Supporting Information: Spatio-temporal dynamics and control of strong coupling in plasmonic nano-cavities

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1 Transformation optics: Nanowire dimer structure

To analytically calculate the plasmonic modes of the 2D nano-wire dimer system and their radiative decay rate, we employ a transformation optics technique. The cylindrical dimer structure can be transformed to a concentric annulus (see figure S1) via the transformation equation: 

\[ r' = R_T^2 / (r - R_0) \]

where \( R_T \) is a transformation parameter that defines the size of the transformed annulus. An incident plane wave with the field polarized along the \( x \)-axis of the dimer structure is transformed to a dipole excitation at \( R_0 \) of the concentric annulus and with polarizability along the \( x \)-axis.

![Figure S1](image_url)

Figure S1: Schematic of the dimer nano-wire structure in physical (left) and transformed (right) space. The dimer structure in physical space is surrounded by an absorbing medium (in purple colour) that transforms to a dot particle in the transformed space.

Here we treat the radiative decay rate (and thus the life-time) of the modes in the physical plane as an absorbing material in the far-field enclosing the dimer and with permittivity:

\[ \varepsilon_{\text{abs}} = \varepsilon_d + i\Delta \]

where \( \varepsilon_d \) is the dielectric permittivity of the dimer’s hosting material. In the transformed frame, this material becomes a point particle at \( R_0 \), whose polarizability is only
imaginary and given by:

\[ \gamma_s = -\frac{i\pi^2\varepsilon_0 k_0^2 g^4}{2} \]  

(S1)

The effective dipole moment of the absorbing particle:

\[ p_s = \gamma_s E(r = R_0) = \hat{r} \left( \frac{i\pi^2\varepsilon_0 k_0^2 g^4}{2R_0} \right) \sum_n n (a_{n}^{s+} - a_{n}^{s-}) \]  

(S2)

The scattering potential for the absorbing particle can be written as:

\[ \phi_s^s = -\frac{p_s}{2\pi\varepsilon_0} \left( \frac{\rho \cos \varphi - R_0}{\rho^2 + R_0^2 - 2\rho R_0 \cos \varphi} \right) \]

\[ = \begin{cases} 
\frac{p_s}{2\pi\varepsilon_0 R_0} \sum_n \left( \frac{\rho}{R_0} \right)^n \cos (n\varphi) & \rho < R_0 \\
-\frac{p_s}{2\pi\varepsilon_0 R_0} \sum_n \left( \frac{\rho}{R_0} \right)^{-n} \cos (n\varphi) & \rho > R_0 
\end{cases} \]  

(S3)

(S4)

The scalar electromagnetic potential for the concentric annulus structure is therefore given by:

\[ \phi = \sum_n \left( \frac{\rho}{R_0} \right)^n a_n e^{in\varphi} \quad \rho < R_1 \]

\[ = \sum_n a_n^+ \left( \frac{\rho}{R_0} \right)^n e^{in\varphi} + a_n^- \left( \frac{\rho}{R_0} \right)^{-n} e^{in\varphi} + a_n^{s+} \left( \frac{\rho}{R_0} \right)^n (e^{in\varphi} + e^{-in\varphi}) \quad R_1 < \rho < R_0 \]

\[ = \sum_n a_n^+ \left( \frac{\rho}{R_0} \right)^n e^{in\varphi} + a_n^- \left( \frac{\rho}{R_0} \right)^{-n} e^{in\varphi} + a_n^{s+} \left( \frac{\rho}{R_0} \right)^{-n} \left( e^{-in\varphi} + e^{in\varphi} \right) \quad R_0 < \rho < R_2 \]

\[ = \sum_n a_n^{\text{out}} \left( \frac{\rho}{R_0} \right)^{-n} e^{in\varphi} \quad \rho > R_2 \]  

(S5)

where \( R_1, R_2 \) are shown on figure ??, and \( a_n^{s+} \) and \( a_n^{s-} \) are the expansion coefficients associated with the absorbing particle at \( R_0 \) and one can define them as:

\[ a_n^{s+} = -a_n^{s-} = \frac{p_s}{2\pi\varepsilon_0 R_0} = \frac{i\pi k_0^2 g^4}{4R_0^3} \]  

(S6)
Using these values for $\alpha_n^{s+}$ and $\alpha_n^{s-}$, we match the scalar potential and $\varepsilon(\mathbf{r})\mathbf{r} \cdot \nabla \phi$ across the two interfaces at the electro-static limit, which leads to two sets of equations for the real parts (i.e. even solutions):

\[
\left( \frac{R_1}{R_0} \right)^n a_n^{in} = (a_n^+ + 2a_n^{s+}) \left( \frac{R_1}{R_0} \right)^n + a_n^-(\frac{R_1}{R_0})^{-n} \quad (S7)
\]

\[
\varepsilon_m \left( \frac{R_1}{R_0} \right)^n a_n^{in} = \varepsilon_d (a_n^+ + 2a_n^{s+}) \left( \frac{R_1}{R_0} \right)^n - \varepsilon_d a_n^- \left( \frac{R_1}{R_0} \right)^{-n} \quad (S8)
\]

\[
a_n^{out} \left( \frac{R_2}{R_0} \right)^{-n} = a_n^+ \left( \frac{R_2}{R_0} \right)^n + (a_n^+ + 2a_n^{s-}) \left( \frac{R_2}{R_0} \right)^{-n} \quad (S9)
\]

\[
-\varepsilon_m a_n^{out} \left( \frac{R_2}{R_0} \right)^{-n} = \varepsilon_d a_n^+ \left( \frac{R_2}{R_0} \right)^n - \varepsilon_d (a_n^+ + 2a_n^{s-}) \left( \frac{R_2}{R_0} \right)^{-n} \quad (S10)
\]

and imaginary parts (i.e. odd solutions):

\[
\left( \frac{R_1}{R_0} \right)^n a_n^{in} = a_n^+ \left( \frac{R_1}{R_0} \right)^n + a_n^- \left( \frac{R_1}{R_0} \right)^{-n} \quad (S11)
\]

\[
\varepsilon_m \left( \frac{R_1}{R_0} \right)^n a_n^{in} = \varepsilon_d a_n^+ \left( \frac{R_1}{R_0} \right)^n - \varepsilon_d a_n^- \left( \frac{R_1}{R_0} \right)^{-n} \quad (S12)
\]

\[
a_n^{out} \left( \frac{R_2}{R_0} \right)^{-n} = a_n^+ \left( \frac{R_2}{R_0} \right)^n + a_n^- \left( \frac{R_2}{R_0} \right)^{-n} \quad (S13)
\]

\[
-\varepsilon_m a_n^{out} \left( \frac{R_2}{R_0} \right)^{-n} = \varepsilon_d a_n^+ \left( \frac{R_2}{R_0} \right)^n - \varepsilon_d a_n^- \left( \frac{R_2}{R_0} \right)^{-n} \quad (S14)
\]

Solving the two sets of equations above, we obtain two resonance conditions:

\[
\left( \frac{R_2}{R_1} \right)^n = \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + \varepsilon_d} \left[ 1 + i \frac{n \pi k_0^2 g^4}{2 R_0^2} \right] \quad (S15)
\]

\[
\left( \frac{R_2}{R_1} \right)^n = \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + \varepsilon_d} \quad (S16)
\]

and assuming that the metal permittivity follows the Drude model: $\varepsilon_m = 1 - \omega_p^2 / (\omega^2 + i \gamma_m \omega)$
and $\varepsilon_d = 1$, we deduce the dispersion relations of the even and odd modes:

$$\omega_{\text{even}}^{n} \approx \sqrt{\left(\frac{R_{1}^{n} - R_{2}^{n}}{2R_{2}^{n}}\right)}\omega_{p} - i\left(\frac{\gamma_{m}}{2} + \frac{n\pi g^{4}\omega_{p}^{3}}{8R_{0}^{6}c^{2}}\left(\frac{R_{1}}{R_{2}}\right)^{n} \sqrt{\left(\frac{R_{2}^{n} - R_{1}^{n}}{2R_{2}^{n}}\right)}\right)$$ \hfill (S17)

$$\omega_{\text{odd}}^{n} \approx \sqrt{\left(\frac{R_{1}^{n} - R_{2}^{n}}{2R_{2}^{n}}\right)}\omega_{p} - i\frac{\gamma_{m}}{2}$$ \hfill (S18)

2 Eigenstates on a 2D-dimer structure over the $y$– mirror axis

A dimer structure has two mirror planes, one along the $y$-axis (green line in figure ??) and one along the x-axis. $E_{y}$-polarized sources (either plane wave or a dipole source) enforce the $y$-axis symmetry. Hence, the set of modes that can be coupled to are shown in figure ??, We show the first-order ($n = 1$ - left figure) and second-order ($n = 2$ - right figure) modes. The even-bonding modes are always bright and radiate effectively to the far-field, and correspond to the dipole and quadrupole modes of a plasmonic dimer structure. The odd-bonding modes are also excited with external radiation and radiate to the far-field, but not as efficiently. The even and odd anti-bonding modes are excited only from a dipole-source placed within the nano-cavity, and not from external illumination. Hence, they are beyond the scope of this paper.
Figure S2: First (left) and second (right) order eigenstates of a dimer structure that can be excited with $E_y$ polarized plane wave or dipole source.

To compare the dynamics of the first-order dipole mode ($n = 1$, even bonding) with higher-order modes such as the quadrupole ($n = 2$, even bonding), we plot the evolution of the normalized $E_y$ for the two eigenstates in figure ???. In figure ??(a), we show the good agreement between the numerical calculations and the analytical predictions of equation (??). Figure ??(b) shows the different decay rate between the $n = 1$ and $n = 2$ modes. As prediction by the transformation optics description, the quadrupole ($n = 2$, even bonding) mode decays faster than the dipole ($n = 1$, even bonding) mode.
Figure S3: The decay rate of the dipole ($n = 1$) and quadrupole ($n = 2$) even eigenstates, calculated numerically and analytically using the transformation optics description (equations (??) and (??)). (a) Comparison between the analytical description and numerical calculations for the dipole (top) and quadrupole (bottom) eigenstates. (b) The quadrupole mode decays faster than the dipole mode for both the analytical (top) and numerical (bottom) calculations.

3 Maxwell-Bloch description for 2-level Quantum Emitters

To study the dynamics between the 2-level QEs and the metallic nanostructure, we employ the semi-classical 2-level Maxwell-Bloch description, which treats the emitters quantum mechanically and the E-field classically. The Hamiltonian describing the QEs and their
interaction with the E-field is given by:

$$\hat{H} = \hat{H}_0 + \hat{V}(t) = \hbar \Omega_{12} \hat{\sigma}^\dagger \hat{\sigma} - \hat{\mu} \cdot \mathbf{E}$$  \hspace{1cm} (S19)$$

where $\hat{\sigma} = |1\rangle \langle 2|$ is the exciton annihilation operator, $\Omega_{12} = (E_2 - E_1)/\hbar$ the transition resonance frequency between the two energy levels $E_2$ and $E_1$ and is a complex: $\Omega_{12} = \omega_{12} - i \delta_{12}$, where $\delta_{12}$ describes the linewidth of the transition under weak applied fields, $\hat{\mu} = \langle 1 | \mathbf{r} | 2 \rangle$ the dipole matrix element of the electronic transition and $\mathbf{E}$ the local E-field calculated using Maxwell equations. Using the density matrix approach, we write the Lindblad equation for an open quantum system:

$$\partial_t \hat{\rho} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] + \frac{\gamma_r}{2} (2 \hat{\sigma} \hat{\rho} \hat{\sigma}^\dagger - \hat{\sigma}^\dagger \hat{\sigma} \hat{\rho} - \hat{\rho} \hat{\sigma}^\dagger \hat{\sigma} + \hat{\sigma} \hat{\rho} \hat{\sigma}^\dagger) + \frac{\gamma_p}{2} (2 \hat{\sigma}^\dagger \hat{\rho} \hat{\sigma} - \hat{\sigma} \hat{\rho} \hat{\sigma}^\dagger) + \frac{\gamma_d}{2} (\hat{\sigma} \hat{\rho} \hat{\sigma}^\dagger - \hat{\rho} \hat{\sigma} \hat{\sigma}^\dagger)$$  \hspace{1cm} (S20)$$

where $\hat{\rho}$ is the density matrix and $\gamma_r$, $\gamma_p$ and $\gamma_d$ denote the incoherent relaxation, pumping and pure dephasing rates respectively. Solving for the above Hamiltonian, we obtain:

$$\partial_t \rho_{12} = -(\Gamma - i \omega_{12}) \rho_{12} - \frac{i \mu \cdot \mathbf{E}}{\hbar} (\rho_{22} - \rho_{11})$$
$$\partial_t \rho_{22} = -\partial_t \rho_{11} = -\gamma \rho_{22} - \frac{2 \mu \cdot \mathbf{E}}{\hbar} Im(\rho_{12})$$  \hspace{1cm} (S21)$$

where $\Gamma = \gamma_d + \frac{\gamma_r}{2} + \frac{\gamma_p}{2}$ and $\gamma = \gamma_p + \gamma_r$. Since the macroscopic polarization $\mathbf{P}_{12} = N_d Tr (\rho_{12} \mu) = 2N_d \mu Re(\rho_{12})$, where $N_d$ is the total density carrier, we obtain:

$$\frac{\partial N_2}{\partial t} = -\frac{\partial N_1}{\partial t} = -\gamma N_2 + \frac{1}{\hbar \omega_{12}} \left( \frac{\partial \mathbf{P}}{\partial t} + \Gamma \mathbf{P} \right) \cdot \mathbf{E}$$  \hspace{1cm} (S22)$$

and

$$\frac{\partial^2 \mathbf{P}}{\partial t^2} + 2 \Gamma \frac{\partial \mathbf{P}}{\partial t} + (\Gamma^2 + \omega_{12}^2) \mathbf{P} = -\frac{2 \omega_{12} |\mu|^2}{\hbar} (N_2 - N_1) \mathbf{E}$$  \hspace{1cm} (S23)$$
Figure S4: The oscillations of the

4 Rabi oscillations

In the main manuscript we discuss extensively the results showing the Rabi oscillations of the system with both $E$-field spatio-temporal maps (figure 1(g) and figure 3(d,e)) and the direct polarization induced by the 2-level system $P_{12}$ (figure 4). In figure ??, we plot both quantities at $x = 3.2\text{nm}$ for the symmetric ($\Delta \phi = 0$) and anti-symmetric ($\Delta \phi = 180$) double excitation and the single excitation. $P_{12}$ describes the polarization of the photons induced by the 2-level system. On the other hand $\Delta E = E_{y}^{SC} - E_{y}^{passive}$ is the general field induced due to the presence of QEs (where $E_{y}^{SC}$ os tje E-field for the strongly coupled system and $E_{y}^{passive}$ is the E-field when no QEs are present) and includes the contribution from $P_{12}$ but also evolving plasmon excitation due to injected $P_{12}$ at earlier times.

5 Nanowire and nanoparticle on mirror structures

In this section, we show for various geometries of nano-cavities with both mirror and rotational symmetries over the $y$-axis, the absorption cross-sections for double-sided and one-sided excitation, and the relevant single-sided spatio-temporal maps. As stated in the main
manuscript, the first even and odd bonding eigenstates are in general spectrally degenerate for mirror symmetric structures, and spectrally separated for rotationally-symmetric structures. The difference between the absorption spectra of the single-sided and the symmetric double-sided excitation demonstrates the impact that the odd-bonding mode has on the far-field spectra recorded, but not on the coupling strength and Rabi-oscillation dynamics of the odd-bonding mode. The nanowire-on-mirror structure shows the largest mode beating between the even and odd bonding modes (larger than the 2D dimer structure). This is due to the two eigenstates being spectrally close, and the odd bonding mode not being as dark as for the 2D-dimer structure.

Figure S5: (a) The 3D spherical dimer structure, (d) the nano-wire on mirror and (g) nanoparticle on mirror structure. (b),(e) and (h) show the absorption spectra for single-sided (green), symmetric (red) and anti-symmetric (blue) double-sided excitation for each structure and (c),(f) and (i) the spatio-temporal maps of the passive system.