

Collectively enhanced resonant photoionization in a multiatom ensemble

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Photoionization of an atom via interatomic correlations to N neighboring atoms may be strongly enhanced due to constructive interference of quantum pathways. The ionization proceeds via resonant photoexcitation of a neighbor atom and subsequent interatomic Coulombic decay. The enhancement can scale with N^2 , leading to “superenhanced photoionization.”

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I. INTRODUCTION

The quantum dynamics of a single fluorescing atom is strongly modified when an additional emitter is located nearby [1]. Furthermore, it is well known that collective interactions between closely spaced particles can lead to a significant modification of spontaneous emission processes—an effect called superradiance. In particular, the quantum dynamics of an excited collective system can be N times faster than for a single particle, and the intensity of the emitted electromagnetic field scales as N^2 in multiparticle samples, where N is the number of radiators. The enhancement occurs due to constructive interference effects. Superradiance was first demonstrated experimentally in an optically pumped hydrogen fluoride gas [2] and the concept was transferred to other branches of physics [3], including sonoluminescence [4], plasmas [5], Bose-Einstein condensates [6], molecular nanomagnets [7], γ -ray lasers [8], and band-gap materials [9].

The process of photoionization may be influenced by the atomic environment as well. Indeed, when photoionization of an atom A occurs in the presence of a neighboring atom B , then—apart from the direct ionization of A without participation of B —there are additional resonant channels for certain photon energies where first B is photoexcited and afterward, upon deexcitation, B transfers the transition energy radiationlessly to A , leading to its ionization. The latter Auger-like step is commonly known today as interatomic Coulombic decay (ICD) [10–12] or, more specifically, as resonant ICD [13,14]. The effect of the environment on photoionization has been observed on core resonances in metal oxides, where it was termed multiatom resonant photoemission (MARPE) [15]. The measured MARPE effects, amounting to about 30%–100% on the resonance and 10%–30% after energy integration, were substantial but did not exceed the direct photoionization.

Recently, it has been shown that—in certain circumstances—the interatomic channel of photoionization via ICD can be very strong and by far the dominant one [16]. In fact, its strength with respect to the direct channel is given by the ratio [16,17]

$$\rho_1 = \frac{\sigma_{\text{interatomic}}^{(N=1)}}{\sigma_{\text{direct}}} \sim \left(\frac{c}{\omega R} \right)^6, \quad (1)$$

where ω denotes the electron transition frequency, R the interatomic distance, and c the speed of light. Equation (1) assumes that the bound-bound transition is dipole allowed and the radiative width in atom B exceeds the interatomic Auger width. The latter will always hold at sufficiently large values of R . When the resonance frequency is not too large, $\omega \lesssim 1\text{--}10$ eV, the ratio ρ_1 exceeds unity for interatomic distances $R \lesssim 1\text{--}10$ nm.

In the present Brief Report, we show that the strength of the interatomic channel of photoionization can be even more greatly enhanced when atom A is surrounded by $N > 1$ atoms B (see Fig. 1). In this case, the photoionization amplitude must be coherently summed over all neighbor atoms, allowing for collective effects via interfering quantum pathways. Under certain conditions, the resulting enhancement can be proportional to N^2 due to fully constructive interference. Conditions under which this effect of superenhanced photoionization may occur will be specified. We also outline the prospects for an experimental observation of collective enhancements in multiatom resonant photoionization.

II. THEORETICAL FRAMEWORK

Our theoretical description of photoionization of atom A in the presence of an electromagnetic wave and N neighboring atoms B relies on the total Hamiltonian

$$\hat{H} = \hat{H}_A + \sum_{j=1}^N \hat{H}_{B_j} + \hat{W} + \sum_{j=1}^N \hat{V}_{AB_j} + \sum_{j>l} \hat{V}_{B_j B_l}. \quad (2)$$

Here, H_A and H_{B_j} are the Hamiltonians of the noninteracting atoms A and B_j ($j = 1, \dots, N$), which are assumed to be at rest. Taking the position of the nucleus of atom A as the origin, we denote the position of the nucleus of atom B_j by \mathbf{R}_j . The coordinates of the electron of atom A and the electron of atom B_j are \mathbf{r} and $\mathbf{r}_j = \mathbf{R}_j + \boldsymbol{\xi}_j$, respectively ($j = 1, \dots, N$).

In Eq. (2), \hat{W} is the interaction of the electrons with the external electromagnetic field. The latter will be taken as a classical, linearly polarized field, described by the vector potential $\mathbf{A} = \frac{c}{\omega} \mathbf{F}_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r})$, where $\omega = c|\mathbf{k}|$ and \mathbf{k} are the angular frequency and wave vector, and \mathbf{F}_0 is the peak field strength. The interaction reads [18]

$$\begin{aligned} \hat{W} &= \hat{W}_0^+ e^{-i\omega t} + \hat{W}_0^- e^{i\omega t}, \\ \hat{W}_0^\pm &= \frac{\mathbf{F}_0}{2\omega} \cdot \left(e^{\pm i\mathbf{k} \cdot \mathbf{r}} \hat{\mathbf{p}} + \sum_{j=1}^N e^{\pm i\mathbf{k} \cdot \mathbf{r}_j} \hat{\mathbf{p}}_j \right), \end{aligned} \quad (3)$$

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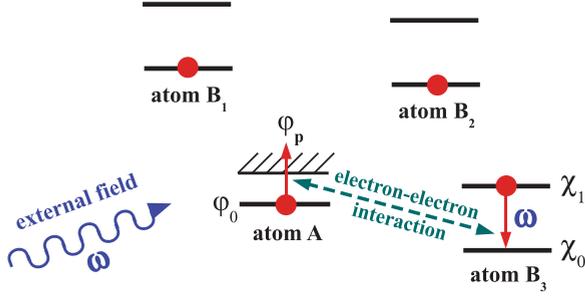


FIG. 1. (Color online) Scheme of photoionization of atom A in the presence of an external laser field and $N = 3$ neighboring atoms B_j ($j = 1, 2, 3$). Apart from the direct photoionization of A , there are interatomic channels via photoexcitation of one of the atoms B_j (here $j = 3$) and subsequent ICD.

where $\hat{\mathbf{p}}$ denotes the momentum operator of the (active) electron in atom A and $\hat{\mathbf{p}}_j$ denotes the momentum operator of the (active) electron in atom B_j . Below we will assume that $kR_j \ll 1$ holds for $j = 1, \dots, N$, so that we may apply the dipole approximation to the interaction (3), ignoring its spatial variation and retardation effects.

The photon field may lead to direct ionization of atom A or resonant excitation of one of the atoms B . In the latter case, atom A can be ionized by radiationless energy transfer upon deexcitation via the (instantaneous) dipole-dipole coupling

$$\hat{V}_{AB_j} = \frac{\mathbf{r} \cdot \boldsymbol{\xi}_j}{R_j^3} - \frac{3(\mathbf{r} \cdot \mathbf{R}_j)(\boldsymbol{\xi}_j \cdot \mathbf{R}_j)}{R_j^5} \quad (4)$$

between the atoms. The analogous term $\hat{V}_{B_j B_l}$ in Eq. (2) describes the dipole-dipole interaction between the atoms B_j and B_l .

In the following, all the interactions will be considered as weak and treated as small perturbations. The photoionization probability will be evaluated within second-order time-dependent perturbation theory.

The total wave function of the multielectron system may be expanded into products of unperturbed eigenstates of the atoms A, B_1, \dots, B_N [19]. In particular, let $\varphi_0(\mathbf{r})$ and $\varphi_p(\mathbf{r})$ denote the ground state and continuum state (with asymptotic momentum \mathbf{p}) of atom A , with corresponding energies ε_0 and ε_p . Similarly, $\chi_0^{(j)}(\boldsymbol{\xi}_j)$ and $\chi_1^{(j)}(\boldsymbol{\xi}_j)$ are the ground state and first excited state in atom B_j , with energies ε_0 and ε_1 (see Fig. 1).

Then in the process under consideration there are essentially three qualitatively different electron configurations: (I) $\Psi_{00} = \varphi_0(\mathbf{r}) \prod_{\ell=1}^N \chi_0^{(\ell)}(\boldsymbol{\xi}_\ell)$, where all electrons are in their corresponding ground states; (II) $\Psi_{01}^{(j)} = \varphi_0(\mathbf{r}) \chi_1^{(j)}(\boldsymbol{\xi}_j) \prod_{\ell \neq j} \chi_0^{(\ell)}(\boldsymbol{\xi}_\ell)$, where the electron in atom B_j is in the excited state and all other electrons are in the ground state; and (III) $\Psi_{p0} = \varphi_p(\mathbf{r}) \prod_{\ell=1}^N \chi_0^{(\ell)}(\boldsymbol{\xi}_\ell)$, where the electron of atom A is in a continuum state and all other electrons are in the ground state. The corresponding energies of these electron configurations are $E_{00} = \varepsilon_0 + N\varepsilon_0$, $E_{01} = \varepsilon_0 + (N-1)\varepsilon_0 + \varepsilon_1$, and $E_{p0} = \varepsilon_p + N\varepsilon_0$, respectively.

Applying perturbation theory up to the second order, we may obtain the amplitude for photoionization of atom A in the atomic ensemble subject to an external electromagnetic field.

The field can ionize atom A directly; this is described by the first-order amplitude

$$S_{p0}^{(1)}(t) = -i \int_{-\infty}^t dt' \langle \Psi_{p0} | \hat{W} | \Psi_{00} \rangle e^{-i(E_{00} - E_{p0})t'} \\ = -\frac{e^{i(\varepsilon_p - \varepsilon_0 - \omega)t}}{\varepsilon_p - \varepsilon_0 - \omega - i0} \langle \varphi_p | \hat{W}_0^+ | \varphi_0 \rangle, \quad (5)$$

where t is the time and the external field is assumed to be switched on adiabatically in the remote past. The last line in Eq. (5) was obtained by applying the rotating-wave approximation, i.e., keeping only the resonant term. The interatomic pathway of ionization via photoexcitation of one of the atoms B_j and subsequent ICD is described by the second-order amplitude

$$S_{p0}^{(2)}(t) = i \sum_{j=1}^N \int_{-\infty}^t dt' \langle \Psi_{p0} | \hat{V}_{AB_j} | \Psi_{01}^{(j)} \rangle e^{-i(E_{01} - E_{p0})t'} \\ \times \langle \Psi_{01}^{(j)} | \hat{W}_0^+ | \Psi_{00} \rangle \frac{e^{i(\varepsilon_1 - \varepsilon_0 - \omega)t'}}{\varepsilon_1 - \varepsilon_0 - \omega - i\Gamma_B}, \quad (6)$$

where we have introduced the radiative width Γ_B of the state $\chi_1^{(j)}$. The total photoionization amplitude up to second order thus becomes

$$S_{p0}^{(1+2)}(t) = -\frac{e^{i(\varepsilon_p - \varepsilon_0 - \omega)t}}{\varepsilon_p - \varepsilon_0 - \omega - i0} \left(\langle \varphi_p | \hat{W}_0^+ | \varphi_0 \rangle \right. \\ \left. - \frac{\langle \chi_1^{(1)} | \hat{W}_0^+ | \chi_0^{(1)} \rangle}{\varepsilon_1 - \varepsilon_0 - \omega - i\Gamma_B} \sum_{j=1}^N \langle \varphi_p \chi_0^{(j)} | \hat{V}_{AB_j} | \varphi_0 \chi_1^{(j)} \rangle \right). \quad (7)$$

The photoionization probability is obtained by taking the modulus squared of the amplitude (7) in the limit $t \rightarrow \infty$ and integrating over the final electron momenta \mathbf{p} .

It is worth mentioning that photoionization of atom A may, in principle, also proceed via photoexcitation of atom B_j , which transfers the energy subsequently to another atom B_l through the dipole-dipole interaction $\hat{V}_{B_j B_l}$, and only afterward is atom A ionized via ICD of atom B_l . In such a case, however, ionization of atom A would require (at least) three interaction steps. This pathway has therefore been ignored in Eq. (7) as a higher-order process. Note that this is justified although the interference term of such a three-step ionization mechanism with the direct ionization channel in $|S_{p0}(\infty)|^2$ is of the same perturbation order as the square of the two-step interatomic channel. The latter will still be significantly larger because we consider a situation where the amplitude of the two-step channel is not only larger than the three-step channel but—due to its resonant character—also much larger than the direct channel.

III. RESULTS AND DISCUSSION

A particularly interesting situation arises when the contributions to the interatomic ionization channel of atom A from

the N neighboring atoms in Eq. (7) add fully constructively. This happens, for instance, when all atoms B_j have almost the same distance $R_j \approx R_0$ to atom A and are in the same plane perpendicular to the field polarization. Then, due to interference, the interatomic channel of photoionization is larger than the direct channel by the factor

$$\rho_N \sim N^2 \left(\frac{c}{\omega R_0} \right)^6, \quad (8)$$

where we omitted a prefactor of order unity.

Let us consider for illustration a simple example. The photoionization cross section of an isolated Li atom amounts to $4.5 \times 10^{-19} \text{ cm}^2$ [20] at $\omega = 21.2 \text{ eV}$, which coincides with the $1s^2 \ ^1S-1s2p \ ^1P$ transition energy in helium. When, instead, the Li atom is surrounded by, say, three He atoms at a distance of $R = 1 \text{ nm}$, the photoionization is enhanced by almost seven orders of magnitude ($\rho_3 \sim 6 \times 10^6$) due to the resonant collective coupling between the Li and He atoms (see Fig. 2). The enhancement is so tremendous that a very substantial effect will still remain when the finite bandwidth $\Delta\omega$ of the external field is taken into account, because of which only a fraction $\Gamma_B/\Delta\omega$ of the incident photons will be resonant. Using $\Gamma_B = 4 \times 10^{-7} \text{ eV}$ and assuming $\Delta\omega \sim 100 \text{ meV}$, the relative enhancement still amounts to one order of magnitude.

The amplification by N^2 in Eq. (8) is reminiscent of superradiance and related collective effects [1–9]. The present phenomenon could therefore be called “superenhanced photoionization.”

In a more general situation, where the interatomic position vectors \mathbf{R}_j significantly differ from each other with respect to their length and orientation to the external field, the photoionization yield will not follow the simple N^2 scaling

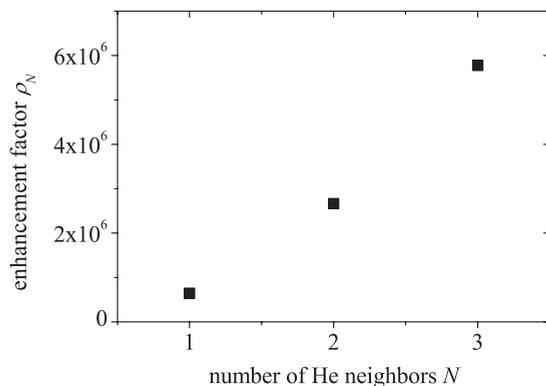


FIG. 2. Resonant photoionization of a Li atom in the presence of neighboring He atoms. Shown is the relative enhancement with respect to the photoionization cross section of an isolated Li atom [see Eq. (8)], for various numbers N of He neighbors. The incident photon energy is resonant with the $1s^2 \ ^1S-1s2p \ ^1P$ transition in helium (i.e., $\omega \approx 21.2 \text{ eV}$). The distance between the Li atom and each of the He atoms is $R \approx 1 \text{ nm}$ and the He atoms are assumed to be located in the plane perpendicular to the photon field polarization. $N = 1$ corresponds to the diatomic case considered in Ref. [16]; $N = 2$ would be realized, e.g., by a linear chain He-Li-He; and $N = 3$ could correspond to a Li atom in the center of an equilateral triangle formed by three He atoms.

of Eq. (8). The photoionization cross section will rather be a complicated function of the precise ensemble geometry. Nevertheless, when all the distances R_j lie in the same range, a pronounced collective enhancement of the photoelectron yield will still result, showing an N scaling between linear and quadratic.

The strong collective enhancement of resonant photoionization in the present study relies on the fact that the spatial extension of the multiatom ensemble is assumed to be smaller than the (reduced) wavelength of the incident laser field. Therefore, the space-dependent factors in Eq. (3) are immaterial and only a relatively weak spatial dependence on the ensemble geometry described by the position vectors \mathbf{R}_j ($j = 1, \dots, N$) remains in Eq. (7). Interestingly, the condition $kR_j \ll 1$ not only favors the appearance of collective effects, but also enables the dominance of the interatomic ionization channel as compared with the direct ionization channel in a system of two atoms A and B_j [see Eq. (1)]. Note that the situation in the MARPE measurements [15] on MnO crystals was very different because the relevant $2p-3d$ transition energy in Mn is very high, amounting to several hundred eV. In combination with the interatomic distance of about 2 \AA , this leads to $kR \sim 1$.

We conclude this section with two additional remarks: First, while the interatomic decay mechanism occurring in the He-Li system of Fig. 2 represents an example of so-called participator resonant ICD [14] (since the photoexcited electron in He itself participates in the ICD process), we point out that the same kind of collective N^2 enhancement may also arise in systems where spectator resonant ICD [14] occurs. The origin of the enhancement is identical in both cases: the process amplitude involves a coherent sum over the N neighboring atoms.

Second, the photoexcited state in atom B could, in principle, also be an autoionizing state which can deexcite via intra-atomic Auger decay. We note that this additional decay channel will not affect the appearance of the N^2 enhancement factor (under optimum conditions) in the photoionization of atom A . In fact, when the corresponding intra-atomic Auger width Γ_{AI} is smaller than the radiative width Γ_B , Eq. (8) will remain unchanged. However, in the opposite case, when $\Gamma_{AI} \gg \Gamma_B$, an additional factor $(\Gamma_B/\Gamma_{AI})^2$ would appear on the right-hand side of Eq. (8). It reflects the fact that, because of the losses arising from the intra-atomic decay channel, a substantial fraction of intermediate states will not contribute to the interatomic ionization channel of atom A .

IV. CONCLUSION

We have studied the collective enhancement of resonant photoionization in an ensemble of atoms. The enhancement relies on the constructive interference of interatomic ionization pathways, involving resonant photoexcitation and subsequent ICD. The amplification of photoionization of an atom A can scale as N^2 with the number N of atoms B surrounding it, leading to superenhanced photoionization.

An experimental observation of the predicted effect may be possible by use of an alkali-metal atom (e.g., Li) attached to a helium cluster or water droplet. The Li photo-ionization yield could be monitored as a function of the applied field

frequency in order to reveal the enhancement at the resonance. Note that experimental photoionization studies on alkali-metal atoms embedded into helium and water droplets have been successfully conducted in recent years [21,22].

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