Supporting Information: Plasmon-Exciton Coupling in Symmetry-Broken Nanocavities

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This Supporting Information provides detailed derivations behind the transformation optics treatment of gap cavities presenting material asymmetry. First, the most relevant steps in the computation of the spectral density for these systems are presented. Next, the iterative calculation of the surface plasmon resonant frequencies in dimers comprising two different (metal-metal and metal-dielectric) materials is described.

Spectral Density in Nanocativies with Material Asymmetry

Figure 1(a), which sketches the most general gap cavity considered in this work, introduces the variables ϵ_1 and ϵ_2. These denote the permittivities of the metal/dielectric nanosphere with radius R_1 and R_2, respectively. Taking into account this asymmetry in the material characteristics of the dimer, we obtain the following expressions for the expansion coefficients

in Equation (2) at the intermediate shell region in the transformed frame

$$\begin{aligned} a_l^+ &= \frac{a_l^{\mathrm{E}+} - e^{-\alpha_1} r_1'^{-(2l+1)} a_l^{\mathrm{E}-}}{e^{-(\alpha_1+\alpha_2)}(r_2'/r_1')^{2l+1} - 1}, \\ a_l^- &= \frac{-e^{-\alpha_2} r_2'^{2l+1} a_l^{\mathrm{E}+} + a_l^{\mathrm{E}-}}{e^{-(\alpha_1+\alpha_2)}(r_2'/r_1')^{2l+1} - 1}, \end{aligned} \tag{S1}$$

where $a_l^{\mathrm{E}+}$ and $a_l^{\mathrm{E}-}$ are given in Equation (3), and $r_1' = (1-\Delta_1)/(1+\Delta_1)$, $r_2' = (1+\Delta_2)/(1+\Delta_1)$, with $\Delta_1 = (\delta+R_2-R_0)/(2R_1+R_2-R_0)$ and $\Delta_2 = \delta/(R_2-R_0)+(\delta+R_2-R_0)/(R_2+R_0)$. Note that $e^{-\alpha_{1,2}} = (\epsilon_{1,2}+\epsilon_{\mathrm{D}})/(\epsilon_{1,2}-\epsilon_{\mathrm{D}})$ reflects the material asymmetry of the system. Importantly, the surface plasmon (SP) resonances sustained by the system are given by the poles of the scattering coefficients above, i.e., by the condition

$$e^{-[\alpha_1(\omega)+\alpha_2(\omega)]}(r_2'/r_1')^{2l+1} - 1 = 0. \tag{S2}$$

Using the relation

$$E_z = \frac{\partial\Phi'}{\partial x'}\frac{\partial x'}{\partial z} + \frac{\partial\Phi'}{\partial y'}\frac{\partial y'}{\partial z} + \frac{\partial\Phi'}{\partial z'}\frac{\partial z'}{\partial z}, \tag{S3}$$

we can derive the scattered electric field in the original frame at the quantum emitter (QE) position, $\mathbf{r}_{\mathrm{E}}$, from the quasi-static potential within the transformed geometry, $\Phi'(\mathrm{r}')$. This way, we obtain

$$\begin{aligned} E_z^{\mathrm{sc}}(\mathbf{r}_{\mathrm{E}}) \;=\; & -\frac{\Lambda^2}{(r_{\mathrm{E}}-R_0)^2}\sum_{l\geq 0}\Big\{a_l^+[(\eta-1)^l + \eta l(\eta-1)^{l-1}] + \\ & + a_l^-[(\eta-1)^{-(l+1)} - \eta(l+1)(\eta-1)^{-(l+2)}\Big\}\mathrm{Y}_{l0}(\pi), \end{aligned} \tag{S4}$$

where the definition of η can be found in the main text. Note that the dependence on Λ in Equation (S4) is removed through the source coefficients, $a_l^{\mathrm{E}\pm}$ also provided in the main text. Once the scattered field is known, the Purcell factor and spectral density can be calculated through Equations (4) and (5).

Iterative Calculation of Surface Plasmon Resonant Frequencies

Equation (S4) serves as an example of the natural way in which our TO approach leads to a decomposition of the spectral density as a sum of terms with different index l. As shown in Ref. 1, each of these terms can be split in single metal cavities. A new index, $\sigma = \pm 1$, can then be used to label the two contributions to $J(\omega)$ with the same index l. This splitting is possible thanks to the relatively simple form that Equations (S1) acquire for $\alpha_1 = \alpha_2$. The method also provides a clear physical interpretation for σ, which gives the parity of the SP modes with respect to the gap center. Finally, this procedure makes it possible to write each contribution (characterized by indices l and σ) to $J(\omega)$ in a Lorentzian-like form.

In nanocavities involving two different metals, or a metal and a dielectric, the division of each l-term in $J(\omega)$ does not occur naturally, and cannot be carried out in a fully analytical and exact form. In the following, we describe briefly the iterative, approximate way in which we introduce index σ in this case. Importantly, this index still indicates the SP parity. However, in our derivations, it appears naturally linked to one of the two particles (or more precisely, permittivities) forming the dimer. For this reason, the two possible values we use for this index are no longer $(+1, -1)$ but $(1, 2)$. This way, we borrow the same notation as in Figure 1(a) to label the two nanospheres in the cavity.

Our objective is splitting the coefficients a_l^+ and a_l^- into two resonant terms, each of them depending on only one of the two metal permittivities. In the case of a single metal, the decomposition is done by writing the denominator in Equations (S1) as

$$e^{-2\alpha}(r_2'/r_1')^{2l+1} - 1 = \left(e^{-\alpha}(r_2'/r_1')^{\frac{l+1}{2}} - 1\right)\left(e^{-\alpha}(r_2'/r_1')^{\frac{l+1}{2}} + 1\right). \tag{S5}$$

In order to mimic this decomposition, we deal with the problem of finding convenient approximate forms for Equation (S2) into two different frequency ranges. If we denote ϵ_1 (ϵ_2) as the metal with a higher (lower) plasma frequency, such as Ag (Au) in the main text, we can proceed as follows.

First, we focus at frequencies $\omega_{l,1}$, which are solutions of Equation (S2) located below the PS for $\epsilon_1(\omega)$. In this regime, we can make $\epsilon_2(\omega_{l,1}) \simeq \epsilon_{\infty,2}$ and

$$e^{-\alpha_2(\omega_{l,1})} = \frac{\epsilon_2(\omega_{l,1}) + \epsilon_{\mathrm{D}}}{\epsilon_2(\omega_{l,1}) - \epsilon_{\mathrm{D}}} \approx \frac{\epsilon_{\infty,2} + \epsilon_{\mathrm{D}}}{\epsilon_{\infty,2} - \epsilon_{\mathrm{D}}}. \tag{S6}$$

Thus, we can write

$$e^{-[\alpha_1(\omega_{l,1})+\alpha_2(\omega_{l,1})]}(r_2'/r_1')^{2l+1} - 1 \simeq e^{-\alpha_1(\omega_{l,1})} \left\{ \left(\tfrac{\epsilon_{\infty,2}-\epsilon_{\mathrm{D}}}{\epsilon_{\infty,2}+\epsilon_{\mathrm{D}}} \right) (r_2'/r_1')^{2l+1} - e^{\alpha_1(\omega_{l,1})} \right\}. \tag{S7}$$

Thus, we can set the initial seed for the calculation of the SP resonant frequencies through any of the two factors above. For simplicity, we take the condition $e^{-\alpha_1(\omega_{l,1})} = 0$, which yields the zero-order approximation for $\omega_{l,1}$,

$$\omega_{l,1} \simeq \omega_{l,1}^{(0)} = \frac{\omega_{\mathrm{p},1}}{\sqrt{\epsilon_{\infty,1} + \epsilon_{\mathrm{D}}}}. \tag{S8}$$

This value can be refined iteratively to i-th order by solving the equation

$$e^{-[\alpha_1(\omega_{l,1}^{(i)})+\alpha_2(\omega_{l,1}^{(i-1)})]}(r_2'/r_1')^{2l+1} - 1 = 0. \tag{S9}$$

We focus next on $\omega_{l,2}$, low frequency solutions of Equation (S2). In this regime, we perform the following zero-order approximation for $e^{-\alpha_1(\omega_{l,2})}$

$$e^{-\alpha_1(\omega_{l,2})} = \frac{\epsilon_1(\omega_{l,2}) + \epsilon_{\mathrm{D}}}{\epsilon_1(\omega_{l,2}) - \epsilon_{\mathrm{D}}} \approx 1, \tag{S10}$$

which assumes that $\epsilon_1(\omega_{l,2}) \ll -\epsilon_{\mathrm{D}}$. Introducing this expression into Equation (S2), we obtain

$$e^{-[\alpha_1(\omega_{l,2})+\alpha_2(\omega_{l,2})]}(r_2'/r_1')^{2l+1} - 1 \simeq e^{-\alpha_2(\omega_{l,2})]}(r_2'/r_1')^{2l+1} - 1 = 0 \tag{S11}$$

This leads to zero-order approximation to $\omega_{l,2}$,

$$\omega_{l,2} \simeq \omega_{l,2}^{(0)} = \frac{\omega_{\mathrm{p},2}}{\sqrt{\epsilon_{\infty,2} + \epsilon_{\mathrm{D}} \dfrac{\xi_l^0 + 1}{\xi_l^0 - 1}}}, \tag{S12}$$

where $\xi_l^0 = \left(\frac{1+\Delta_2}{1-\Delta_1}\right)^{\frac{2l+1}{2}}$. Again, this value can be refined by solving iteratively

$$e^{-[\alpha_1(\omega_{l,2}^{(i-1)}) + \alpha_2(\omega_{l,2}^{(i)})]} (r_2'/r_1')^{2l+1} - 1 = 0. \tag{S13}$$

Once the SP resonant frequencies $\omega_{l,1}$ and $\omega_{l,2}$ are converged (typically within ~ 10 iterations), the Lorentzian decomposition of $J(\omega)$ can be also applied to nanocavities with material asymmetry. This acquires the form of Equation (9), where the width of each the different terms is given by the Drude damping of the corresponding permittivity (γ_1, γ_2), and the coupling strengths are calculated as

$$\begin{aligned} g_{l,1}^2 &= \frac{\gamma_1 \pi}{2} J_l(\omega_{l,1}), \\ g_{l,2}^2 &= \frac{\gamma_2 \pi}{2} J_l(\omega_{l,2}), \end{aligned} \tag{S14}$$

where $J_l(\omega)$ is the l-contribution to the spectral density (which emerges naturally in our TO approach) and the high quality resonator limit[2] is implicit.

The derivations above can be easily adapted to treat cavities formed by metallic, $\epsilon_1(\omega)$, and dielectric, ϵ_2, spheres. In this case, Equation (S2) admits only one solution, which makes the index σ redundant. The SP frequencies for such system can be written as

$$\omega_l = \frac{\omega_{\mathrm{p}}}{\sqrt{\epsilon_\infty + \epsilon_{\mathrm{D}} \frac{\xi_l + 1}{\xi_l - 1}}}, \tag{S15}$$

where $\xi_l = \xi_l(\epsilon_2) = e^{-\alpha_2} \left(\frac{1+\Delta_2}{1-\Delta_1}\right)^{\frac{2l+1}{2}}$.

References

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(2) Waks, E.; Sridharan, D. Cavity QED treatment of interactions between a metal nanoparticle and a dipole emitter. *Phys. Rev. A* **2010**, *82*, 043845.