On the use of Purcell factors for plasmon antennas

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The Purcell factor is the standard figure of merit for spontaneous emission enhancement in microcavities and has also been proposed to describe emission enhancements for plasmonic resonances. A comparison of quality factor, mode volume, and Purcell factor for single and coupled plasmon spheres to exact calculations of emission rates shows that a Purcell factor derived from quality factor and mode volume does not describe emission changes due to plasmon antennas. © 2010 Optical Society of America
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It is a paradigm of quantum optics that the internal dynamics of a quantum system can be controlled by placing the quantum system in a photonic environment that is resonant with radiative transitions of the source [1]. Indeed, according to Fermi's Golden Rule, the spontaneous emission decay rate is proportional to the density of photon states that the photonic environment offers for spontaneous decay [1]. A resonant microcavity with a high quality factor Q and a mode confined in an ultrasmall volume V enhances the density of photon states by a factor $F = 3/4\pi^2(\lambda/n)^3 Q/V$, known as the *Purcell factor* [1–3]. Creating microcavities with the highest Q/V is a central target in solid-state quantum optics, with success being reported with photonic crystals, micropillars, and SiO_2 microspheres and microtoroids [2,3].

Recent advances in nanofabrication have provided new impetus to the field of plasmonics, which creates highly confined electromagnetic resonances by using the response of free electrons in metals [4]. In particular, there are widespread activities that exploit plasmon antennas for enhanced fluorescence and quantum optics [4–12]. Because of absorption and radiative loss, the quality factor of plasmonic devices is extremely low $(Q < 10^2)$. Nonetheless, truly nanoscale confinement leads to estimates for the Purcell factor of the order of $F = 10^3$, competitive with dielectric cavities [12–14]. Motivated by the tremendous success of the Purcell factor as a quantitative, easily evaluated figure of merit for cavity QED, several workers have also adopted this figure of merit for plasmonics [13–15]. Here, I assess whether the Purcell factor derived by Purcell for high Q cavities provides a quantitative gauge for plasmon-enhanced emission.

The spontaneous emission rate Γ of a dipole emitter (transition frequency ω, transition dipole moment d) is governed by the local density of photonic states (LDOS) $N(\omega, \mathbf{r}, \mathbf{e}_d)$ that enters Fermi's Golden Rule (see pp. 273–275 in [1]) through $\Gamma(\omega, \mathbf{r}, \mathbf{e}_d) = \frac{\pi d^2 \omega}{3\hbar\epsilon_0} N(\mathbf{r}, \omega, \mathbf{e}_d)$. Here, $\mathbf{r}$ is the source position and $\mathbf{e}_d$ is the dipole orientation. In terms of the electric field Green dyadic $\mathbb{G}(\mathbf{r}, \mathbf{r}', \omega)$, the LDOS equals [1,16]

$$N(\omega, \mathbf{r}, \mathbf{e}_d) = \frac{6\omega}{\pi c^2}(\mathbf{e}_d^T \cdot \text{Im}(\mathbb{G}(\mathbf{r}, \mathbf{r}, \omega)) \cdot \mathbf{e}_d). \qquad (1)$$

This formalism rigorously describes the *total decay rate* in any photonic system. If the nanophotonic system is dissipative, the total decay rate Γ is the sum of radiative decay and the quenching rate induced by the lossy environment [1,8,9]. The Purcell factor for dielectric cavities is an approximation to the LDOS that rests on two assumptions. First, in nondissipative systems, normal modes can be defined, and the LDOS in Eq. (1) can be rewritten as a sum over all normal modes:

$$N(\omega_0, \mathbf{r}, \mathbf{e}_d) = 3\sum_{\lambda,\omega}|\mathbf{e}_d^T \cdot \mathbf{E}_\lambda(\mathbf{r}, \omega)|^2\delta(\omega - \omega_0). \qquad (2)$$

The second assumption (see Gérard and Gayral [3]) is that the sum over all modes in Eq. (2) is dominated by just a single term. The δ function is replaced by a Lorentzian spectrum of width $\Delta\omega = \omega/Q$ centered on the cavity resonance, and the spatial profile is set by the eigenfunction $|E|^2$ of the cavity, normalized to contain a single photon. Within this approximation, the LDOS for a dipole (at the spatial and spectral mode maximum, aligned with the mode field) normalized to the LDOS of the host (index n) simplifies to the Purcell factor:

$$F = \frac{3Q}{4\pi^2 V}\left(\frac{\lambda}{n}\right)^3 \text{with} V = \frac{\int \epsilon|E|^2 d\mathbf{r}}{\max(\epsilon|E|^2)}. \qquad (3)$$

Sometimes, the term "Purcell factor" is used to indicate the rigorous LDOS in Eq. (1). To avoid any confusion, in this Letter, "Purcell factor" strictly refers to F in Eq. (3). Maier has previously noted [14] that the textbook definition for mode volume V in Eq. (3) cannot be retained for plasmons, as the integrand becomes negative when $\epsilon < 0$. Instead, he proposed that the energy density $\epsilon|E|^2$ that enters the mode volume should be redefined [14] to account for energy stored in the metal [17,18]. I, hence, use the energy density in [17] $(\text{Re}\epsilon + 2\omega\text{Im}\epsilon/\gamma)|E|^2$, which is positive and real, and is appropriate for a Drude model $\epsilon = 1 - \omega_p^2/\omega(\omega + i\gamma)$ for the dielectric constant ϵ of Ag $(\omega_p = 7.9 \text{ eV}, \gamma = 0.06 \text{ eV})$.

In this work, the commonly employed procedure to obtain F from Q and V (using the energy density described above) is compared with exact calculations of the LDOS for the textbook case of metal spheres. First, I consider calculation of the mode volume. For dielectric cavities, one typically resorts to a numerical solver to obtain $|E|^2$. As long as the excitation has spatial and spectral overlap with the cavity mode, a high F ensures that the calculated

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spatial distribution will be almost exactly the true mode field $|E|^2$. The numerically calculated mode (total field minus excitation) is inserted in the mode volume integral, with integration limits truncated at the computation domain. Also for plasmon antennas, far-field excitation yields near-field patterns with large local field enhancements, representative of the resonance mode profile. In this work, the exact Green function for a sphere [16] is used to find the energy density upon plane wave excitation. Figure 1(a) shows a strongly confined field ($\sim 10^2$ enhancement relative to incident $|E|^2$) just outside the sphere (radius 35 nm).

In Fig. 1(b), a plot is shown of the mode volume integral evaluated over a truncated integration domain of radius R around the plasmon sphere. The mode volume integral shows a linear divergence with the truncation radius R. Thus, Fig. 1(b) exemplifies a second problem with the textbook definition of mode volume, which is not related to the definition of energy density, but that is generic for all leaky cavities [19], including plasmon antennas and dielectric cavities. Several workers in cavity QED [20,21] have already noted that a normalizable true mode, as required for the Purcell factor, does not exist for leaky cavities that are coupled to a universe of radiative modes. Indeed, the linear divergence in Fig. 1(b) is understood by noting that radiative loss signifies constant integrated far-field flux, and, hence, only a $1/R^2$ asymptotic falloff of $|E|^2$. This divergence is always ignored when determining V from numerical calculations for high Q cavities, since high Q factors imply a very small slope of the linear tail that is often not noticed

in a finite computation domain. Leaving the fundamental treatment aside [19], I note that subtracting the linear divergence defines a rigorous mode volume for leaky cavities. For dielectric cavities, this volume is rigorously identical to the mode volume required for Eq. (3) to be equal to Eq. (1) [19]. Figure 1(c) shows the divergence-corrected mode volume for Ag spheres of different sizes. The mode volume is generally comparable to, or even smaller (large spheres) than, the physical volume, because field energy is mainly stored near the metal surface.

To obtain the quality factor Q, Mie extinction cross sections [16] are analyzed. By dividing out the nonresonant ω^4 scaling, Lorentzian line shapes are retrieved from which Q factors are extracted between $Q \sim 40$ (limited by absorption) in very small particles and $Q \sim 3$ for larger particles [Fig. 1(c)]. Combining Q and V in Fig. 1(d) reveals predicted Purcell factors from 10^5 for the smallest spheres to below 10^2 for the 50 nm spheres. The key question is in how far this Purcell factor F correctly predicts the total decay rate enhancement calculated rigorously from Eq. (1), i.e., from Im$\mathbb{G}$ [16]. The Purcell factor is expected to be an upper bound for the total decay rate, with equality exactly at the mode maximum and for dipole orientation along the mode field (perpendicular to the sphere). For comparison, the total decay rate enhancement almost at the particle surface (separations shown: 1 and 0.1 nm, dipole along the mode field) is plotted in Fig. 1(d). The Purcell factor *underestimates* the total decay rate by 1 order of magnitude.

One might argue that single plasmon spheres set a poor example, as they do not provide very high local field enhancements typical for plasmonics. Figure 2 presents an analysis of the Purcell factor for two spheres with a narrow gap. The calculation uses a multipole expansion multiple scattering code provided by García de Abajo [22] to analyze a dimer of two 25 nm radius silver spheres separated by a 10 nm gap, in a $n = 1.5$ host medium. A scattering resonance with $Q = 5.7$ occurs near $\lambda = 506$ nm, with a 1890 times $|E|^2$ enhancement polarized along the dimer axis. Purcell analysis predicts a mode volume $V = 1.32 \cdot 10^{-5}$ μm^3 and a Purcell factor $F \sim 1300$. Purcell theory hence predicts an LDOS $F \times |E|^2$ of $F \sim 1300$ at
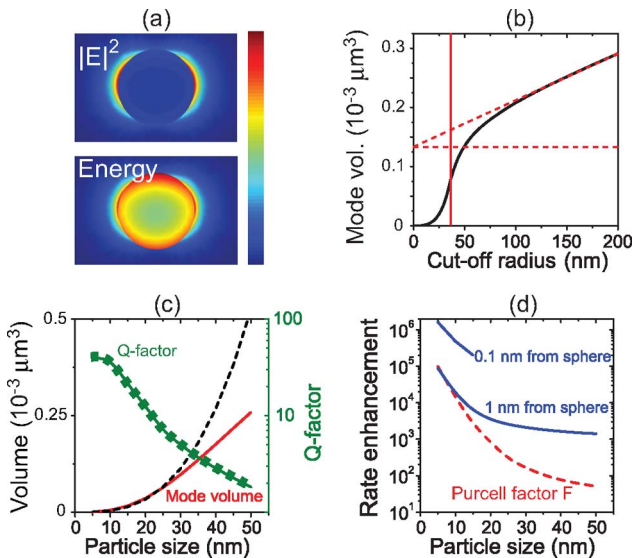

Fig. 1. (Color online) Contour plots of $|E|^2$ and energy density W for a 35 nm radius Ag sphere in vacuum. The color bar ranges from 0 to 107 (respectively, 0 to 118) in units of $|E|^2$ (respectively, W) of the incident plane wave (from below, horizontal polarization). (b) Mode volume $\int W \mathrm{d}\mathbf{r}/\max(W)$ evaluated over a spherical integration domain truncated at R, plotted versus R. Vertical line, particle radius. Dashed line, linear divergence due to radiation loss. Red dashed horizontal line, mode volume. (c) Mode volume (red solid curve) and physical volume (dashed curve) versus sphere (Ag in vacuum) radius. Green curve with symbols, quality factor Q (right-hand axis). (d) Dashed curve, F from Q and V. Solid curves, total decay rate at 1 and 0.1 nm from the sphere.
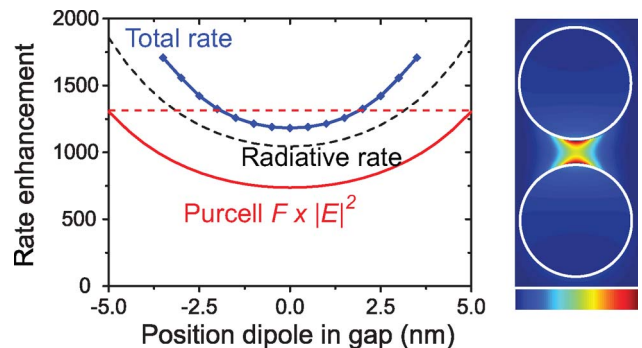

Fig. 2. (Color online) Radiative decay rate (dashed curve) and total decay rate (joined symbols) along the centerline joining two 25 nm silver spheres with a 10 nm gap. Rates are relative to the rate in the $n = 1.5$ host medium. Red solid line, prediction from Purcell theory. The dipole is oriented along the centerline. Right, contour plot of $|E|^2$ (scale from 0 to 1890 in units of incident $|E|^2$) upon illumination by a vertically polarized plane wave).

the sphere surface and about 700 times exactly in between the spheres. The rigorous calculation based on Eq. (1) predicts a rate enhancement of ∼1200 times for a dipole oriented along the mode field, positioned exactly in the middle of the gap. Again, the Purcell factor underestimates the rigorously calculated total decay rate enhancement.

Referring to the two assumptions underlying the Purcell factor, in general, both will break down. First, a set of normal modes can generally not be defined for dispersive absorbing media. Second, if an expansion in modes can be generalized (as in the case of multipole expansion for the Green function of a plasmon sphere), no single term is dominant, even if the resonance is clearly due to one term. For instance, at the dipolar plasmon sphere resonance, the LDOS is dominated by nonresonant coupling of the emission dipole to higher-order multipole moments of the plasmon sphere [8,23]. This nonresonant coupling is not contained in a Purcell factor estimate based on Q and V of the dipolar mode field and corresponds to quenching of emission when very close to the metal. The total decay rate diverges as z^{-3}, where z is the separation between dipole and metal surface [9,23]. Such quenching occurs generally in both planar and curved plasmonic structures [23], and, unfortunately, always exactly coincides with the field maximum where one seeks to apply the Purcell factor. Since the z^{-3} divergence is general [9], the Purcell factor is expected to underestimate Im$\mathbb{G}$ for any plasmon resonator, although the mismatch may differ from structure to structure.

Based on the above, one is led to conclude that the Purcell factor [Eq. (3)] is not adequate for plasmon antennas. One might expect that moving the emitter away from the extreme near-field limit allows one to retrieve the Purcell prediction, taking into account that displacement and detuning of the emitter reduces the enhancement in proportion to the mode field and the Lorentzian cavity line shape [1,3]. Contrary to Purcell theory, however, the emission rate of a dipole near a nanoantenna generally does not have a Lorentzian line shape. As first discussed by Dulkeith et al. [24], emission enhancement by antennas can be understood in an image dipole picture as constructive or destructive interference of radiation emitted by the emitter with that radiated by the antenna. Because the antenna response flips phase exactly on resonance, such interference leads to a non-Lorentzian, dispersive frequency dependence, in which coupling to the antenna actually leads to inhibition of emission on one side of the resonance (see Fig. 10 in [8]). This phenomenon occurs for all antennas that radiate strongly. In this regime, the physics can often be understood in a point dipole model [25] in which the gauge for interaction strength is the polarizability, not a mode volume.

In closing, the Purcell factor as defined by Purcell for microcavities [Eq. (3)] appears unsuited to determine quantitative total decay rate enhancements experienced by emitters near plasmonic resonances, because the two approximations break down that there is a normal mode expansion with a single dominant term. While Purcell factors may be a qualitative design guideline, one always needs a full calculation to confirm the actual total decay rate enhancements.

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