex way, they support each other in creating entanglement, as documented in figure 8.

Spectral distribution of entanglement can be conveniently visualized using negativity $N_{ab}$ defined in equation (49). It characterizes a common state of both ionized electrons obtained by filtering the energies of electrons. The comparison of graphs shown in figures 9(a) and 6(b) and also in figures 9(b) and 3(c) reveals that the negativity $N$ is concentrated in the areas with higher intensities.

Also when the energy of only one electron is filtered, highly entangled states are obtained in the central part of the spectrum (see figure 10 for negativity $N_a$). We note that the values of negativity $N_{ab}$ as well as negativity $N_a$ depend on the length $\Delta E$ of the interval of measured energies [see equations (48) and (49)]. The wider the interval $\Delta E$ the greater the values of negativities. However, this dependence is weak.

6. Ionization in molecular condensates

The dipole–dipole interaction is usually much weaker than the dipole interaction of atoms or molecules with external coherent fields. It is also much weaker than the Coulomb configuration interaction. This means that only weak modifications of the ionization spectra discussed in section 4 are expected in real systems. For example, energy shifts of the ionization peaks in the spectra plotted in figure 2 are comparable to the value of the dipole–dipole interaction energy. On the other hand, strongly correlated pairs of ionized electrons can be obtained in real systems provided that the process of ionization is sufficiently slow compared to the timescale characterizing the dipole–dipole interaction.

Molecular condensates [56] represent a typical example. In molecular crystals, energies of discrete excited states are in $1\text{ eV}$, Coulomb configuration interaction energies in $10\text{ meV}$ and dipole–dipole interaction energies in $0.1 \sim 1$ meV. Typical values of dipole moments are expressed in $10^8 \text{ V/m}$ are therefore necessary to arrive at the comparable dipole and Coulomb configuration interaction energies needed for the observation of the Autler-Townes splitting. If the Coulomb configuration interaction energy ($V_a$) and the direct dipole interaction energy ($\tilde{\mu}_a\tilde{\mu}_b$) have equal strengths, also the ionization process considerably slows down. Electrons then tend to occupy their ground states and discrete auto-ionizing states, i.e states mutually interacting through the dipole–dipole interaction. Alternatively, the electrons can undergo ionization caused by the dipole–dipole interaction with the continua. In both cases, the influence of dipole–dipole interaction to the ionization process dramatically increases. This results in greater values of negativities $N$ (see figure 11(a) for the interaction with the continua and figure 11(b) for the interaction between the auto-ionizing levels).
Considering fixed values of parameters $V$ and $\tilde{\mu}$, the conditions maximizing negativity $N$ and discussed above can be reached choosing suitably the pump-field amplitude $\tilde{\alpha}_L$. This is possible because negativity $N$ as a function of pump-field amplitude $\tilde{\alpha}_L$ exhibits a well-formed maximum (see figure 12).

7. Conclusions

An analytical solution of the model of two auto-ionization systems interacting through the dipole–dipole interaction has been found using the Laplace transform of the dynamical equations. Quadratic negativity together with its spectral density have been defined to quantify the entanglement between two ionized electrons developed due to the dipole–

Figure 7. Quadratic negativity $N$ (curve without symbols) and covariance $C$ (curve with *) as they depend on (a) parameter $\tilde{\gamma} \equiv \tilde{\gamma}_a = \tilde{\gamma}_b$ and (b) parameter $J_{ab}$. Values of the other parameters are written in the caption to figure 2.

Figure 8. Topo graph of quadratic negativity $N$ as it depends on dipole–dipole interaction parameters $\tilde{\gamma} \equiv \tilde{\gamma}_a = \tilde{\gamma}_b$ and $J_{ab}$. Values of the parameters are written in the caption to figure 2.

Values of the other parameters are written in the caption to figure 2.

Figure 9. Topo graphs of quadratic negativity $N_{ab}$ depending on normalized energies $(E_a - E_b^0)/\Gamma_a$ and $(E_b - E_a^0)/\Gamma_b$ for (a) $\tilde{\gamma}_a = \tilde{\gamma}_b = 1$, $J_{ab} = 0$, $\Delta E = 0.005$ [$N = 0.98$] and (b) $\tilde{\gamma}_a = \tilde{\gamma}_b = 0$, $J_{ab} = 1.68$, $\Delta E = 0.01$ [$N = 1.79$]. Values of the other parameters are written in the caption to figure 2.
Figure 10. Quadratic negativity $N_a$ as a function of normalized energy $(E_a - E_a^0)/\Gamma_a$ of atom $a$; $\Delta E = 0.01$, $I_{ab} = 1.68$ and values of the other parameters are written in the caption to figure 2; $N = 1.79$.

dipole interaction. The dipole–dipole interaction with the continua weakens the interference of direct and indirect ionization paths. This results in spectral shifts of the peaks in the long-time photoelectron ionization spectra towards the energy of the auto-ionizing state. On the other hand, the dipole–dipole interaction between the auto-ionizing states leads to the occurrence of an additional peak in the long-time ionization continua weakens the interference of direct and indirect ionization paths. This results in spectral shifts of the peaks in the long-time photoelectron ionization spectra towards the energy of the auto-ionizing state. When the auto-ionizing states play a dominant role in ionization and a strong field induces the Autler–Townes splitting of the ionization peak, the dipole–dipole interaction with the continua weakens this splitting. Balancing the dipole–dipole interactions with the continua and between the auto-ionizing states leads to the occurrence of a minimum in the long-time photoelectron ionization spectrum of an individual atom that resembles the Fano zero. The dipole–dipole interactions are responsible for strong anti-correlations in the ionized electrons. They originate in the energy conservation. Both dipole–dipole interactions participate together in the creation of entanglement. The stronger the dipole–dipole interactions are, the more entangled the state is. Optimal conditions for entanglement creation occur when the direct and indirect ionization paths are balanced and slow ionization is observed. The ‘distribution of entanglement’ in the state of two ionized electrons as described by the density of quadratic negativity reflects the shape of the corresponding joint photoelectron ionization spectrum.

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Appendix A. Solution for two independent auto-ionization systems

If atoms $a$ and $b$ are independent the quantum state $|\psi\rangle(t)$ in equation (5) can be written as

$$|\psi\rangle^{\text{ind}}(t) = |\psi^a\rangle(t) |\psi^b\rangle(t).$$  \hspace{1cm} (A.1)

In equation (A.1) states $|\psi^j\rangle(t)$, $j = a$, $b$, describe electrons at individual atoms:

$$|\psi^j\rangle(t) = c^j_0(t) |0\rangle_j + c^j_1(t) |1\rangle_j + \int dE_j d^j(E_j, t) |E_j\rangle.$$  \hspace{1cm} (A.2)

The corresponding differential equations for the coefficients in equation (A.2) are derived as follows:

$$i \frac{d}{dt} \begin{bmatrix} c_j(t)
\end{bmatrix} = \begin{bmatrix}
K_j & \int dE_j I_j
\end{bmatrix} \begin{bmatrix} c_j(t)
\end{bmatrix}$$  \hspace{1cm} (A.3)

using vectors $c_j = (c^j_0, c^j_1)$ for $j = a$, $b$, and matrices $K_j$ and $I_j$ defined in equation (7).

The Laplace transform leaves equations (A.3) in the form:

$$\left[\epsilon I - K_j\right] \tilde{c}_j(\epsilon) - \int dE_j I_j \tilde{d}_j(E_j, \epsilon) = i \tilde{c}_j(0),$$

$$\left(\epsilon - E_j + E_L\right) \tilde{d}_j(E_j, \epsilon) - \frac{i}{\epsilon - E_j + E_L} \tilde{c}_j(0) = 0, j = a, b.$$  \hspace{1cm} (A.4)

Applying the approach similar to that used in section 2 the solution of equations (A.4) is revealed in the form:

$$\tilde{c}_j(\epsilon) = i \sum_{k=1,2} L^j_k(\epsilon) \left[\epsilon + \lambda_k^j\right]^{-1},$$

$$\tilde{d}_j(E_j, \epsilon) = \frac{i}{\epsilon - E_j + E_L} \sum_{k=1,2} \frac{L^j_k(\epsilon)}{\epsilon + \lambda_k^j}, j = a, b.$$  \hspace{1cm} (A.5)

Matrices $L^j_k$ and eigenvalues $\lambda_k^j$ used in equation (A.5) are given in equations (19) and (20), respectively. The inverse Laplace transform provides this solution in the time domain:

$$c_j(t) = \sum_{k=1,2} L^j_k(0) \exp\left(i\lambda_k^j t\right),$$

$$d_j(E_j, t) = \sum_{k=1,2} \frac{L^j_k(0)}{E_j - E_L + \lambda_k^j} \left[\exp\left[-i(E_a - E_L)t\right] - \exp\left(i\lambda_k^j t\right)\right], j = a, b.$$  \hspace{1cm} (A.6)

Considering the common state $|\psi\rangle^{\text{ind}}$ of both atoms defined in equation (A1), the Laplace transform of coefficients $c(t)$ defined by direct product $c_a(t) \otimes c_b(t)$ is
expressed as:

\[
\sum \varepsilon \lambda \varepsilon \lambda = \varepsilon' \lambda' = \lambda' \varepsilon' = \lambda \varepsilon.
\]

Similarly, the Laplace transform of coefficients \( E_t (a) \) determined by direct product \( \otimes \) takes the form:

\[
\tilde{d}_a (E_a, \varepsilon) = i \sum_{k,k=1,2} \left[ \begin{bmatrix} L_k^a c_a(0) \\ L_k^b c_b(0) \end{bmatrix} \right] \left[ \begin{bmatrix} L_k^a c_a(0) \\ L_k^b c_b(0) \end{bmatrix} \right] \frac{1}{\varepsilon + \lambda_k^a + \lambda_k^b}.
\]

Using solutions (A.7) and (A.8), the first term in equation (13) can be treated as follows:

\[
\left[ (\varepsilon - E_a + E_L) \mathbf{1} + \mathbf{L}_b \right] \tilde{d}_a (E_a, \varepsilon) = \sum_{k=1,2} \left( \varepsilon - E_a + E_L + \lambda_k^b \right) \mathbf{L}_k^b \tilde{d}_a (E_a, \varepsilon)
\]

\[
= i \sum_{k,k=1,2} \left[ \begin{bmatrix} L_k^a \mathbf{c}_a(0) \\ L_k^b \mathbf{c}_b(0) \end{bmatrix} \right] \left[ \begin{bmatrix} L_k^a \mathbf{c}_a(0) \\ L_k^b \mathbf{c}_b(0) \end{bmatrix} \right] \frac{1}{\varepsilon + \lambda_k^a + \lambda_k^b} = \mathbf{B}_a \tilde{c}(\varepsilon). \quad (A.9)
\]

The following relations have been used in equation (A.9),

\[
\mathbf{L}_k^a \mathbf{L}_k^b = \delta_{kk} \mathbf{L}_k^a, \mathbf{B}_a = \begin{bmatrix} \mathbf{I}_a & 0 \\ 0 & \mathbf{I}_a \end{bmatrix}. \quad (A.10)
\]

The equality expressed in equation (A.9) implies that the integral term in equation (13) is zero when independent atoms \( a \) and \( b \) are considered. The same holds also for the integral term in equation (14) owing to the symmetry \( a \leftrightarrow b \). We note that this conclusion can be achieved also by direct integration of the solution written in equation (A.8).

**Appendix B. Competition of the discrete and continuum dipole–dipole interactions**

Spectra in auto-ionization systems are formed by mutual interference of two types of ionization paths. One of them is based upon direct ionization originating from the ground state. The other uses an excited auto-ionizing discrete level that mediates auto-ionization of the system. These two ionization paths may interfere destructively. The presence of the Fano zero in the ionization spectra [14] represents a clear evidence of such quantum interference. Similarly, the dipole–dipole interaction of an auto-ionization system with its neighbor can be divided into two parts [46]. One part influences the discrete auto-ionizing level, states of the continuum...
are modified by the other. Also these two parts of the interaction compete. However, this competition occurs at the level of population of the involved quantum states as the dipole–dipole interaction means energy transfer. This competition naturally modifies photoelectron spectra. The greatest changes in photoelectron spectra are observed when both parts of the dipole–dipole interaction have comparable strengths.

Suitable conditions for this case can be described as follows. First, we apply the usual Fano unitary transformations of excited/ionized states at atoms $a$ and $b$. The appropriate values of parameters are then found from the requirement that the interaction Hamiltonian $\hat{H}_{\text{trans}}$ given in equation (4) is zero. In this case, two parts of the dipole–dipole interaction related to the discrete and continuum states of both atoms are equally strong but with the opposed signs.

Invoking the Fano unitary transformations [14, 54] on both atoms, Hamiltonians $\hat{H}^{a}_f$, written in equation (2) are transformed into their diagonal forms,

$$\hat{H}^{a}_f = \int dE_i |E_i\rangle \langle E_i|, \quad j = a, b.$$  \hspace{1cm} (B.1)

In equation (B.1), states $|E_i\rangle$ arise from the Fano diagonalization,

$$|E_i\rangle = f_j(E_i) |1\rangle_j + \int dE'_j g_j(E_i, E'_j) |E'_j\rangle,$$  \hspace{1cm} (B.2)

and

$$f_j(E_i) = \frac{V_j(E_i)}{E_i - \bar{E}_j^0 + i\gamma_j},$$

$$g_j(E_i, E'_j) = \frac{V_j(E_j) f_j(E_i)}{E_i - E'_j + i\epsilon} + \delta(E_i - E'_j).$$  \hspace{1cm} (B.3)

Damping constants $\gamma_j, \gamma' = \pi |V_j|^2$, and shifted energies $\bar{E}_j^0, E'_j = E_j^0 + P \int dE[V(E)]^2/(E_j^0 - E)$, have been introduced in equation (B.3). Symbol $\epsilon$ denotes a small positive number and limit $\epsilon \rightarrow 0$ is assumed at the end of calculations.

After the transformations, Hamiltonians $\hat{H}^{a}_f$ defined in equation (3) attain the form:

$$\hat{H}^{a}_f = \int dE_i \tilde{\mu}_j(E_i) \alpha_L \exp(-iE_L t) |E_i\rangle \langle 0| + \text{H.c.}$$  \hspace{1cm} (B.4)

Dipole moments $\tilde{\mu}_j(E_i)$ describing excitation/ionization of states $|E_i\rangle$ inside the structured continua are derived in the form

$$\tilde{\mu}_j(E_i) = \tilde{\mu}_j \left\{ e_j(E_i) + q_j \right\},$$  \hspace{1cm} (B.5)

$$e_j(E) = (E - \bar{E}_j^0)/\gamma_j, \quad q_j = \mu_j \langle \sigma \tilde{\mu} \tilde{V}_j \rangle,$$  \hspace{1cm} (B.5)

and $i$ stands for the imaginary unit. If the dipole–dipole interaction between two atoms is neglected, we have $\tilde{\mu}_a(E''_a) = \tilde{\mu}_b(E''_b) = 0$ for $E''_a - \bar{E}_a^0 = -\gamma_a q_a$ and $E''_b - \bar{E}_b^0 = -\gamma_b q_b$. Thus, there occurs one Fano zero with energy $E''_a$ in the photoelectron ionization spectrum of atom $a$ and one Fano zero with energy $E''_b$ in the spectrum of atom $b$.

These Fano zeros are concealed by the dipole–dipole interaction. The greatest competition of two parts of the dipole–dipole interaction is observed provided that the matrix element of transfer Hamiltonian $\hat{H}_{\text{trans}}$ between states $|E^{f}_a\rangle$ and $|E^{f}_b\rangle$ equals zero, Hamiltonian $\hat{H}_{\text{trans}}$ given in equation (4) is expressed in these bases as

$$\hat{H}_{\text{trans}} = \int dE_a \int dE_b \tilde{J}(E_a, E_b) |E_b\rangle \langle E_a| + \text{H.c.},$$  \hspace{1cm} (B.6)

where

$$\tilde{J}(E_a, E_b) = J_{ab} \tilde{\mu}_a^* (E_a) \tilde{\mu}_b^* (E_b)$$

$$+ \int dE'_a J_{ab}^* \tilde{\mu}_a^* (E_a) \tilde{\mu}_b^* (E_b)$$

$$+ \int dE'_b J_{ab}^* \tilde{\mu}_a^* (E_a) \tilde{\mu}_b^* (E_b).$$  \hspace{1cm} (B.7)

The use of expressions written in equations (B.3) transforms equation (B.7) into the form:

$$\tilde{J}(E_a, E_b) = \frac{J_{ab} V_a}{\gamma_a [\bar{E}_a(E_a) - i]} + \frac{J_{ab} V_b^*}{\gamma_b [\bar{E}_b(E_b) + i]}$$

$$+ \frac{J_{ab} V_a^*}{\gamma_a \gamma_b} \left( e_a(E_a) + i \right) \left( e_b(E_b) - i \right).$$  \hspace{1cm} (B.8)

The requirement $\tilde{J}(E_a^f, E_b^f) = 0$ results in the following condition for the values of dipole–dipole interaction constants $J_{ab}, J_a$ and $J_b$:

$$J_{ab} \mu_a^* + J_a \mu_b^* = J_{ab}.$$  \hspace{1cm} (B.9)

Assuming identical atoms $a$ and $b$ and real interaction constants, the condition in equation (B.9) simplifies

$$J_{ab} = \frac{\mu_a}{\mu_b}.$$  \hspace{1cm} (B.10)

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