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Letter

Polariton entering a continuum: Giant diffuse polaritonic resonance

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Polaritons arise due to a light-matter interaction and have been amply investigated for atoms and molecules in a quantum field. By increasing the coupling between the atom/molecule and the cavity, the upper polariton penetrates into the continuum (i.e., ionization continuum of atoms or molecules or dissociation continuum of molecules) within the standard two-level approach. We investigate what happens to the polaritons in reality. We first show that the upper polariton cannot enter the continuum if the atomic or molecular system itself does not support metastable states, often called resonances, and instead becomes a giant diffuse bound polariton which can be extended in space to any size one wishes. Then, we show how external perturbations can enable such a diffuse polariton to penetrate into the continuum and turn it into a metastable polariton, i.e., into a polaritonic resonance. In order to achieve these results the coupling of the bound states to the continuum induced by the quantum light has to be taken into account. We discuss how such giant diffuse bound polaritons as well as polaritonic resonances including their finite lifetime can be calculated and present explicit numerical examples. The results provide a complete picture of what happens to the upper polariton in the vicinity of the continuum and may be utilized to enhance ionization or dissociation inside the cavity.

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Introduction and motivation. The spectra of atoms and molecules change dramatically in confined geometries such as nanoscale cavities. Perhaps the most striking example is the ability to vary the rate of spontaneous emission (see, e.g., Ref. [1] and references therein). Another result of general interest is the formation of atomic and molecular polaritons which are hybrid photon-matter quantum states. An extensive amount of literature (both theoretical or experimental) focuses on studying the energy splitting between polaritons [2–19].

Commonly, theoretical studies of energy splitting between polaritons employ the two-level-system (TLS) approximation [20–25]. When the Rabi frequency (field intensity times dipole transition between the two bound states coupled by the cavity) is larger than the energy gap between the upper polariton (UP) and the continuum threshold, the question arises what happens in reality with this polariton. Answering this basic question is the subject of our present Letter.

In general, one would expect that the UP penetrates into the continuum and becomes a metastable polariton of finite lifetime if the TLS model will be extended to include also the continuum of the system. However, as we will show here, the polariton cannot enter the continuum (i.e., the ionization of an atom or dissociation of a molecule cannot occur) as expected if the atomic/molecular system itself does not support any metastable states, often called resonances. This impossibility to penetrate the continuum will be shown to give birth to the creation of a giant diffuse bound polariton.

As we will theoretically demonstrate here, there are well-defined cases which are neither accidental nor rare where the formed giant diffuse bound polaritons can be as large as one wishes. Once these objects are sizable, they become sensitive to external perturbations, and as we will show below, such perturbations will turn them into metastable polaritons, i.e., into giant diffuse polaritonic resonances.

Formation of a giant diffuse bound polariton. Let us first illustrate the effect of the continuum on the polaritons for a simple model of a one-dimensional (1D) potential that supports only two bound states. For reasons that will be clarified later, we have selected a potential whose continuum density of states $\rho(E)$ changes monotonically with the energy. In other words, $\rho(E)$ does not contain any structures (signatures of resonances), and describes thus the so-called "white" continuum as for the Morse-type potentials [26]. Specifically, we have employed the Rosen-Morse potential [27,28] supporting just two bound states with energies $E_0 < E_1 < 0$, which is defined as

$$V_{\mathrm{RM}}(x) = -V_0/\cosh^2(ax), \tag{1}$$

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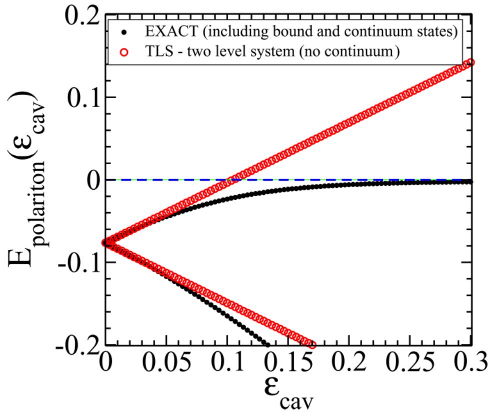

FIG. 1. The energies of the polaritons plotted as a function of the system-cavity coupling parameter ϵ_{cav} [see the Hamiltonian (3)]. Our calculations employ the Rosen-Morse potential [27,28] as defined in the text. The energies of the TLS polaritons are presented in red color, and their counterparts computed including the continuum states are depicted in black color. As a reference, the threshold energy is marked by a dashed blue color. Atomic units are used throughout.

where, in atomic units, $V_0 = 10$ and $a = \sqrt{V_0/6}$. The two bound states have energies $E_0 = 1.41$ and $E_1 = 0.07$, in hartree units. The frequency of the cavity was chosen to be $\omega_{\mathrm{cav}} = E_1 - E_0$. The associated coupling parameter is denoted by ϵ_{cav}.

Although the theoretical background and the details of the numerical calculations are presented below and in the Supplemental Material [29], respectively, we show the results found for the polaritons already now as they clearly demonstrate one of our main findings. Figure 1 depicts the energies of the upper and lower polaritons as a function of the coupling strength of the cavity. We show both the outcome of the two-level-system (TLS) approximation, and of the full treatment including the atomic/molecular continuum. As expected, the TLS upper polariton (briefly TLS-UP) freely crosses the dissociation threshold and penetrates into the continuum. In contrast, the exact UP remains a bound state and approaches asymptotically the threshold energy to become an extremely diffuse (i.e., spatially delocalized) polariton. Such a state remotely reminds of an extremely diffuse Rydberg state [30,31]. As we will demonstrate explicitly below, the just mentioned giant diffuse bound state is extremely sensitive to any small external perturbation due to its interactions with the environment (e.g., with other atoms or molecules, or with the cavity itself) and, therefore, eventually does penetrate into the continuum to become a finite lifetime resonance polariton. Again, we remind in this context an analogy with a highly excited Rydberg electron which is detached by a slight perturbation [30,31].

Theoretical description. Let us open our theoretical discussion by emphasizing that the problem of a matter-radiation interaction (and polaritons in particular) can be studied using different mutually equivalent gauges. Specifically, the momentum (MG), length (LG), and acceleration (AG) gauges come into consideration; these are outlined in the Supplemental Material [29] where also their exact mathematical equivalence is highlighted. Here, we provide just a concise discussion. The standard length gauge (LG) representation of the relevant Hamiltonian reads as follows [32]:

$$\hat{H}_{\mathrm{SC}}^{\mathrm{LG}} = \hat{H}_{\mathrm{S}} + \hbar\omega_{\mathrm{cav}}\left(\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right) + \frac{\left(\epsilon_{\mathrm{cav}}^{\mathrm{LG}}\right)^2}{\hbar\omega_{\mathrm{cav}}}\hat{d}_{\mathrm{LG}}^2 + \epsilon_{\mathrm{cav}}^{\mathrm{LG}}\,\hat{d}_{\mathrm{LG}}\, i(\hat{a} - \hat{a}^{\dagger}). \tag{2}$$

Here, $\hat{H}_{\mathrm{S}} = \frac{\hat{p}^2}{2m} + V_{\mathrm{S}}(\hat{x})$ is our model Hamiltonian of the atomic/molecular system, $\hat{d}_{\mathrm{LG}} \sim \hat{x}$ represents the electric dipole operator, and $\epsilon_{\mathrm{cav}}^{\mathrm{LG}}$ stands for the pertinent LG coupling constant (see the Supplemental Material for more details [29]). The dipole approximation is used here as usual (see also Refs. [34,35]), but we stress that long before the size of our considered polariton is comparable to the cavity size, this polariton becomes extremely sensitive to any small perturbation and stops growing, and penetrates the continuum to become a metastable state.

The Hamiltonian $\hat{H}_{\mathrm{SC}}^{\mathrm{LG}}$ of Eq. (2) does not lend itself well for our subsequent considerations involving the atomic/molecular continuum. Indeed, the electric dipole operator $\hat{d}_{\mathrm{LG}}$ grows linearly with distance from the considered atom or molecule, i.e., it does not vanish outside the cavity inside which our studied material system is placed. Yet there is also the dipole self-energy term containing $\hat{d}_{\mathrm{LG}}^2$ which grows quadratically with $\hat{x}$. An existence of the atomic/molecular continuum is thus camouflaged in the LG representation. In addition, the just presented LG picture seems to contradict an intuitive expectation that the coupling of our atom or molecule to the radiation field should be localized only inside the cavity. For the just mentioned reason, we have decided to switch in all our calculations from the length gauge into the so-called acceleration gauge (AG) description, in which the electric dipole operator is replaced by an equivalent term $\hat{d}_{\mathrm{AG}} = \partial V_{\mathrm{S}}(x)/\partial x$. The resulting Hamiltonian valid in the regime of the coupling ϵ_{cav} used here reads

$$\hat{H}_{\mathrm{SC}}^{\mathrm{AG}} = \hat{H}_{\mathrm{S}} + \hbar\omega_{\mathrm{cav}}\left(\hat{a}^{\dagger}\hat{a} + \tfrac{1}{2}\right) + \epsilon_{\mathrm{cav}}\,\hat{d}_{\mathrm{AG}} i(\hat{a} - \hat{a}^{\dagger}). \tag{3}$$

Note that an existence of the atomic/molecular continuum becomes manifest in AG, as opposed to LG. Also the matter-radiation AG coupling is manifestly confined only to a small region of nonvanishing $\partial V_{\mathrm{S}}(x)/\partial x$. More details regarding the AG representation and the relationship between the $\epsilon_{\mathrm{cav}}^{\mathrm{LG}}$ given in Eq. (2) and ϵ_{cav} given in Eq. (3) are provided in Ref. [33] and in the Supplemental Material [29].

The corresponding AG dipole transitions between the bound states and the "white" continuum of $V_{\mathrm{S}}(x)$ are also plotted in the Supplemental Material (see Fig. S1) [29]. It is seen that the magnitude of the dipole transition moments between the bound states and the continuum is comparable to those between the two bound states.

Let us point out that all the considerations and calculations presented here are such that the matter-cavity interaction is facilitated via exchanging a single photon only. We have confirmed the validity of the single-photon picture by carrying out computations going beyond the single-photon approximation (accounting for an exchange of two or more photons did not affect the obtained results). In passing, we note also that the single-cavity mode approximation, used implicitly in our treatment, is justified when dealing with phenomena which are energetically below the excitation energies of all the other cavity modes.

As clearly seen in Fig. 1, the energies of the exact polaritons are lower than their TLS counterparts. Indeed, this interesting observation is general as is proven in the Supplemental Material [29]. Moreover, Fig. 1 demonstrates that the exact polaritons remain as bound states, as also indicated by the numerical results of recent pioneering work on the impact of including the continuum in the calculations of polaritons in electron-hole models [34,35]. This essential result is analyzed and explained below. In particular, we answer the fundamental and tantalizing question concerning the penetration of a polariton into the continuum and demonstrate the general finding by explicit examples. In our opinion, our theory also explains the numerical result found in Refs. [34,35], namely, that the polariton does not enter the continuum there.

The exact polaritons avoid penetration into the white continuum. Let us explain now why the exact polaritons of Fig. 1 do not enter the white continuum (e.g., dissociation of a molecule inside a cavity cannot occur). The eigenvalue problem of the AG Hamiltonian (3) in the single-photon approximation simplifies and decouples into two mutually independent one-dimensional eigenproblems. Following the theoretical analysis developed in Ref. [36] and adapting it to our present situation, one obtains, as shown explicitly in the Supplemental Material [29], the two eigenvalue equations

$$\left(-\frac{\hbar^2}{2\,m}\,\partial_{xx}+V_{\rm SC}^{0,1}(x)-E\right)\chi_{0,1}(x)=0, \tag{4}$$

where

$$V_{\rm SC}^{0}(x)=V_{\rm S}(x)-\epsilon_{\rm cav}\,\partial V_{\rm S}/\partial x+\hbar\omega_{\rm cav}/2,$$
$$V_{\rm SC}^{1}(x)=V_{\rm S}(x)+\epsilon_{\rm cav}\,\partial V_{\rm S}/\partial x+\hbar\omega_{\rm cav}/2.$$

In the cavity, the potential $V_{\rm S}(x)$ of the system is modified by the term $\epsilon_{\rm cav}\,\partial V_{\rm S}/\partial x$. What are the conditions at which this modification of the potential does not enable penetration of the polaritons into the continuum? This question is equivalent to asking for the conditions that the modified potential does not support resonance states [as is the case for the original potential $V_{\rm S}(x)$]. From the condition derived in Ref. [36] to support resonances for two coupled potentials, we can deduce the condition for which resonances do not appear in the present situation in a cavity, more specifically, the condition for the barrier described in Ref. [36] and for that in our paper to not introduce new types of resonances. This condition is indeed fulfilled in the first example we have discussed here of a Rosen-Morse potential in a cavity, at least in the weak-coupling regime which is tacitly assumed in the present Letter. Our finding also explains the results presented in Ref. [35], since the above term, $\epsilon_{\rm cav}\,\partial V_{\rm S}/\partial x$, for a hydrogen atom is $\epsilon_{\rm cav}\,x/r^3$ (x is the polarization direction of the cavity mode) which does not lead to the creation of a barrier that might form resonances. Reference [36] states that resonances are not supported by the modified potential as long as it does not possess a barrier whose maximum value reaches above the dissociation threshold of the original $V_{\rm S}(x)$. In other words, resonances appear only if there exists a value of x such that

$$V_{\rm S}(x)\pm\epsilon_{\rm cav}\,\partial V_{\rm S}/\partial x>0 \tag{5}$$

is fulfilled.

Resonances induced by our polariton entering the white continuum may be formed only if the coupling strength $\epsilon_{\rm cav}$ is large enough. For our model Rosen-Morse potential, the above inequalities (5) are satisfied for $\epsilon_{\rm cav}\geqslant 0.5$ a.u. (see the Supplemental Material for details [29]). Inspection of Fig. 1 indeed shows that our upper polariton cannot enter the white continuum since the required coupling strength $\epsilon_{\rm cav}$ would have to be increased to an unrealistic magnitude. Note, however, that our theoretical analysis presented here concerns only the weak-coupling regime, so it is therefore in principle possible that the upper polariton may enter the continuum at such large values of $\epsilon_{\rm cav}$ where the weak-coupling approximation does not apply. Moreover, the just provided explanation does not concern such situations when the continuum of $\hat{H}_{\rm S}$ is not "white" (i.e., it contains resonances). This issue will be discussed further below.

Importantly, there exist prominent examples of physically relevant potentials which do not support any metastable states, e.g., the ubiquitous Morse potential describing molecular vibrations. Hence, as we have just shown above, for Morse-type potentials the upper polariton cannot enter the continuum for physically realistic values of $\epsilon_{\rm cav}$. This finding seems to contradict the claim for dissociation of $\mathrm{W(CO)_6}$ in a cavity as recently measured and attributed to a Morse potential [37,38]. The observed penetration of the upper polariton into the continuum results from the fact that the actual vibrational potential of $\mathrm{W(CO)_6}$ is only approximately of Morse type. Indeed, we show below that by adding tiny bumps or barriers to the relevant atomic/molecular potential $V_{\rm S}(x)$ (which itself supports only the white continuum) one generates resonances. These interact with the giant diffuse bound polariton of the Morse potential and enable its penetration into the continuum, forming a giant diffuse polaritonic resonance which is extremely spatially delocalized.

Penetration of the giant diffuse polariton into the "nonwhite" continuum. As the upper polariton approaches the dissociation threshold, its wave function becomes extremely spatially delocalized (it corresponds to a large de Broglie wavelength). Such a weakly bound and spatially delocalized polaritonic bound state is extremely sensitive to any small perturbations included in the Hamiltonian. Such perturbations may correspond, e.g., to the effects of the environment. Essentially, any long-distance interaction of our system with the environment (i.e., with the neighboring atoms/molecules) introduces tiny bumps and barriers into the potential, and these tiny effects enable the upper polariton to penetrate into the continuum and form the polaritonic resonance. Another kind of small perturbations may arise, e.g., due to intramolecular interactions with other vibrational modes.

We note in passing that a strong impact of tiny bumps and barriers on the properties of resonances has already been demonstrated elsewhere, in a somewhat different context (see Fig. 3 of Ref. [39]). Another insightful example is provided by Ref. [26] where a simple step potential is studied. It is shown that, even in the case when the height of the step is smaller by many orders of magnitude than the width of the step, broad shape-type resonances are born (see Fig. 4.1 in Ref. [26]).

To demonstrate explicitly our claim of penetration of the giant diffuse polariton into the "nonwhite" continuum, we

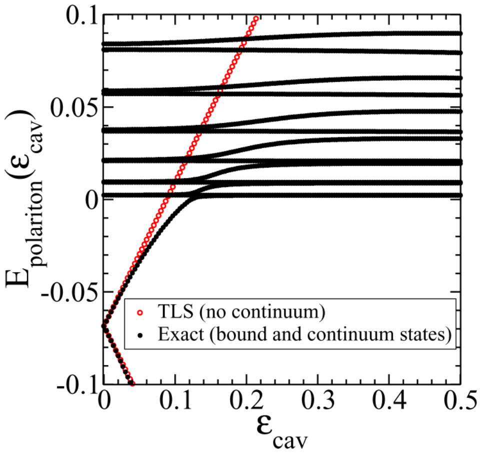

FIG. 2. The energies of the TLS polaritons and the numerically exact eigenvalues of $\hat{H}_S$ + perturbation. Here, $\hat{H}_S$ corresponds to Fig. 1, and the perturbation consists of two tiny potential barriers which generate shape-type resonances of the atomic/molecular system. The exact UP remains still lower in energy than the TLS UP, much as in Fig. 1. On the other hand, contrary to Fig. 1, the exact UP penetrates into the continuum, giving rise to a giant polaritonic resonance, manifested here by a series of avoided crossings. Atomic units are used throughout.

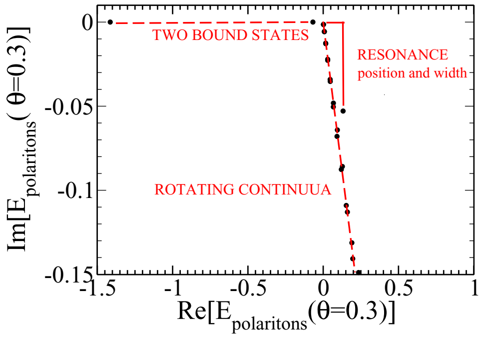

FIG. 3. The UP resonance calculated by means of the complex scaling method [26] for $\epsilon_{cav} = 0.15$ for the same potential $\hat{H}_S$ + perturbation as in the calculation shown in Fig. 2. In this method, the bound states stay on the real energy axis, the continuum states rotate into the complex energy plane and align along a straight line in this plane depending on the scaling, and the resonances are uncovered as isolated points in this plane. The value of energy along the real axis provides the energetic position of the resonance and the imaginary part is half the width of the resonance. The plot shows the bound LP, the rotated continuum states, and the uncovered UP resonance as black dots. The red lines are drawn to guide the eye. Atomic units are used throughout.

modify the Rosen-Morse potential by adding two small barriers which have a negligible effect on the two bound states. The modified Rosen-Morse potential is given explicitly by

$$V_{\text{modified}-\text{RM}}(x) = V_{\text{RM}}(x) + 0.1[e^{-(x+5)^2/2} + e^{-(x-5)^2/2}]. \quad (6)$$

Atomic units are again tacitly adopted here.

As we show, these two barriers do introduce resonance structures into the continuum, in consistency with our discussion pursued above. For the explicit details of the calculation, see the Supplemental Material [29].

In Fig. 2, we plot the resulting eigenvalue spectrum of $\hat{H}_S$ + perturbation as a function of ϵ_{cav}. Contrary to Fig. 1, the UP indeed does cross the dissociation threshold and penetrates into the continuum. The giant polaritonic resonance is thus born, as indicated by the series of avoided crossings appearing in Fig. 2.

This result is confirmed also by another independent calculation, where the polaritonic resonance is computed explicitly by means of the complex scaling method [26] (see Fig. 3). The resonance state is represented here by a single eigenstate of the complex scaled non-hermitian Hamiltonian of our atomic/molecular system in a cavity, and its pertinent energy eigenvalue is complex. The real part of this eigenvalue corresponds to energy of the considered polaritonic resonance, and the imaginary part to its width.

Summary. In this Letter, we have examined the impact of the continuum of an atomic/molecular system on the upper and lower polaritons due to the interaction of the material system with the cavity modes. For potentials which do not support resonances (such as Morse-like potentials), one finds, in contrast to the expectations based on the two-level-system (TLS) approximation, that the upper bound polariton (UP) does not penetrate into the continuum and does not become a finite lifetime resonance state if the interaction with the continuum is taken into account. This statement holds more generally for any number of bound-state approximations. It is shown here that the continuum of the system, neglected in the TLS model, always (not only for potentials that do not support resonances) lowers the energies of the upper and lower polaritons in comparison to their TLS values.

For potentials that intrinsically do not support resonances, the UP approaches asymptotically the threshold energy for ionization/dissociation, and becomes a giant diffuse bound state. In such cases, ionization and/or dissociation takes place only due to weak perturbations (e.g., due to the interaction of the giant diffuse upper polariton with the neighboring atoms or molecules) which introduce resonances into the “white” continuum of the atomic/molecular Hamiltonian. This mechanism leads to the formation of giant polaritonic resonances enabling ionization or dissociation induced by the cavity. Such a giant polaritonic resonance (both its energy and its width) has been calculated explicitly (see Fig. 3). Therefore our present work gives a complete picture of what happens to the upper polariton in a cavity as it penetrates into the continuum and becomes a metastable polaritonic resonance of a finite lifetime. We hope that these findings will stimulate experiments and further theoretical studies.

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