Emitter-Vacuum coupling through a leaky metal nanostructure and the role of dynamics in density of optical states

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We show a break down of the conventional partition of density of optical states into radiative and non-radiative parts, when dynamics of fluctuations becomes important even in the weak vacuum-coupling regime. Here, non-radiative absorption due to a nanostructure as predicted by conventional theory can vanish significantly with an equivalent increase in the density of radiative states. Large divergence of experimental observations from current theory in the case of emitters interacting with fully absorbing plasmonic nanoparticles only a few nanometers in dimensions, are now evident. A detailed model of fluctuation-dissipation by an emitter-nanoparticle quantum system demands a non-local behavior in the limit of very small metal nanoparticles, and this effect is also notable for an emitter located very close to larger metal nanostructures. Thus we point that widely used techniques to enhance optical sensing such as surface-enhanced-Raman-spectroscopy (SERS) would not have been feasible but for this effect. Qualitatively, this quantum effect presents itself only when the classical probability of emitted photon scattering off a proximal metal nanostructure approaches zero. Hence, though different in origin and scale, this effect has an interesting analogy with quantum effects resulting in Hawking radiation near a black-hole.

INTRODUCTION

Spontaneous emission is typically elucidated as a function of vacuum fluctuations and proximal matter, and its nature in the weak vacuum-coupling regime is predicted by the density of optical states. Increasing density of radiative states relative to the non-radiative states using appropriate nanostructures placed near emitters can result in significant gains in power and even efficiency of emission; and this is broadly referred to as Purcell enhancement [1–8]. This work shows a break down of the current theory of local density of optical states when the dynamics of fluctuations between the emitter and a nanostructure becomes important. We point to anomalies of a few orders of magnitude in the observed decay rates reported in the last two decades by researchers studying emission in the presence of metal nanoparticles, and the corresponding theoretical predictions. Especially, the gains in emission observed in presence of plasmonic nanoparticles of limiting small dimensions (<15 nm), directly contradicts our current understanding [9–13]. Some of these theoretical evaluations were available in their original reports but this divergence was probably overlooked, while our evaluations are presented here. In conjunction, we also report predictions of the proposed theory that remove any contradictions and divergence.

Note that in this weak vacuum-coupling regime, the relevance of experiments have been limited to steady-state solutions of the field even when the emitters and metal particles may be quantized. This is unlike in the strong vacuum-coupling regime of electrodynamics, where experiments in micro-cavities have been used to establish vacuum-Rabi oscillations and other effects of the fluctuations [14]. Here, we consider the case when probability of dissipation of the photon by a metal nanoparticle is not much larger than the probability of exchange of excitations between its dipole mode and the dipole emitter. In this case, creation and annihilation of plasmons can be virtual and averages to a lower net dissipation by the dipole mode of the metal particle, with an equivalent increase in stimulation of the emitter by virtual photons. This behavior can also be modeled as fluctuations in the metal nanostructure leaking to the emitter due to the relatively high rate of exchange of virtual excitations i.e a leaky metal particle. It is predicted for limiting small dimensions of a plasmonic nanoparticle, and to a notable degree for even a larger metal nanoparticle when distances less than its radius separate the emitter i.e. a regime that coincidentally supports absorption and a near-zero probability of classical scattering of the photon by the metal nanoparticle. Thus, it is well distinguished from Purcell enhancement where the emitter is at resonance with a relatively large plasmonic particle 50 - 200 nm in dimensions, and is separated by distances on the order of its radius or larger. There, the interaction is dominated by elastic scattering, adding significantly to the relative density of radiative states as in the conventional theory. In many cases of sensing fluorescence and Raman signals, near-field enhancement of radiation exciting the emitter accompanies this possible enhancement of its emission. We show that widely used techniques such as surface-enhanced-Raman-scattering (SERS) exhibit gains up to $10^{10}$ in magnitude [17–21] primarily due to this effect discussed in this work, which otherwise would be restricted to a factor of $10^3$ at most. Typically, a larger metallic surface or a nanostructure hosts smaller (sharper) nano features that result in this near-field enhancement in addition to the large non-radiative
dissipation. The observed factors of enhancement of Raman signals are much greater than the combined amplification possible due to relative increase in intensity of excitation and density of radiative states available, for both resonant and off-resonant emissions. The large enhancements of Raman signals observed has so far lead to tentative mechanisms proposed that do not submit to classical electrodynamics and quantum models. This divergence of theory from experiments is sometimes classified into a chemical enhancement of unknown origin. Further, measurements resolved with a varying distance from the nanostructure have shown that the SERS effect has a longer range than that is possible by just near-field enhancement of the surface features or any chemical effects. This conundrum is answered by vanishing of non-radiative absorption of the dipole mode and its appearance as a stronger radiative mode for emitters close to the plasmonic surface.

A NON-LOCAL THEORY FOR DENSITY OF OPTICAL STATES

We describe the known methods used to evaluate the modified self-energy of a point dipole in an inhomogeneous medium, in the supplementary material. This problem may not have closed-form analytical solutions in general, and a quasi-static solution in the long wavelength limit has been typically preferred. As noted before, this may result in significant errors in the estimated energy shifts, and in a underestimation of non-radiative decay rates in metal nanostructures. Hence, we have resorted to more computationally intensive full-wave approaches to include retardation for finite wavelengths. The decay rate representing the local density of optical states is given by \( \Gamma = -2\Im(\Sigma) \), where \( \Sigma \) is the self-energy in presence of the nanostructure. \( \Gamma^r_0 \) and \( \Gamma^r_0 \) are known radiative and non-radiative decay rates of the isolated emitter adding to \( \Gamma_0 \). The total radiative and non-radiative parts are a sum of the free-space and metallic components as below.

\[
\Gamma^r_{total} = \Gamma^r_0 + \Gamma^r
\]

(1)

where \( \Gamma^r_0 = \frac{2\sqrt{\pi} \mu^2 k^3}{3\hbar} \) and \( \mu \) is the electric dipole moment of the emitter; \( k, \epsilon \) and \( \hbar \) are the wave number, free-space permittivity and reduced Planck’s constant. Note that a dipole oscillator with energy of one quantum represents the emitter as a two-level system in this weak vacuum-coupling regime.

\[
\Gamma^{nr}_{total} = \Gamma^{nr}_0 + \Gamma^{nr}
\]

(2)

where \( \Gamma^{nr} \) and \( \Gamma^{nr} \) are additional radiative and non-radiative decay rates of emitter in the presence of metal nanostructure. The optical theorem for a point source establishes that the evaluated self-interaction of an emitter due to a proximal body represents the total radiative (scattering) and non-radiative (absorption) states of the body. Further, reflection-symmetry of the Green dyadic allows us to equally interpret this perturbation to self-energy, as additional action of vacuum on the emitter due to presence of the body. The real part of self-energy represents the energy shift in the emission due to the nanostructure.

\[
\Re(\Sigma) = \frac{\Delta E}{\hbar}
\]

(3)

Compared to the isolated emitter, the energy of emission is shifted by \( \Delta E \) and more importantly, \( |\Delta E|/\hbar \) is the rate of exchange of excitation between emitter and nanostructure, or the frequency of Rabi oscillations. This exchange in the form of emission and absorption of virtual photons is accompanied by the creation and annihilation of virtual plasmons in the metal particle. Typically, \( \Gamma^{nr} >> |\Delta E|/\hbar \) resulting in a negligible probability of virtual decay of a plasmon in metals (and this regime is irrelevant for dielectric materials where \( \Gamma^{nr} << \Gamma^r \)), except in the case of the smallest metal nanoparticles where they are comparable in magnitude. Also, in the case of an emitter very close to a large metallic nanostructure the above inequality weakens significantly. Note that this is especially pertinent for the dipole mode of a nanostructure which represents most of its coupling to vacuum modes. The generation of photons by virtual plasmon annihilation should not be distinguished from its scattering of virtual photons originating from vacuum, as far as the dipole mode is concerned. Only the latter effect due to a nanostructure is included in the increase of radiative states in conventional theory. In such cases, the following extension of the local density of optical states becomes necessary. To make this distinction between modes, the dipole mode contributions are numbered ‘1’ in the subsequent part of this section. The probability of virtual photons resulting from the creation and annihilation of dipolar plasmons can be non-negligible and is given by \( 1 - \exp(-|\Delta E_1|/\hbar \Gamma^{nr}_1) \). The effect of additional fluctuations on the rates of emission is trivially evaluated using work done on the dipole emitter (as in the classical optical theorem):

\[
\Gamma_{leak}^{nr} = (1 - e^{-|\Delta E_1|/\hbar \Gamma^{nr}_1}) \cdot \Gamma_1^{nr}
\]

(4)

The effective decay rates thus become:

\[
\Gamma^{eff}_r = \Gamma_0^r + \Gamma^r + \Gamma_{leak}^{nr}
\]

(5)

and

\[
\Gamma^{eff}_r = \Gamma_0^{nr} + \Gamma^{nr} - \Gamma_{leak}^{nr}
\]

(6)

The observed quantum efficiency is then:

\[
Q = \frac{\Gamma_{eff}^r}{\Gamma_{eff}^r + \Gamma_{eff}^{nr}}
\]

(7)
RESULTS AND DISCUSSION

An increase in radiative states can be inferred as the increase in vacuum fluctuations coupled to the emitter due to elastic scattering of virtual photons from the proximal nanostructure. The smaller nanoparticles can absorb light well in the plasmonic range increasing non-radiative states notably, but have a negligible scattering efficiency and do not add to the density of radiative states. But they have been observed to increase rates of spontaneous emission from proximal emitters significantly more than theoretical evaluations, and in cases even notably increase their efficiency of emission in a direct contradiction with theory. Moreover, we point that the same applies in a lesser degree to an emitter separated from large plasmonic nanostructures by distances less than its radius. This effect thus becomes crucial for techniques such as surface-enhanced-Raman-spectroscopy (SERS) using plasmonic nanostructures, which would not be otherwise feasible.

First, we begin with the experiments of fluorescence and photo-luminescence enhancements using metal nanoparticles of limiting small sizes. The excitation is off-resonant, and thus near-field enhancement of excitation due to the nanoparticle plays a negligible role here. The rates of radiative and non-radiative processes were estimated using independent life-time measurements in many cases, in addition to the measurement of gain in photons emitted. The measured gains are relatively robust and repeatable, while the decay rate is more sensitive to any uncertainty in distances. Figure 1 presents the measured gains for varying separations of the emitter from a gold nanoparticle of 5 nm radius. We present evaluations of both relative quantum efficiency $Q$ and relative power of emission $Q_{\text{r}}^\Gamma$, with respect to the emitters not interacting with metal nanostructures. The former represents the increase in probability of radiative decay of the excited emitter, while the latter also includes increase in ground-state population for emitters that can be excited continuously. The large divergence of the predictions of conventional theory from the observations are clear.

Figure 2 and Figure 3 present experiments of quenched emission from two different types of emitters. Here the nanoparticles are marginally larger at 6.5 nm radii and the quenching in the experimental results is significantly less than the expected values of the conventional theory. In contrast these experiments have a reasonable agreement with the predicted range of this extended theory. Note that quenching due to polymer molecules binding the emitter-particle system has not been included in both the theoretical models of relative emissions. When this is included, both theoretical predictions should reduce notably at larger distances due to the larger effect of polymer molecules. Thus one can infer a better agreement of experiments with the proposed theory, than reflected by these Figures 2 and 3.

Many experiments by other researchers on even smaller...
gold nanoparticles using self-assembled films and monolayers with quantum dot emitters, are summarized in Figure 4. Note that for the smaller metal nanoparticles discussed in Figures 1 and 4, the experiments present a direct contradiction; theory predicts quenching while experiments report significant enhancements of emission. Monolayers with smaller separations of emitters and gold nanoparticles of a smaller radii of 1.75 nm, have larger divergence with conventional theory as expected (section on the left in figure 4). But the large enhancement up to a factors of 3 for the dots embedded in films due to sparsely doped and well separated 2.5 nm radii gold nanoparticles are equally unexpected (on the right in figure 4). In this section on the right, four experiments with nearly overlapping gain values are marked along with the predictions of theory. Our modified theory of local density of optical states predicts these experiments reasonably well. One notable aspect of the experiments with limiting small metal nanoparticles of 1.75 nm radii, is the sensitivity to the number-ratio of emitters and metal particles in the monolayer, and this is not discussed here. The significant effect of virtual plasmons in this case may necessitate the inclusion of any collective behavior among emitters, that has been suggested in the presence of plasmonic nanoparticles [30], phonon interactions [31] and otherwise at low temperatures [32]. But the theoretical works involved long-wavelength approximations and more importantly neglected any thermal effects; while other experimental indications of such collective behavior of emitters in the weak vacuum-coupling regime are few so far [33, 34]. Hence, we believe our understanding of this more sensitive additional effect is preliminary.

In the case of SERS, we summarize many observations to compare predictions of the proposed theory. These enhancements were typically approximated by the \((E_{\text{local}}/E_\alpha)^4\) rule for nanostructures of various geometries. Note that difference between excitation and emission energies are not large in SERS measurements, and we ignore this difference in the following interpretation of this rule. The local enhancement of excitation, represented by a incident plane wave typically, is given by \((E_{\text{local}}/E_\alpha)^2\) and indicates the increase in probability of excitation of emitters due to the nanostructure. For the \((E_{\text{local}}/E_\alpha)^4\) rule to be valid in general, we have to infer an additional enhancement of emission by the same factor. Interestingly, the sum of densities of radiative and non-radiative states of the body available for the emission is also represented by \((E_{\text{local}}/E_\alpha)^2\), up to a constant of multiplication. Thus SERS experiments can be inferred to demonstrate a significant loss of distinction between the radiative and total density of states for emitters close to the nanostructure that are predominantly excited; as predicted by the proposed theory of density of optical states. Figure 5 shows the predictions and experimental measurements of a few distance dependent SERS measurements [17, 18], along with a few reported experiments without any spacers between the SERS sur-
face and the emitters. The latter are marked closest to a distance of zero where the probability of excitation is highest. Here, we have plotted the numerical results of the emission near a plane surface at plasmon resonance (permittivity $\epsilon \approx -1 + 0.33i$) with near-field enhancement of the excitation due to nano features ranging in size from 2 to 50 nm marked by error bars. A closer view of the short-range results, and a comparison of the quasi-static and full-wave solutions are relegated to the supplementary. Overall, the proposed theory removes the large divergence observed in the measured enhancements of Raman signals over many decades, and is also supported by the more recent experiments with metal nanoparticles of limiting small dimensions. We believe further sensitive experiments may be required in firmly establishing the full theory defining density of optical states.

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1. E. M. Purcell, Phys. Rev. 69, 681 (1946).
2. K. Drexhage, J. Luminescence 1, 693 (1970).
3. S. Kühn, U. Håkanson, L. Rogobete, and V. Sandoghdar, Phys. Rev. Lett. 97, 017402 (2006).
4. P. Bharadwaj and L. Novotny, Opt. Exp. 15, 14266 (2007).
5. D. Cheng and Q.-H. Xu, Chem. Commun. 0, 248 (2007).
6. D. Kim, H. Yokota, T. Taniguchi, and M. Nakayama, J. Appl. Phys. 114, 154307 (2013).
7. E. Dulkeith, A. Morteani, T. Niedereichholz, T. Klar, J. Feldmann, S. Levi, F. Van Veggel, D. Reinhoudt, M. Möller, and D. Gittins, Phys. Rev. Lett. 89, 203002 (2002).
8. E. Dulkeith, M. Ringler, T. Klar, J. Feldmann, A. Munoz Javier, and W. Parak, Nano Lett. 5, 585 (2005).
9. L. Tripathi, M. Praveena, and J. Basu, Plasmonics 8, 657 (2013).
10. M. Haridas, J. Basu, A. Tiwari, and M. Venkatapathi, J. Appl. Phys. 114, 064305 (2013).
11. M. Haridas, L. Tripathi, and J. Basu, Appl. Phys. Lett. 98, 27 (2011).
12. M. Haridas, J. Basu, D. Gosztola, and G. Wiederecht, Appl. Phys. Lett. 97, 189 (2010).
13. M. Haridas and J. Basu, Nanotechnol. 21, 415202 (2010).
14. J. Raimond, P. Goy, M. Gross, C. Fabre, and S. Haroche, Phys. Rev. Lett. 49, 1924 (1982).
15. G. Kovacs, R. Loutfy, P. Vincett, C. Jennings, and R. Aroca, Langmuir 2, 689 (1986).
16. Q. Ye, J. Fang, and L. Sun, J. Phys. Chem. B 101, 8221 (1997).
17. A. D. McFarland, M. A. Young, J. A. Dieringer, and R. P. Van Duyne, J. Phys. Chem. B 109, 11279 (2005).
18. J. A. Dieringer, A. D. McFarland, N. C. Shah, D. A. Stuart, A. V. Whitney, C. R. Younson, M. A. Young, X. Zhang, and R. P. Van Duyne, Faraday Discussions 132, 9 (2006).
19. D. Wang, W. Zhu, M. D. Best, J. P. Camden, and K. B. Crozier, Sci. Rep. 3, 2867 (2013).
20. A. M. Gabudean, M. Focsan, and S. Astilean, J. Phys. Chem. C 116, 12240 (2012).
21. V. Ivanov, N. Todorov, L. Petrov, T. Ritacco, M. Giocondo, and E. Vlahov, in J. Phys.: Conference Series (IOP Publishing, 2016), vol. 764, p. 012023.
22. B. Kennedy, S. Spaeth, M. Dickey, and K. Carron, J. Phys. Chem. B 103, 3640 (1999).
23. E. Le Ru and P. Etcheogin, Chem. Phys. Lett. 423, 63 (2006).
24. Supplementary material at [URL of Journal] for additional information on used methods and cited experimental results (2018).
25. V. N. Pustovit and T. V. Shahbazyan, Phys. Rev. B 82, 075429 (2010).
26. C. Van Vlack, P. T. Kristensen, and S. Hughes, Phys. Rev. B 85, 075303 (2012).
27. M. Venkatapathi, J. Opt. Soc. Am. B 31, 3153 (2014).
28. V. N. Pustovit and T. V. Shahbazyan, Phys. Rev. Lett. 102, 077401 (2009).
29. E. O. Potma and D. A. Wiersma, J. Chem. Phys. 108, 4894 (1998).
30. M. Gross and S. Haroche, Phys. Rep. 93, 301 (1982).
31. M. Scheibner, T. Schmidt, L. Worschech, A. Forchel, G. Bacher, T. Passow, and D. Hommel, Nat. Phys. 3, 106 (2007).
32. A. Goban, C. L. Hung, J. D. Hood, S. P. Yu, J. A. Muniz, O. Painter, and H. J. Kimble, Phys. Rev. Lett. 115, 063601 (2015).
[35] M. L. Juan, C. Bradac, B. Besga, G. Molina-Terriza, and T. Volz, Nat. Phys. 13, 241 (2017).

[36] M. Praveena, A. Mukherjee, M. Venkatapathi, and J. Basu, Phys. Rev. B 92, 235403 (2015).