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Theoretical study of enhancement and suppression of the fluorescent spectra of dye molecules in a photonic crystal with a pseudogap*

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We have investigated the analytical forms of the photonic density of states (DOS) in a photonic crystal in the interested frequency regime according to the rule of state conservation in a photonic crystal with pseudogaps, which states that, if a valley of the DOS appears in some range of frequencies, it must be compensated for by increasing over some other ranges. By using a model DOS with a state-conservative photonic pseudogap, we have also investigated the enhancement and suppression of spontaneous emission of two-level atoms with different frequency positions and widths of emission spectra in a state-conservative electromagnetic reservoir; and the DOS-induced suppression, enhancement, narrowing and redshifting or blueshifting of spontaneous emission spectra are naturally obtained.

Keywords: photonic crystal, spontaneous emission, density of states, pseudogap
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Spontaneous emission is a fundamental and unavoidable consequence of the quantum nature of the interaction between an excited atom and an electromagnetic reservoir.[1] The existence of a modified electromagnetic reservoir must affect the process of the spontaneous emission of an atom, e.g., it may enhance or inhibit the spontaneous emission to some extent.[2] For this, a photonic crystal (PC), which has a periodic dielectric structure and thus may have a photonic band gap (PBG), was just proposed to modify the spontaneous emission and to localize the light.[3−6] A dielectric structure with a complete PBG is known to affect spontaneous emission most when the transition frequency of an atom is close to the PBG edge. Up to now, a few dispersion models near band edges have been extensively employed to study the spontaneous emission problems in the PC with absolute PBGs.[3,4] Clearly, PCs with absolute PBGs are difficult to fabricate on the sub-micron length scale in the optical and near-infrared (IR) frequency ranges, although much progress has recently been made in fabricating three-dimensional (3D) PBG crystals at near-IR wavelengths.[7] Therefore, most of the experimental works on radiative emission from active materials embedded in optical PCs have been performed using the PCs with photon propagation pseudogaps, i.e. materials that prohibit photon propagation in only certain directions.[8−10] In fact, many types of research do not require a complete PBG, but only a strong pseudogap, or even not so strong.

Many studies show that the inhibition of spontaneous emission rates (SER) for one range of transition frequencies tends to be accompanied by an enhancement of emission rates at other frequencies. It follows that any reduction in SER over some range of frequencies, is necessarily compensated by the increase over some other range of transition frequencies, that is, the sum rule for modified SER called by Barnett and Loudon.[11] This suggests that it is better to use a model photonic total DOS with both a valley over some range of frequencies and a peak over some other range of frequencies relative to that in vacuum. But to the best of our knowledge, all of the theoretical studies using a pseudogap model deal with a model DOS only with one or two valleys, although it is expressed by an analytical function different in different study.[12,13]

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A two-level atom is the simplest possible model of any real atom. It has a distinguished history in theoretical laser physics and still more so generally in theoretical quantum optics.[14] As pointed out in Ref.[12], the description of fluorescence from optically active materials (dye molecules) embedded in a PC can be demonstrated by a two-level atom system, and almost every experiment studying the spontaneous emission in a PC up to now uses dye molecules because of their wide fluorescence spectra up to 10%. In this paper, we select a state-conservative model DOS pseudogap according to the rule of state conservation within a modified frequency regime shown in our previous work[15] and investigate the enhancement and inhibition of fluorescent spectra of dye molecules in this electromagnetic environment using a two-level atom model.

As is known, the 3D photon DOS in a PC is defined by[16]

$$\rho(\omega) = \frac{2V}{(2\pi)^3} \sum_n \int_{1\mathrm{BZ}} \mathrm{d}^3k \delta(\omega - \omega_{n,k}), \qquad (1)$$

where V is the sample volume in 3D space, $\omega_{n,k}$ is the photon dispersion relation in the PC, and 1BZ means the first Brillouin zone of the PC. The factor 2 in Eq. (1) denotes the two polarizations that are degenerate in energy.

According to the physical meaning of the DOS in a system, which is the number of allowed states per unit increase in ω, the total number of states in the system may be the integration of DOS over all the allowed frequency regimes $\omega \in [0, \omega_M]$, where ω_M is large enough and far away from the modified regime of interest but not very large so as to maintain the effective refractive index of the system n_{eff}, i.e. the average refractive index that is close to the calculated value according to Maxwell–Garnett theory is constant. This choice of ω_M is similar to that in Refs. [2] and [17], which is chosen approximately equal to the electron Compton frequency $\omega_M = mc^2$ that probes the relativistic aspects of the electron wavepacket, and remains independent of its precise value in the scope of our analysis. Therefore, the total number of states in the system below the truncated frequency (or its corresponding wavevector) is

$$\int_0^{\omega_M} \rho(\omega)\mathrm{d}\omega = \frac{2V}{(2\pi)^3} \sum_n \int_{1\mathrm{BZ}} \mathrm{d}^3k \int_0^{\omega_M} \mathrm{d}\omega \delta(\omega - \omega_{n,k}). \qquad (2)$$

It is of utmost importance to note that no matter what form the dispersion curve $\omega_{n,k}$ has, the following integration is always valid

$$\int_0^{\omega_M} \rho(\omega)\mathrm{d}\omega = \frac{2V}{(2\pi)^3} \sum_n \int_{1\mathrm{BZ}} \mathrm{d}^3k = 2MN. \qquad (3)$$

Here, M is the truncated number of photonic bands corresponding to the truncated frequency ω_M, N is the number of unit cells in the PC, and we use the well-known relation in solid-state physics that the product of the volume of a unit cell and the volume of the first Brillouin zone equals $(2\pi)^3$ for all time. On the other hand, for its effective medium, the integral DOS truncated at frequency ω_M becomes

$$\frac{2V}{(2\pi)^3} \sum_n \int_{1\mathrm{BZ}} \mathrm{d}^3k = \frac{2Vn_{\mathrm{eff}}^3\omega_M^3}{3\pi^2} \equiv \int_0^{\omega_M} \rho_0(\omega)\mathrm{d}\omega, \qquad (4)$$

where $\rho_0(\omega) = 2Vn_{\mathrm{eff}}^3\omega^2\pi^{-2}$ is the density of states in the effective medium. In this paper, we have let the velocity of light in vacuum and Dirac constant $\hbar = c = 1$. Therefore, we call Eq.(3) or (4) the rule of total state conservation, which states that the total number of states in a PC in the entire allowed frequency regime will always be conservative to that in its corresponding effective medium.

Surely, for the problem of the spontaneous emission of a specific active atom or molecule, model DOSs are generally invalid to account quantum optical phenomena of this atom or molecule in 3D PCs, and the projected local density of states (PLDOS) should be used. However, if there is a collection of dependently emitting atoms or molecules with essentially random dipole orientations in a small volume, then in order to describe the mean emission characteristics of the system, we should average over all the solid angles, and the local density of states (LDOS) $\rho(r, \omega)$ may be used.[12] The relation between the LDOS and the total DOS is given by

$$\rho(\omega) = \frac{1}{V_{\mathrm{WSC}}} \int_{\mathrm{WSC}} \mathrm{d}r\varepsilon(r)\rho(r, \omega), \qquad (5)$$

where WSC and V_{WSC} denote the Wigner–Seitz cell and its volume, respectively. This relation shows that for a small dielectric modulation in the PC, which implies a weak interaction between the dielectric and the electromagnetic field, the total DOS can provide a reasonable description of the field at any point in the PC. Clearly, a crystal exhibiting a strong pseudogap or a full PBG does not satisfy such a condition. Therefore, we can say that a model total DOS can be used in the problem of spontaneous emission of a collection

of dependently emitting atoms or molecules with essentially random dipole orientations in a small volume or even in the whole PC with a small dielectric modulation, i.e. the PC has a photonic pseudogap. Many authors have investigated the emission features assuming that the forms of the DOS only exhibit an inverse Lorentzian-like or inverse Gaussian pseudogap.[12,18] If we abide by the rule of total state conservation, the following forms, for example, will be appropriate for the situation when a peak and a pseudogap are expected

$$\rho(\omega) = \rho_0(\omega)[1+aG(\omega,\omega_{c1},\Gamma_1)-bG(\omega,\omega_{c2},\Gamma_2)], \quad (6)$$

where $G(\omega,\omega_c,\Gamma)$ is the Gaussian function, and a, Γ_1 and ω_{c1} are, respectively, parameters describing the height, width and central frequency of the peak of the DOS; b, Γ_2 and ω_{c2} are parameters describing the depth, width and central frequency of the pseudogap, respectively. In the above-mentioned equation, a and b are dimensionless, $\Gamma_{1,2}$ and $\omega_{c1,2}$ are in units of ω_0 which is the central frequency of the interested modified region of the DOS, not the central frequency of the valley or peak of the DOS. This DOS has the features that it approaches the free- space DOS far away from ω_c, i.e. $\rho(\omega\to 0) = 2Vn_{\rm eff}^3\omega^2\pi^{-2}$, $\rho(\omega \gg \omega_c) = 2Vn_{\rm eff}^3\omega^2\pi^{-2}$. The parameters in Eq.(6) should be determined by the condition

$$\int_0^\infty [\rho(\omega)-\rho_0(\omega)]{\rm d}\omega = 0. \quad (7)$$

For example, b=1.491a when $\omega_{c1,2} = 1 \pm 0.1$, $a < 1.025$, $\Gamma_{1,2}$=0.1 for a Gaussian-like DOS $\rho(\omega)$ in Eq.(6). Here, it must be noted that the model DOS in this paper has a strong pseudogap in order to demonstrate our viewpoints clearly, $\Gamma_{1,2}$=0.1 is a typical bandwidth of the fluorescence spectra of most efficient organic fluorescent materials although $\Gamma_{1,2}$ is very small for most single atoms and molecules.

State conservative form of the DOS of a PC, which exhibits significant oscillation over a wide range and on average follows the DOS of the effective medium, can always be seen from almost all the theoretical outcomes calculated according to realizable PCs[5] and experimental results.[10]

Among several models for the spontaneous emission of a two-level atom, we adopt the theory developed by Woldeyohannes *et al*,[16] which is a theory for a three-level atom, and let two lower levels $|1\rangle$ and $|0\rangle$ equal to one $|1\rangle$. We also adopt the symbol system to describe our two-level atom,[16] that is, $|2\rangle$ is the excited level, $|1\rangle$ is the ground state; γ_{21} is the radiation linewidth that can be as wide as up to 10%, like that of a photoluminescence spectrum or Raman spectrum, etc.; ω_{21} is the transition frequency and is also in units of ω_0. Given a model DOS $\rho(\omega)$, we can deduce the "atom form factor" $z(\omega)$ expressed in terms of the photon DOS $\rho(\omega)$

$$z(\omega) = \frac{{\rm d}k(\omega)}{{\rm d}\omega} = (6\pi^2)^{1/3}\rho(\omega)\left[\int_0^\omega \rho(\omega'){\rm d}\omega'\right]^{-2/3}. \quad (8)$$

For simplicity, we study the enhancement and suppression of SE of a two-level atom in a PC with the model DOS expressed by Eq.(6) using the parameters b=1.488 for $\omega_{c1,2}$=1$\pm$0.1, a=1, $\Gamma_{1,2}$=0.1. Here, we consider first the case where the radiation linewidth γ_{21}=0.1. It should be noted that the central frequency of the pseudogap is, more accurately, 1.105ω_0, which is numerically the zero point of the DOS.

As has been shown in the experimental investigation,[9] either enhancement or inhibition of the spontaneous decay of a molecule with a wide spontaneous emission spectrum can be observed in a PC, depending on the relative position of the photonic band gap / pseudogap and fluorescence spectrum. Usually, ω_{21} is situated around ω_{c2}, and δ_λ is the detuning frequency of ω_{21} from the frequency ω_{c1}, i.e. δ_λ=ω_{21} $-$ ω_{c2}.

Figures 1(a) and 1(b) show the plots of the spontaneous emission spectra $S_\rho(\omega)$ of two kinds of two-level molecules in a PC with the model DOS for the cases of δ_λ=$-$0.1, and 0, respectively, each of them is accompanied by a standard Lorentzian spectrum centred at its corresponding radiation frequency $1+\delta_\lambda$. From Fig. 1, one can see that significant enhancement and suppression do occur at the frequencies corresponding to the DOS peak and valley, respectively, and complete suppression occurs at the zero-DOS frequency. This is in agreement with the Fermi golden rule. Especially, if the radiation transition frequency $\omega_{21} = 1+\delta_\lambda$ is situated near the low frequency side of this model pseudogap, both significant enhancement and suppression result in a dark line at the zero-DOS frequency ω_{c1}, a clear redshift of the maximum frequency and a significant narrowing of the emission spectrum. Similarly, if the DOS has a peak situated at the high frequency side of its pseudogap, and the radiation transition frequency $\omega_{21} = 1+\delta_\lambda$ is also situated near the high frequency side, they will result in a clear blueshift. The redshift has just been detected by Koenderink *et al* but the blueshift has not been yet.[10]

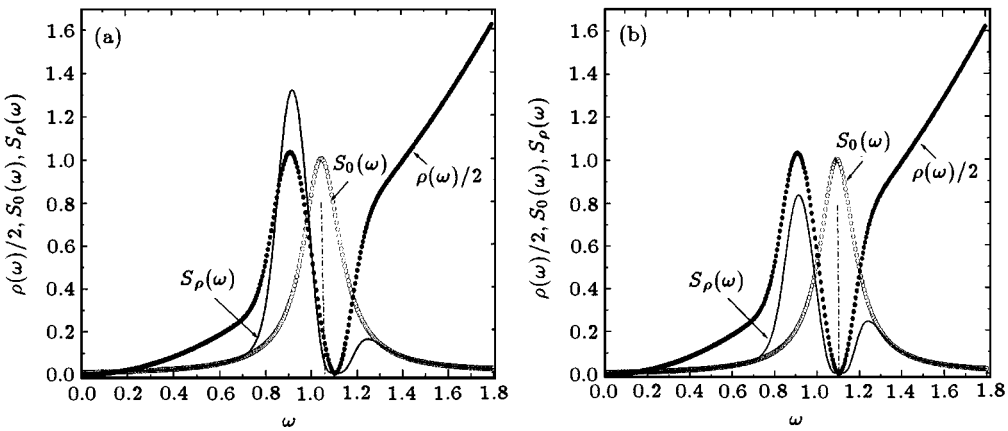


Fig. 1. Plots of spontaneous emission spectra $S_\rho(\omega)$ of two kinds of two-level dye molecule with (a) γ_{21}=0.1, δ_λ=–0.1, (b) γ_{21}=0.1, δ_λ=0 in a PC with the model DOS expressed by Eq.(6) using the parameter b=1.488 for $\omega_{c1,2} = 1 \pm 0.1$, a=1, $\Gamma_{1,2}$=0.1. Both (a) and (b) are accompanied by a standard Lorentzian spectrum $S_0(\omega)$ centred at its corresponding radiation frequency $1 + \delta_\lambda$, and half of the model DOS.

If the linewidth of the spontaneous emission spectrum of an atom is smaller or larger than the width of the photonic pseudogap, the results will have some qualitative differences. For example, when γ_{21}=0.05 and δ_λ=0, i.e. the intrinsic spontaneous emission spectrum of a molecule is almost situated in the photonic pseudogap (its width $\Gamma_2 \approx 0.1$), the modified spontaneous emission spectrum of the atom is suppressed significantly, as shown in Fig. 2(a). When γ_{21}=0.15 and δ_λ=0, i.e. the intrinsic spontaneous emission spectrum of a molecule and the enhanced DOS overlap largely although the central frequency of the spectrum is located at the centre of the DOS pseudogap, a redshifted and an enhanced spontaneous emission spectrum still appears, as shown in Fig. 2(b). Similar results can be demonstrated when the central frequency of the spectrum is slightly less than that of the DOS pseudogap, e.g., for the cases of γ_{21}=0.05, δ_λ=–0.05, and γ_{21}=0.15, δ_λ=–0.05, as shown in Figs 3(a) and (b), respectively.

When the atoms or molecules are placed in PCs with different modified widths of the DOS pseudogaps and peaks, the analysis method and the corresponding results resemble those stated, i.e. the modified spontaneous emission spectrum depends strongly on the relative position of the photonic DOS pseudogap/peak and emission spectrum, as well as on their relative widths.

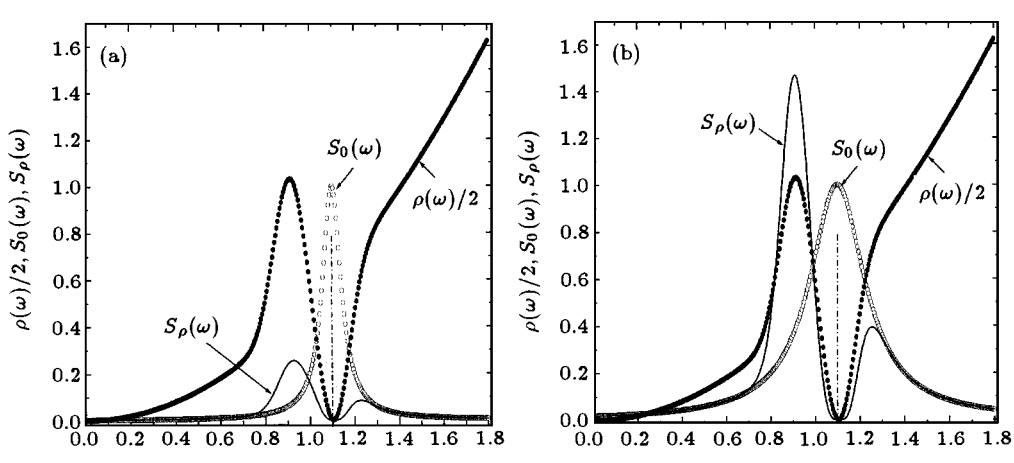


Fig. 2. Plots of spontaneous emission spectra $S_\rho(\omega)$ of two kinds of two-level dye molecule with (a) γ_{21}=0.05, δ_λ=0, (b) γ_{21}=0.15, δ_λ=0, respectively, in a PC with the model DOS demonstrated in the Fig. 1. Both (a) and (b) are accompanied by a standard Lorentzian spectrum $S_0(\omega)$ centred at its corresponding radiation frequency $1 + \delta_\lambda$, and half of the model DOS.

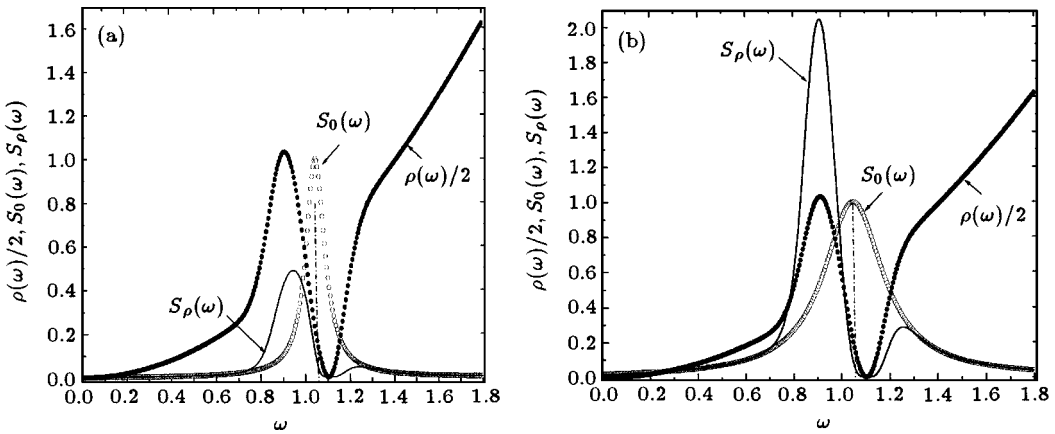


Fig. 3. Plots of spontaneous emission spectra $S_\rho(\omega)$ of two kinds of two-level dye molecule with (a) γ_{21}=0.05, δ_λ=–0.05, (b) γ_{21}=0.15, δ_λ=–0.05, respectively, in a PC with the model DOS demonstrated in the Fig. 1. Both (a) and (b) are accompanied by a standard Lorentzian spectrum $S_0(\omega)$ centred at its corresponding radiation frequency $1+\delta_\lambda$, and half of the model DOS.

Theoretical enhancement and suppression of spontaneous emission are significant, but it is not easy to observe because the results reflect the effect from the whole PC and are the average of all directions, although, strictly speaking, enhancement and suppression of spontaneous emission depend on the local DOS. This can be detected by using an integral-sphere technology. In a given direction, the SE spectrum is usually different from the others, i.e. it is angle-dependent just as most reported experiments detected;[10] therefore, it is not surprising that a possible phenomenon may appear that the emission is enhanced at some frequencies according to the above calculations, while relatively suppressed emission occurs at these frequencies in some directions. There may be some directions in which the detected spectra may be representative for the angle-averaged total emission spectrum.

In conclusion, we have shown that the total number of states in a PC in the entire allowed frequency regime will be conservative to the value in its corresponding effective medium. From the conservation rule, we have deduced the theorem of state conservation within a modified frequency regime in PCs with pseudogaps. This theorem has a very important application in developing a model DOS for a pseudogap of a PC because not every paper in the literature gives a correct pseudogap model of the DOS. Assuming a state-conservative DOS, we have naturally obtained DOS-induced suppression, enhancement and redshift or blueshift in the fluorescent spectra of dye molecules.

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