Molecular Polaritonics 2019

Plasmon-Exciton Polaritons at the Single-Molecule Level

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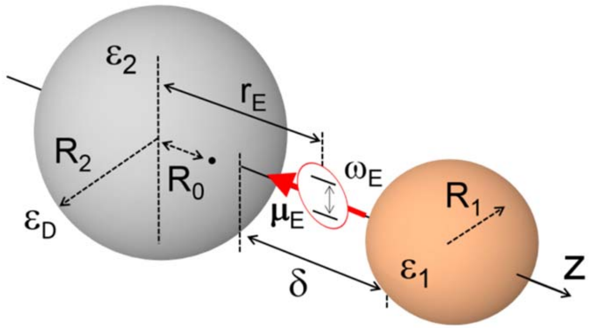
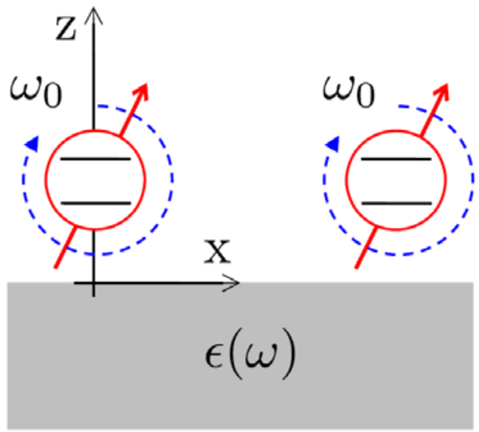
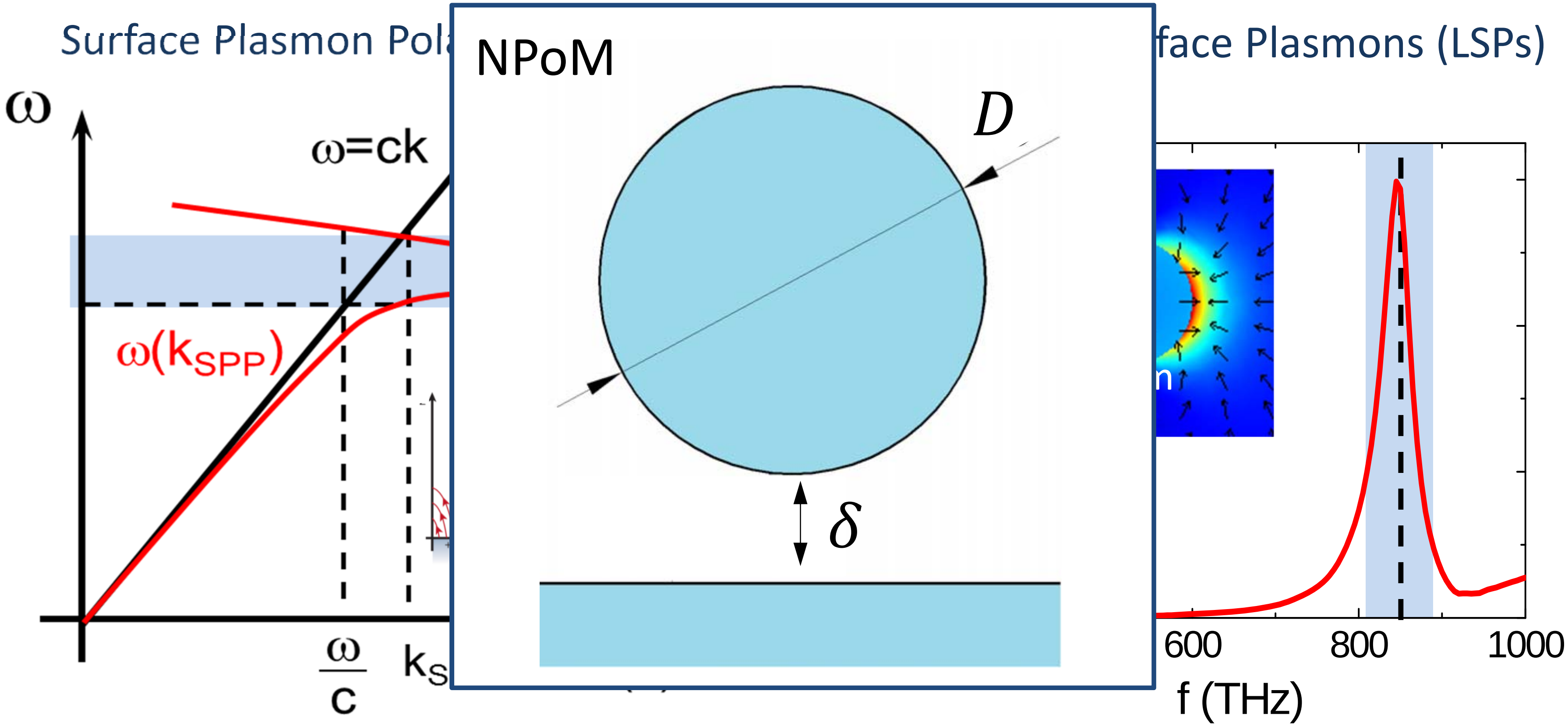
Universidad Autónoma de Madrid, Spain





Surface Plasmons

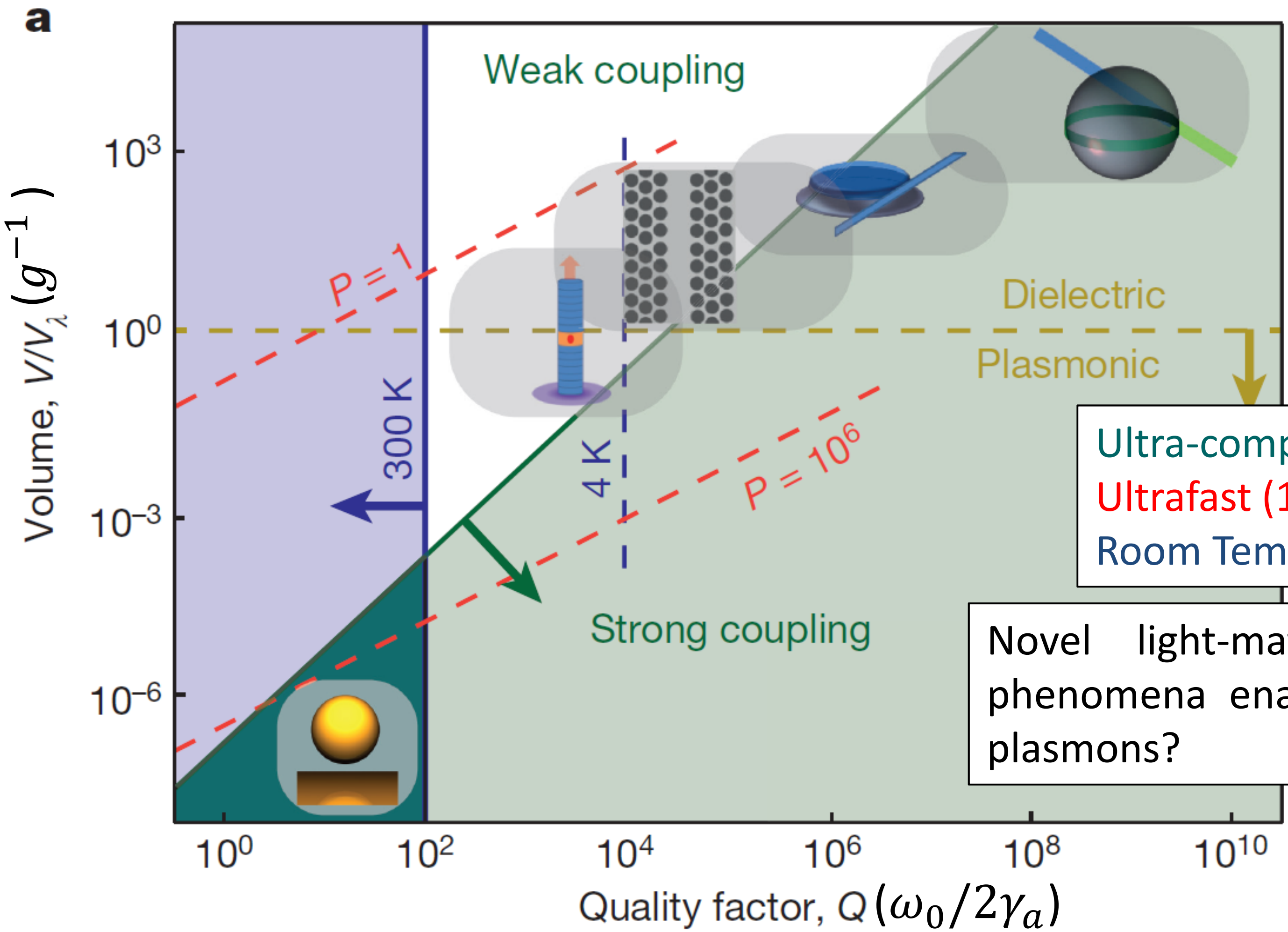
Collective conduction electron oscillations at metal-dielectric interfaces, can couple to electromagnetic fields. Two families:



Limitation: Narrow-band operation → Plasmon hybridization through nm gaps

Baumberg et al. Nature Materials 18, 668 (2019)

Plasmonic nanocavities:



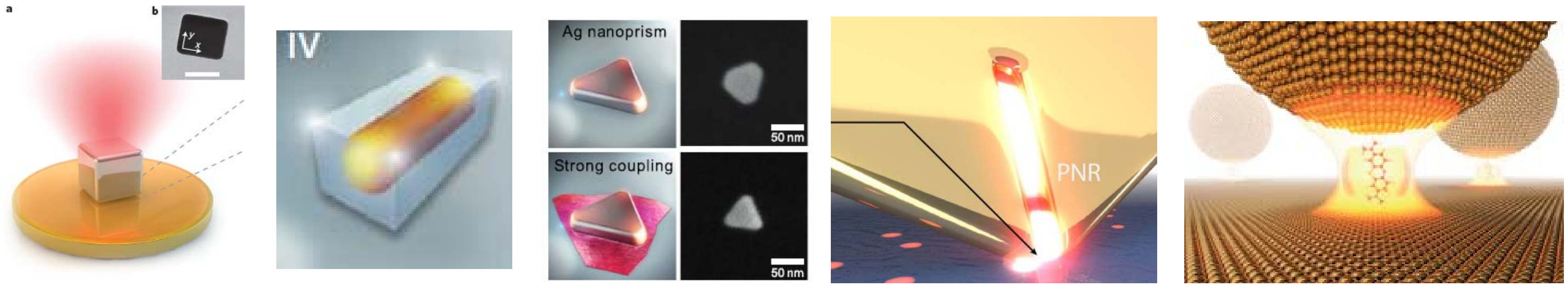
Ultra-compact (V~sub-nm),
Ultrafast ($1/\gamma_a$~ fs),
Room Temperature (g~eV)

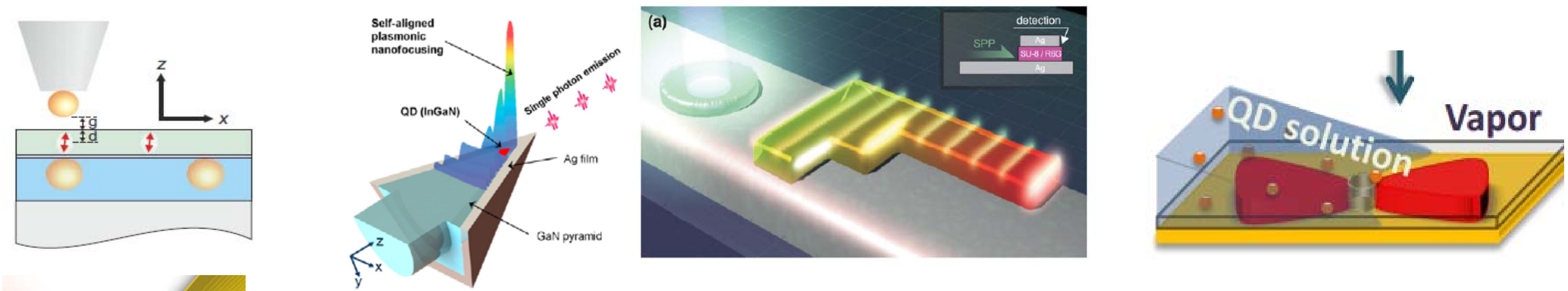
Novel light-matter interaction phenomena enabled by surface plasmons?

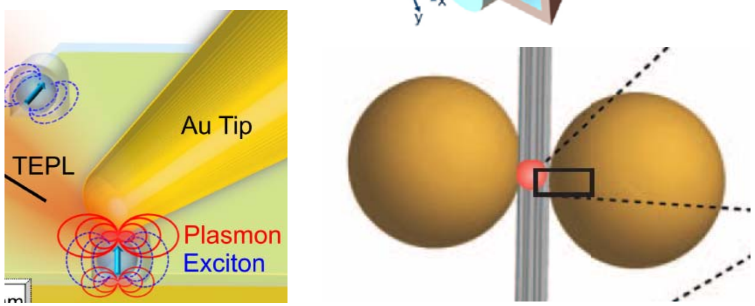
Chikkarady et al. Nature 7, 535 (2016)

Towards plasmonic nanocavities and single emitters:

QEs: quantum dots, diamond vacancies, dye molecules, J-aggregates, TMDs…







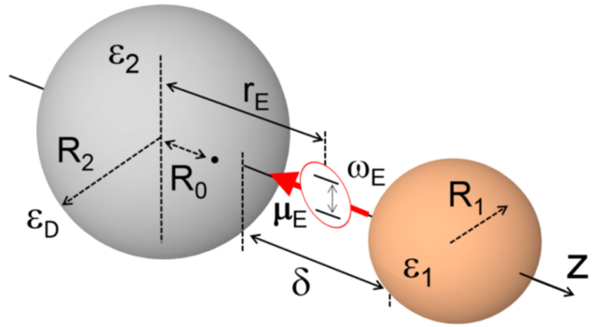
Maximizing coupling in small emitter ensembles: $\Omega_R = \sqrt{N}(\vec{\mu} \cdot \vec{E}_C)$

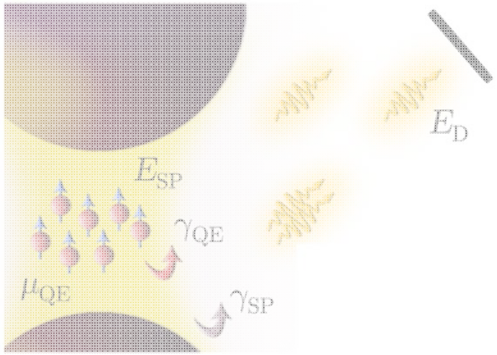
Shegai, Pelton, Sandhogar, Bozhevolnyi, Lukin, Sanvitto, Liedl, Raschke, Mikkelsen, Hecht, Baumberg…

Complementary problems around $\Omega_R = \sqrt{N}(\vec{\mu} \cdot \vec{E}_C)$

Single QE strong coupling in plasmonic gap cavities

- exploring $\vec{E}_C$



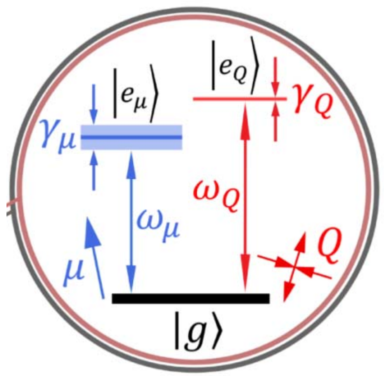


Photon correlations in QE ensembles coupled to a single SP

- exploring N

Chirality and light-forbidden transitions in QE-SP coupling

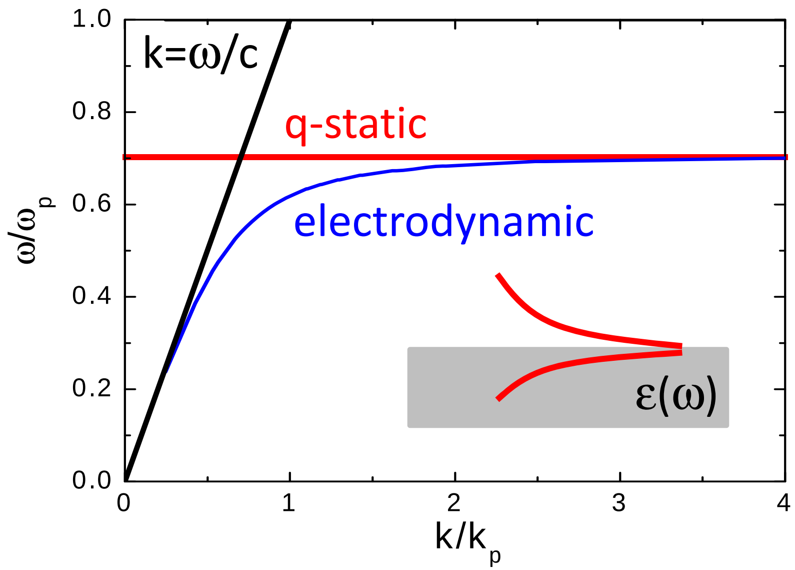
- exploring $\vec{\mu}$

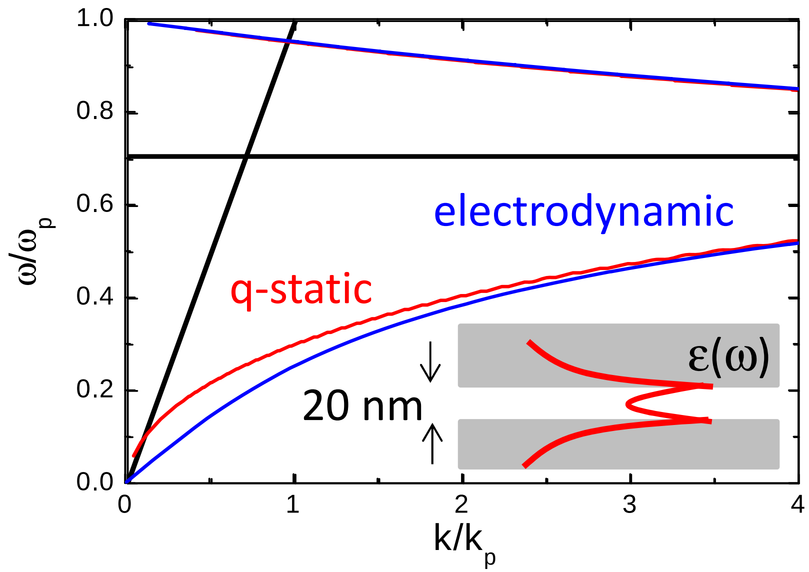


What kind of EM solutions are we interested in?

Strong light-matter interactions require sub-wavelength confinement of electromagnetic fields: **quasi-static regime**.

$$\boldsymbol{E}(t) = \boldsymbol{E}(\omega)e^{-i\omega t} \text{ with } \boldsymbol{E}(\omega) = -\nabla\varphi(\omega) \text{ and } \nabla[\epsilon(\omega)\nabla\varphi(\omega)] = 0$$

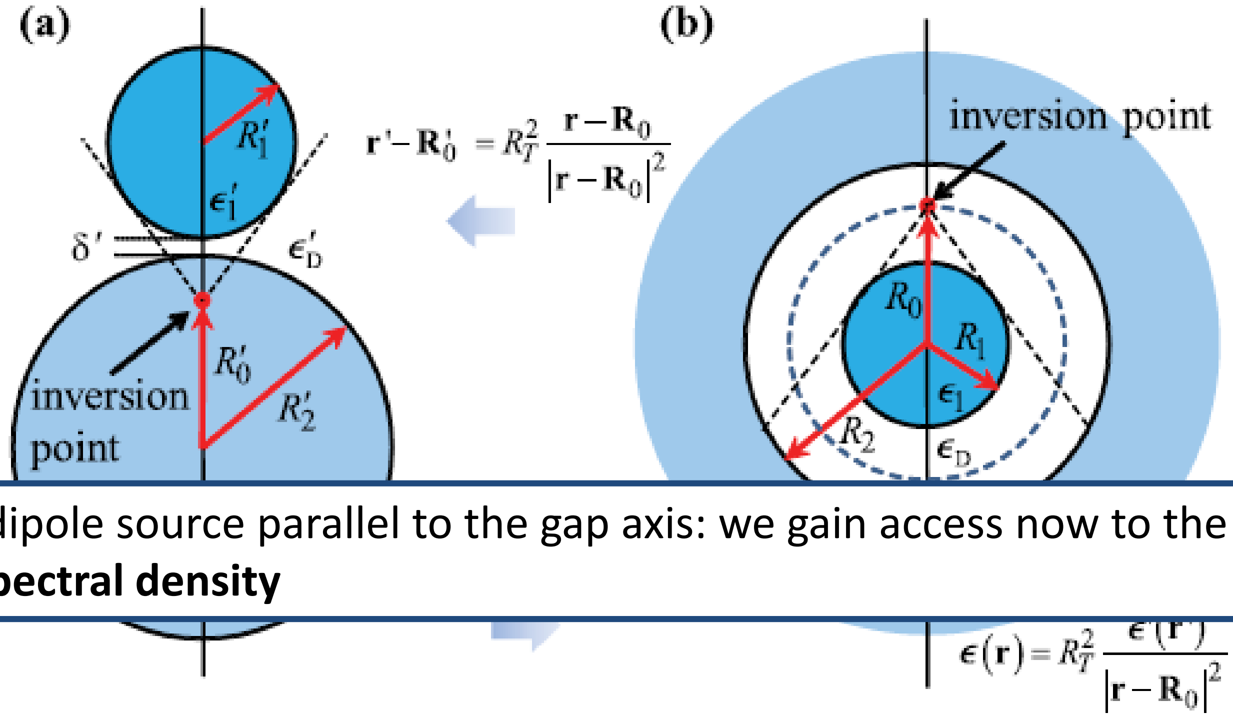




Radiative losses:

Correction due to the self-field: $\boldsymbol{\mu} = \alpha_0(\omega)[\boldsymbol{E}_{\text{inc}} + \boldsymbol{E}_{\text{self}}] = \alpha_{\text{corr}}(\omega)\boldsymbol{E}_{\text{inc}}$

Transformation Optics description of plasmonic dimers



$a_{lm}{}^{s}$ for a dipole source parallel to the gap axis: we gain access now to the Green's function: **Spectral density**

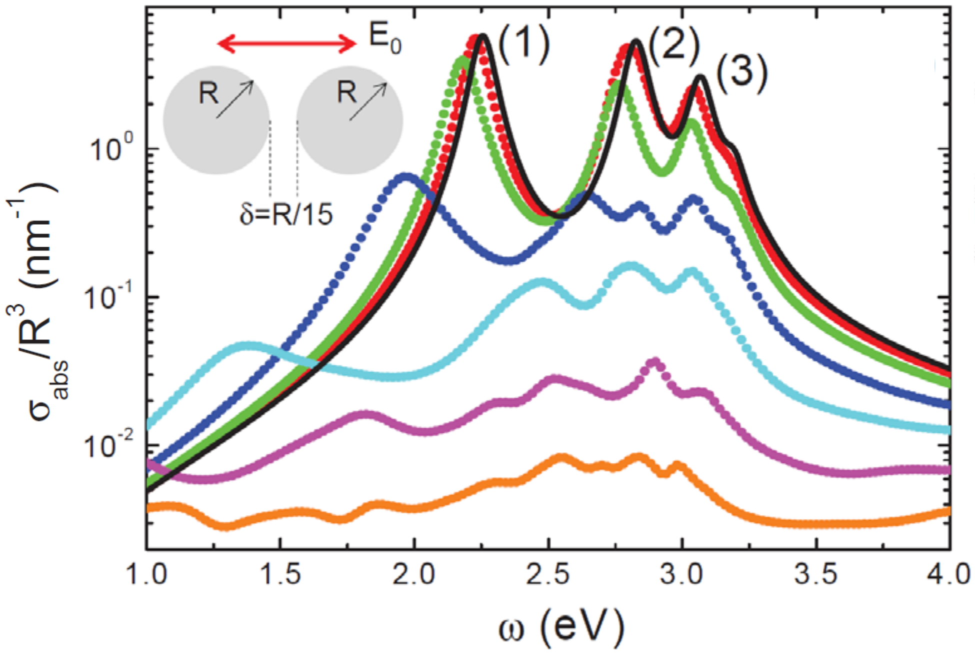
$$\varphi = a_{\ell m}^{in} |\boldsymbol{r}-\boldsymbol{R}_0| r^{\ell} Y_{\ell m}(\theta,\phi), \quad r < R_1$$
$$\varphi = |\boldsymbol{r}-\boldsymbol{R}_0| [(a_{\ell m}^{+} + a_{\ell m}^{s+}) r^{\ell} + a_{\ell m}^{-} r^{-(\ell+1)}] \times Y_{\ell m}(\theta,\phi), \quad R_0 > r > R_1$$
$$\varphi = |\boldsymbol{r}-\boldsymbol{R}_0| [a_{\ell m}^{+} r^{\ell} + (a_{\ell m}^{-} + a_{\ell m}^{s-}) r^{-(\ell+1)}] Y_{\ell m}(\theta,\phi), \quad R_2 > r > R_0$$
$$\varphi = |\boldsymbol{r}-\boldsymbol{R}_0| a_{\ell m}^{out} r^{-(\ell+1)} Y_{\ell m}(\theta,\phi), \quad r > R_2$$

Source terms

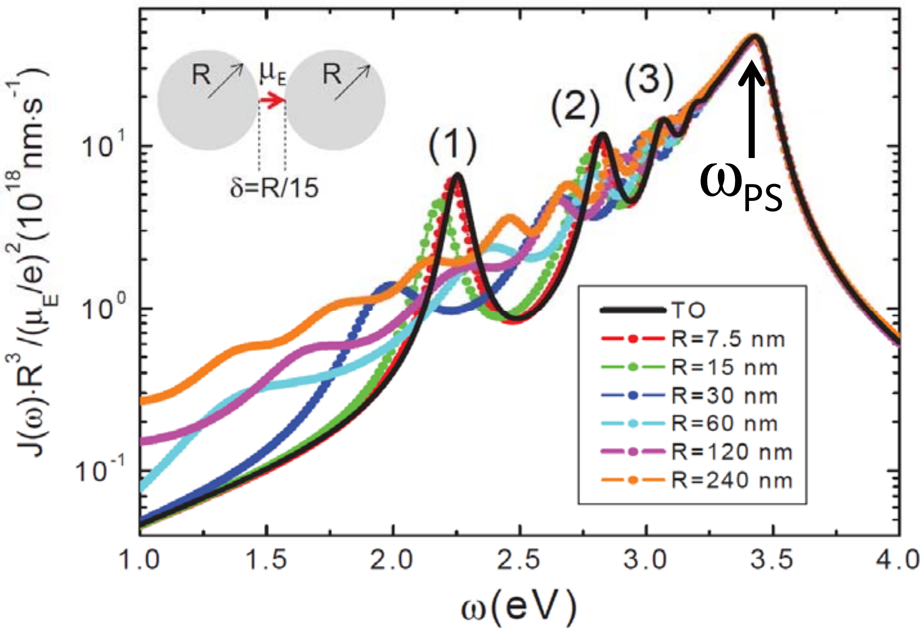
J. Pendry et al., Nat. Phys. 9, 518 (2013), R. Zhao et al., Phys. Rev. Lett. 111, 033602 (2013)

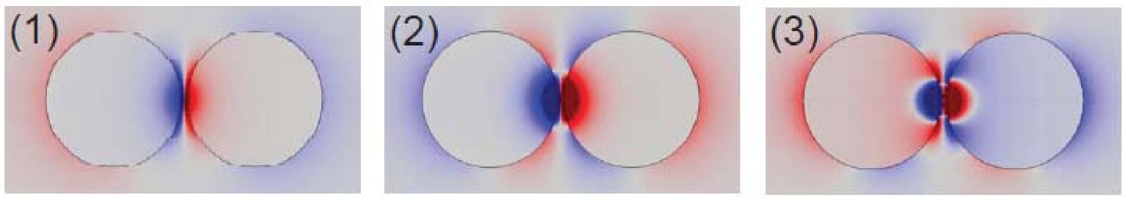
Plasmonic dimers as nanocavities and nanoantennas ($R_{1,2}$=R, δ=R/15)

$\sigma(\omega) \propto \mathrm{Im}\{\alpha_{\mathrm{dim}}(\omega)\} \propto R^3$



$J(\omega) \propto \mathrm{Im}\{G_{zz}(\boldsymbol{r}_E, \boldsymbol{r}_E, \omega)\} \propto 1/R^3$





Different role of SP modes.
Different scaling with R.

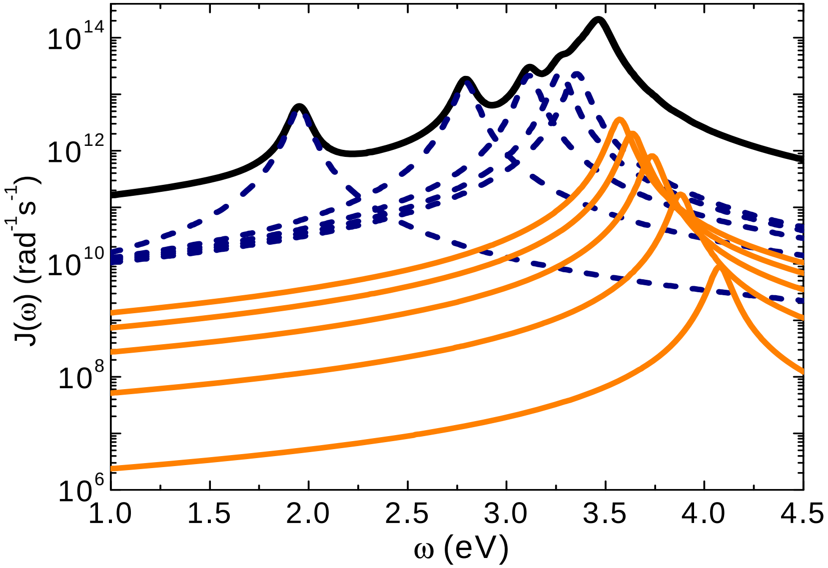
R.-Q. Li et al., Phys. Rev. Lett. 117, 107401 (2016); ACS Photonics 5, 177 (2018).

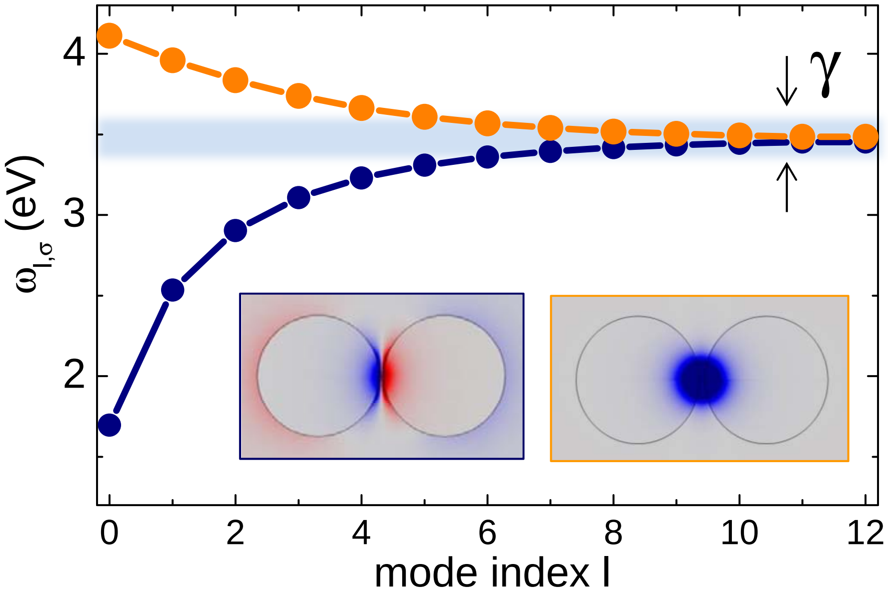
Transformation Optics description of plasmonic cavities

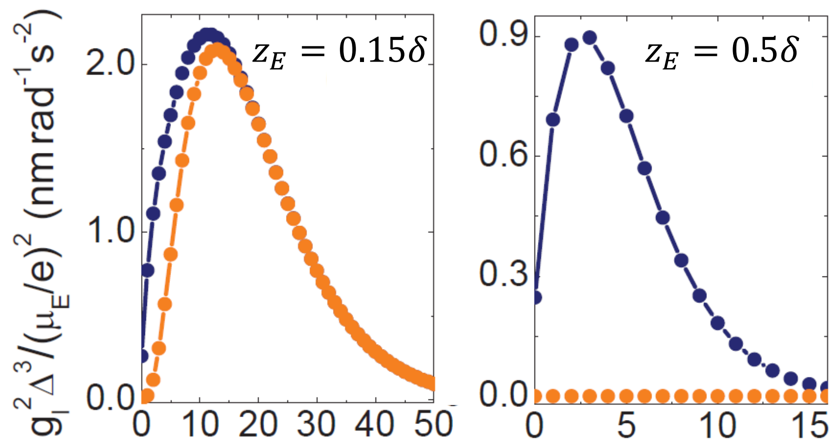
Analytical expressions for $J(\omega)$:

$$J(\omega) = \frac{\mu_{\rm E}^2 \omega^2}{\pi \epsilon_0 \hbar c^2} {\rm Im}\{G_{zz}(z_{\rm E}, z_{\rm E}, \omega)\}$$

$$J(\omega) = \sum_{l=0}^{\infty} \sum_{\sigma=\pm1} \frac{g_{l,\sigma}^2}{\pi} \frac{\gamma/2}{(\omega - \omega_{l,\sigma})^2 + (\gamma/2)^2}$$







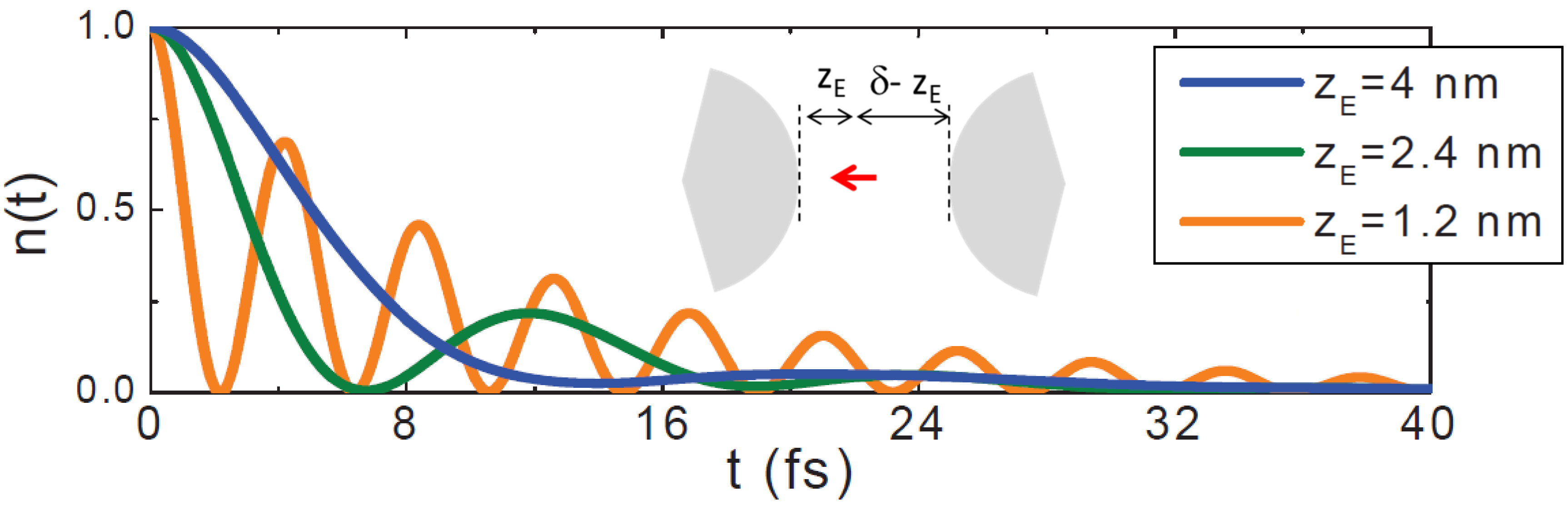
Transformation Optics description of plasmonic cavities

Master equation parametrization ($\omega_{l,\sigma}$, γ, $g_{l,\sigma}$).

$$\hat{H}_{\rm sys} = \omega_i \hat{\sigma}_i^\dagger \hat{\sigma}_i + \sum_{n,\sigma} \omega_{n,\sigma} \hat{a}_{n,\sigma}^\dagger \hat{a}_{n,\sigma} + \sum_{n,\sigma} g_{n,\sigma} [\hat{\sigma}_i^\dagger \hat{a}_{n,\sigma} + \hat{\sigma}_i \hat{a}_{n,\sigma}^\dagger],$$

$$\frac{\partial \hat{\rho}}{\partial t} = i[\hat{\rho}, \hat{H}_{\rm sys}] + \sum_{n,\sigma} \frac{\gamma_m}{2} \mathcal{L}_{\hat{a}_{n,\sigma}}[\hat{\rho}],$$

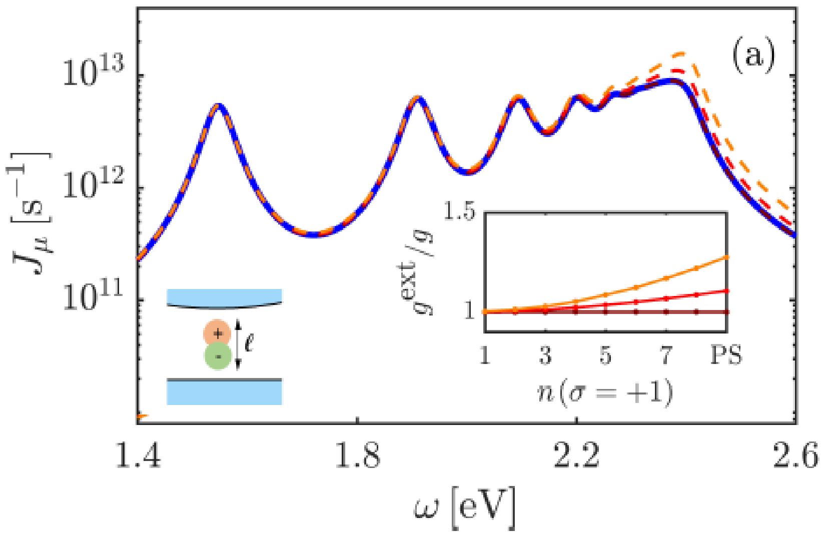
Conditions for plasmon-exciton strong coupling:



R.-Q. Li et al., Phys. Rev. Lett. 117, 107401 (2016); ACS Photonics 5, 177 (2018).

A step backwards to move forward: 2D model

Finite-size effects in the emitter:

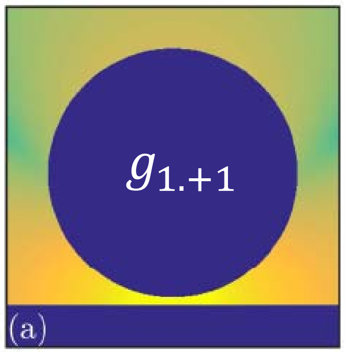


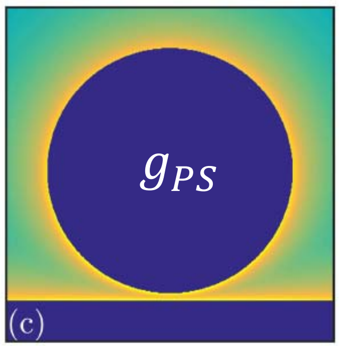
Multipolar sources:

$$P_\mu(\omega) = \frac{8}{\mu^2}\mathrm{Im}\{\boldsymbol{\mu}\mathbf{G}(\mathbf{r},\,\mathbf{r}_{QE})\boldsymbol{\mu}\}_{\mathbf{r}=\mathbf{r}_{QE}},$$

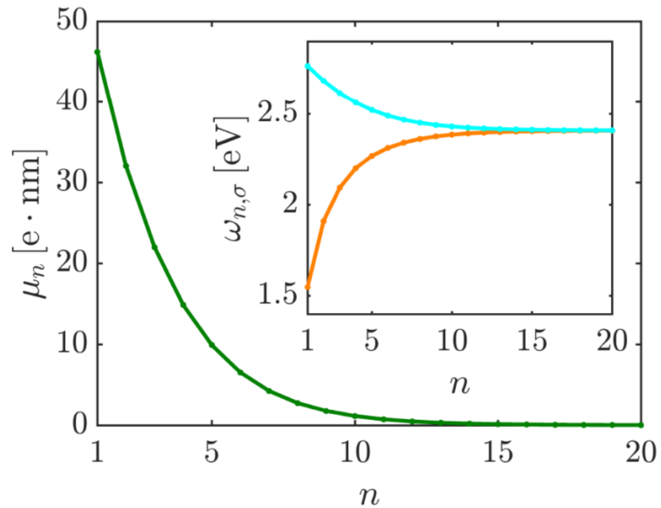
$$P_Q(\omega) = \frac{16c^2}{\omega^2 Q^2}\mathrm{Im}\{(\mathbf{Q}\nabla)(\nabla'\mathbf{G}(\mathbf{r},\,\mathbf{r}'))\mathbf{Q}\}_{\mathbf{r},\mathbf{r}'=\mathbf{r}_{QE}}.$$

Full spatial and orientation dependence:





Radiative reaction: dipolar moments



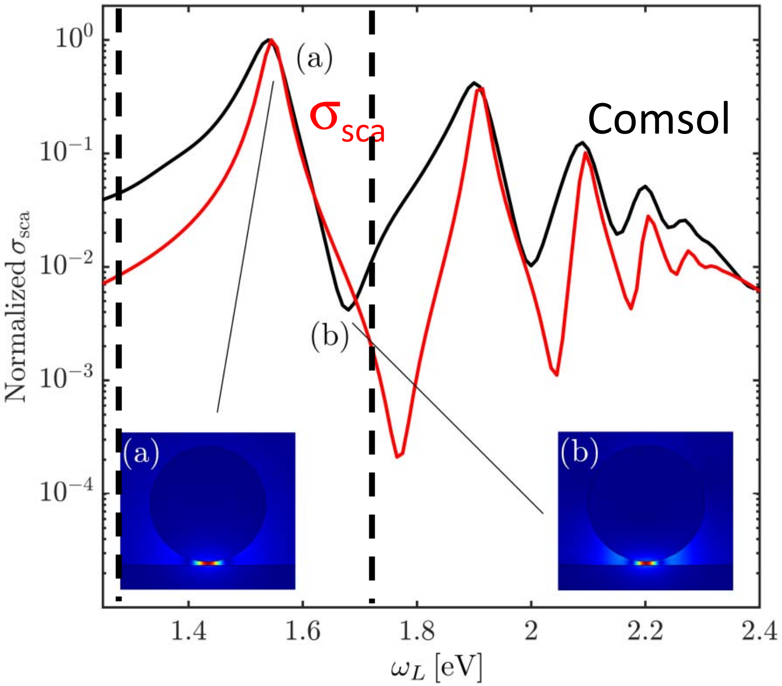
A. Cuartero-Gonzalez et al. arXiv:1905.09893 (2019)

Dark-field spectroscopy

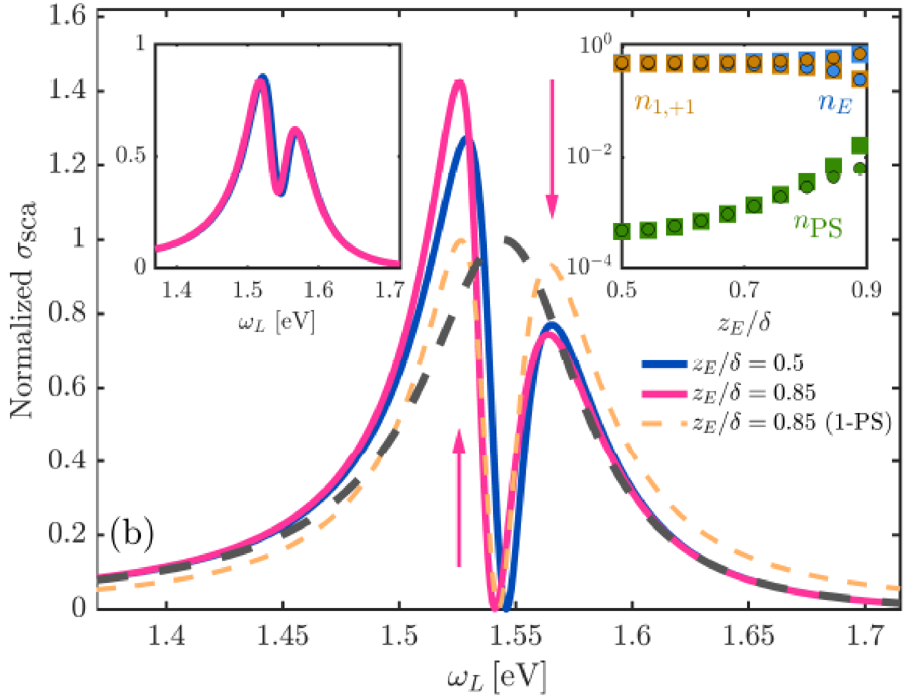
Master Equation: $$\frac{\partial \hat{\rho}'}{\partial t} = i[\hat{\rho}', \hat{H}'_{\exp}] + \sum_{n,\sigma} \frac{\gamma_{n,\sigma}}{2} \mathcal{L}_{\hat{a}_{n,\sigma}}[\hat{\rho}'] + \frac{\gamma_i^{\mathrm{r}}}{2} \mathcal{L}_{\hat{\sigma}_i}[\hat{\rho}']$$

Dipolar moment and cross section: $\hat{M} = \sum_n \mu_n \hat{a}_{n,+1} + \mu \hat{\sigma}_\mu$ $\sigma_{\mathrm{sca}}(\omega_L) = \mathrm{Tr}\{\hat{\rho}'_{\mathrm{SS}}(\omega_L)\hat{M}\}^2$

Bare nanocavity



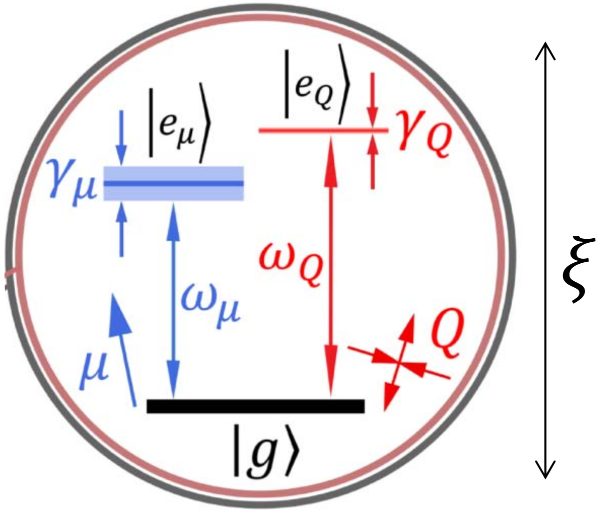
Hybrid system: emitter+nanocavity



A. Cuartero-Gonzalez et al. arXiv:1905.09893 (2019)

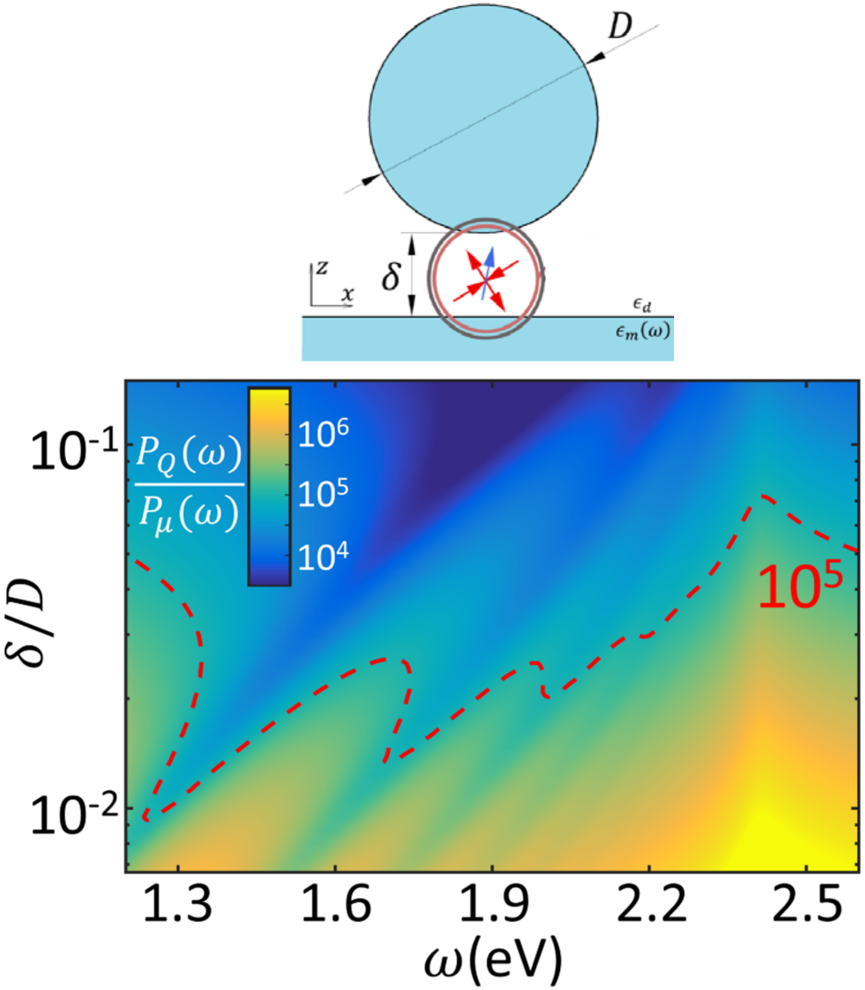
Purcell enhancing light-forbidden transitions

Rivera et al., Science 353, 6296 (2016)



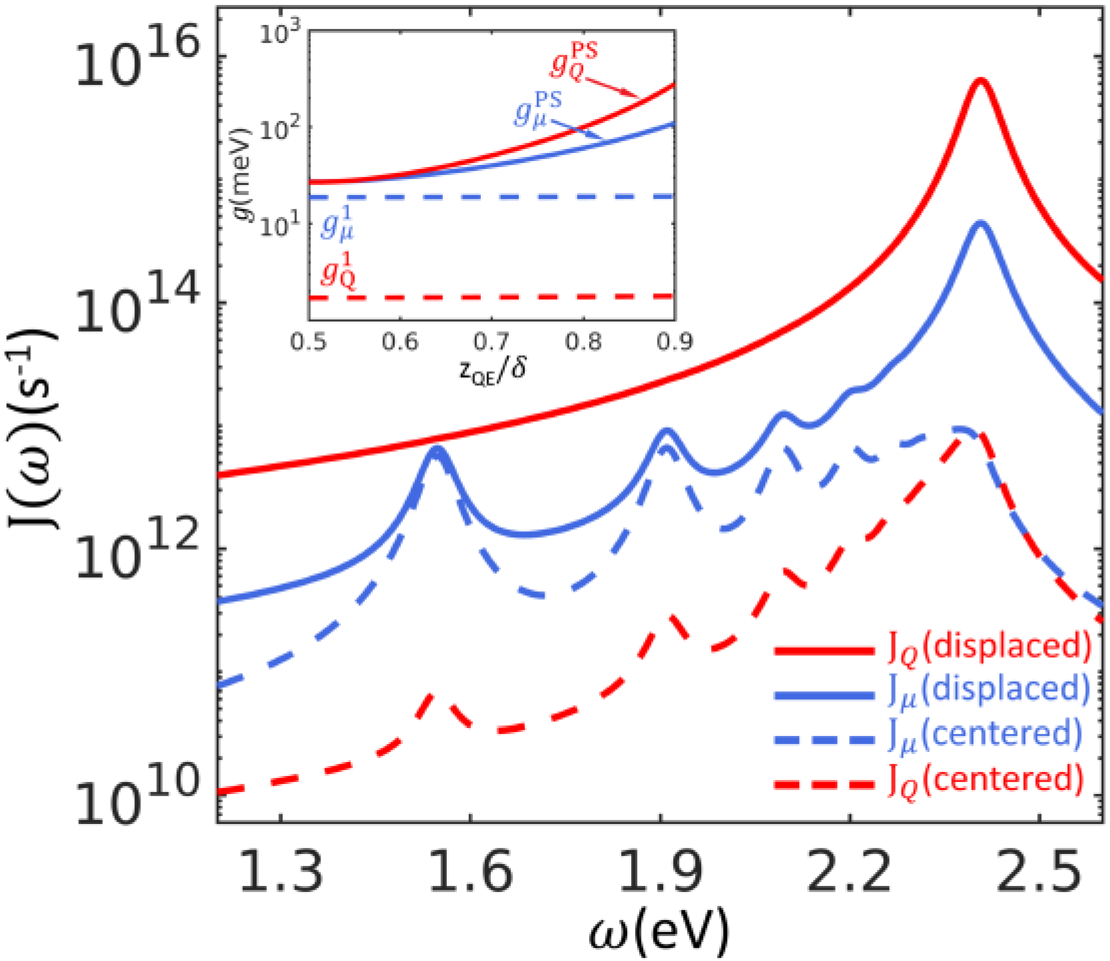
$$\frac{\gamma_Q}{\gamma_\mu} \sim \left(\frac{\xi}{\lambda}\right)^2 \sim 10^{-5}$$

$$H_I = \vec{\mu}\vec{E} + (\vec{Q}\vec{\nabla})\vec{E}$$

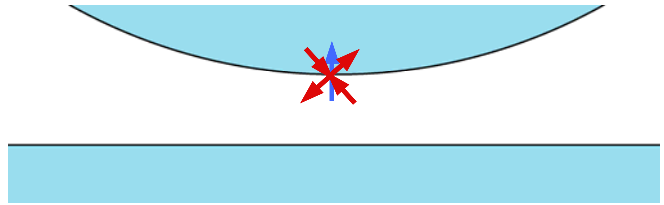


A. Cuartero-González et al., ACS Photonics 5, 3415 (2018).

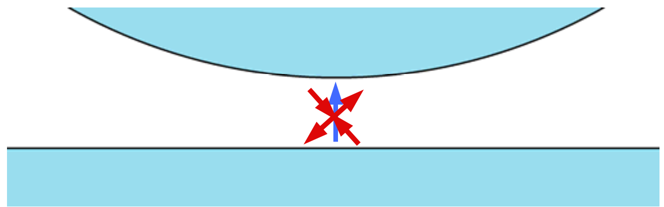
Spectral density for dipolar and quadrupolar excitons:



Displaced:

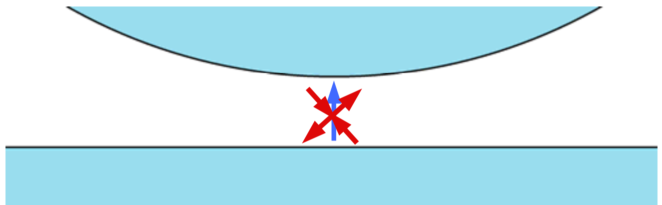


Centered:

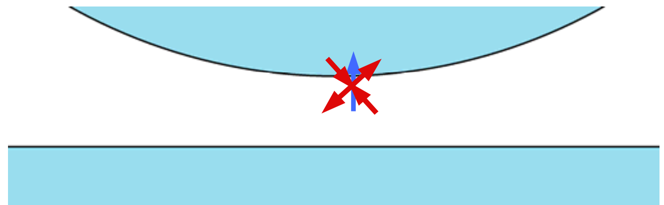


A. Cuartero-González et al., ACS Photonics 5, 3415 (2018).

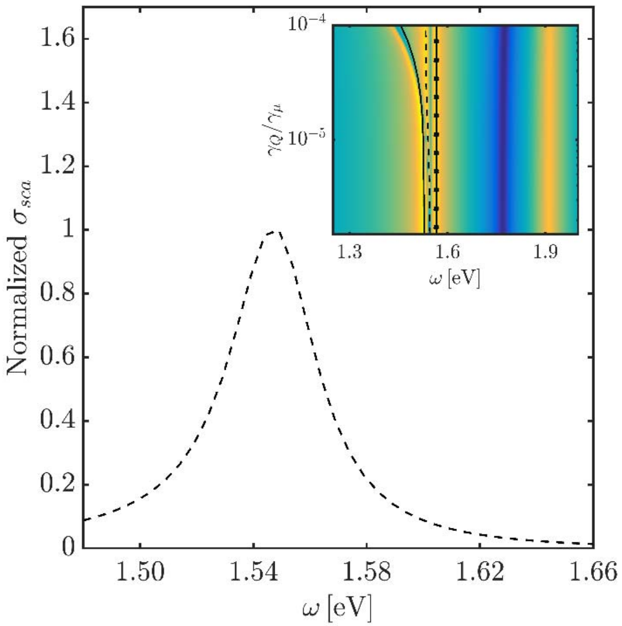
Dark-field scattering spectrum ($D = 30$ nm, $\delta = 1$ nm)

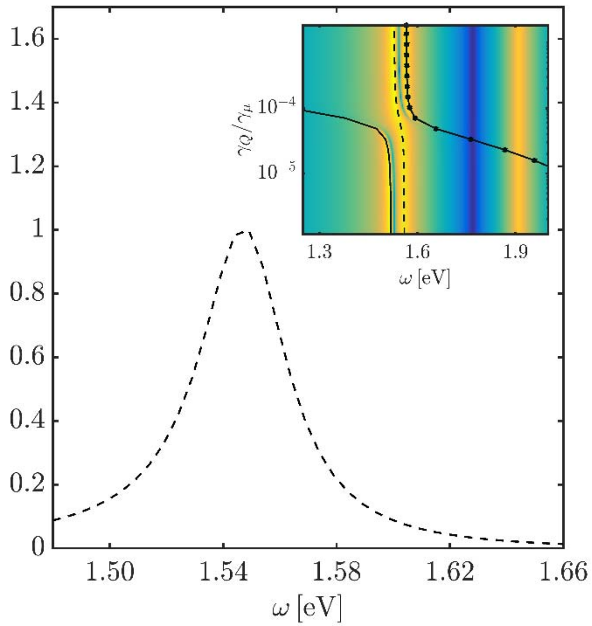


a) $z_E = \delta/2, \omega_\mu = \omega_1, \quad \omega_Q = \omega_1$



b) $z_E = 7\delta/8, \omega_\mu = \omega_1, \quad \omega_Q = \omega_{\mathrm{PS}}$





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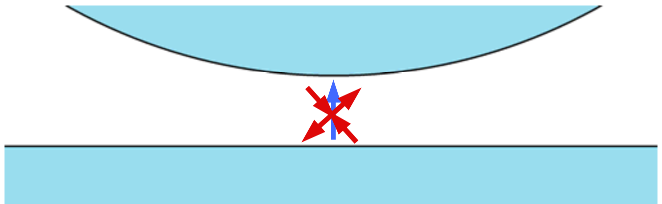
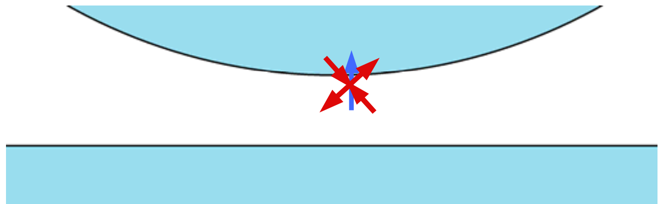
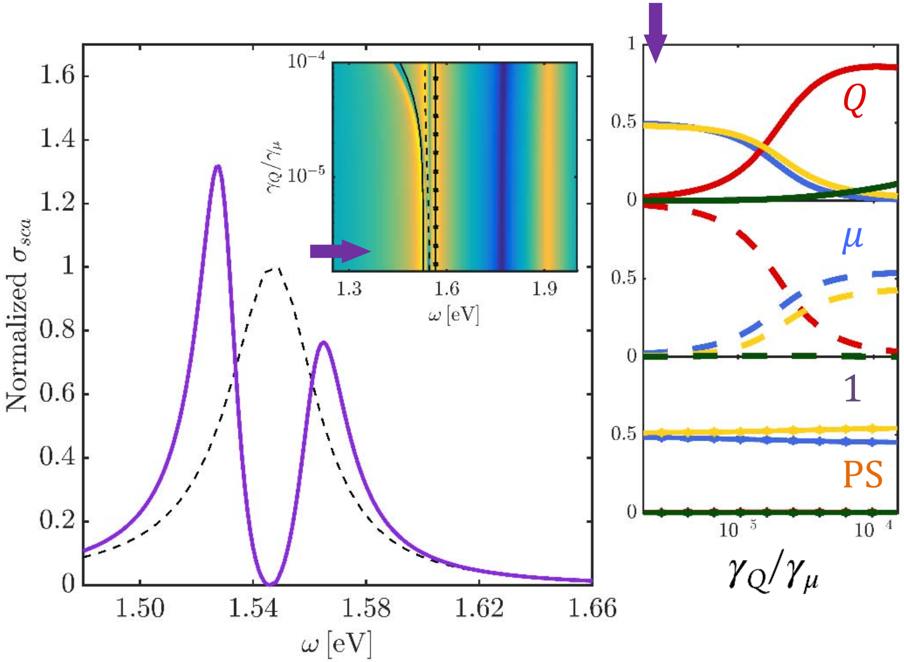
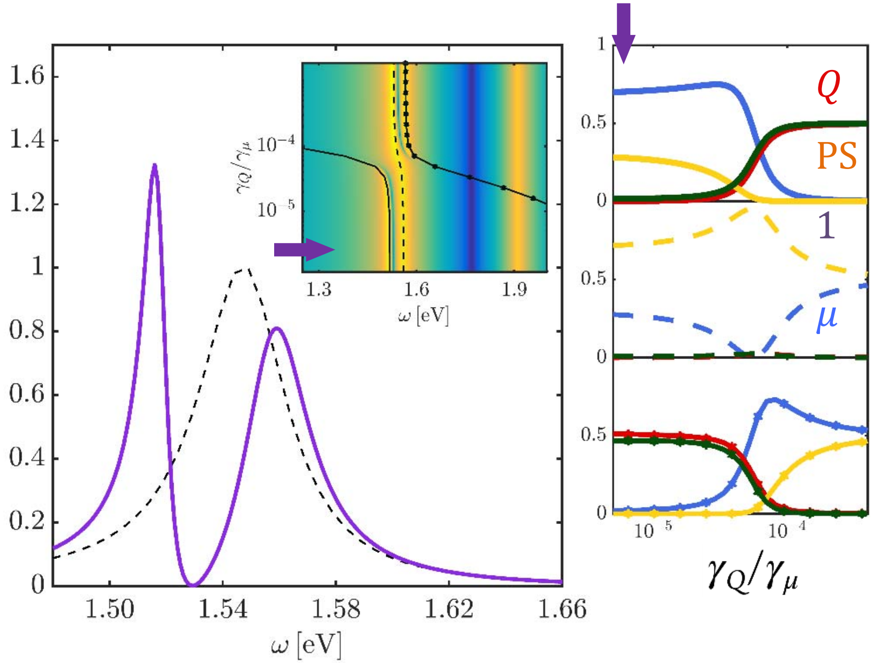




a) $z_E = \delta/2, \omega_\mu = \omega_1, \ \ \omega_Q = \omega_1$

b) $z_E = 7\delta/8, \omega_\mu = \omega_1, \ \ \omega_Q = \omega_{\mathrm{PS}}$





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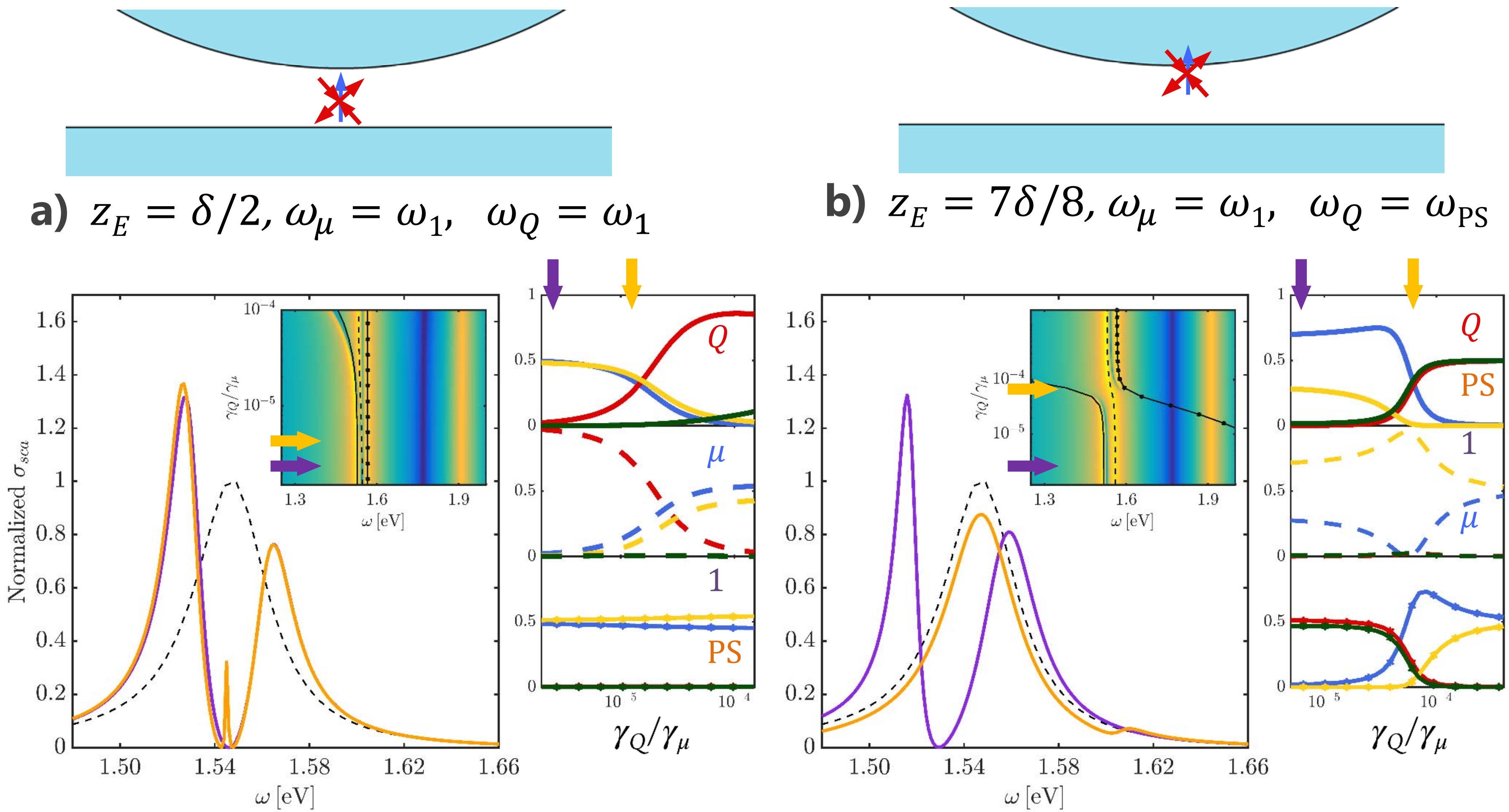

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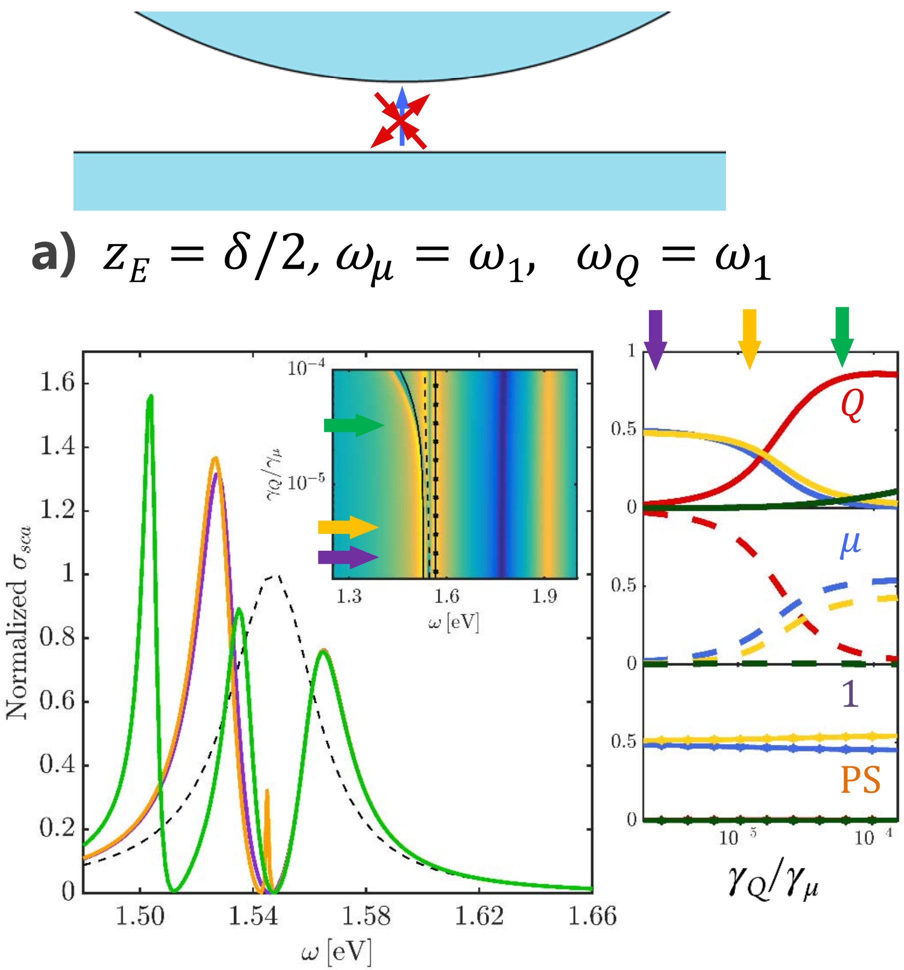
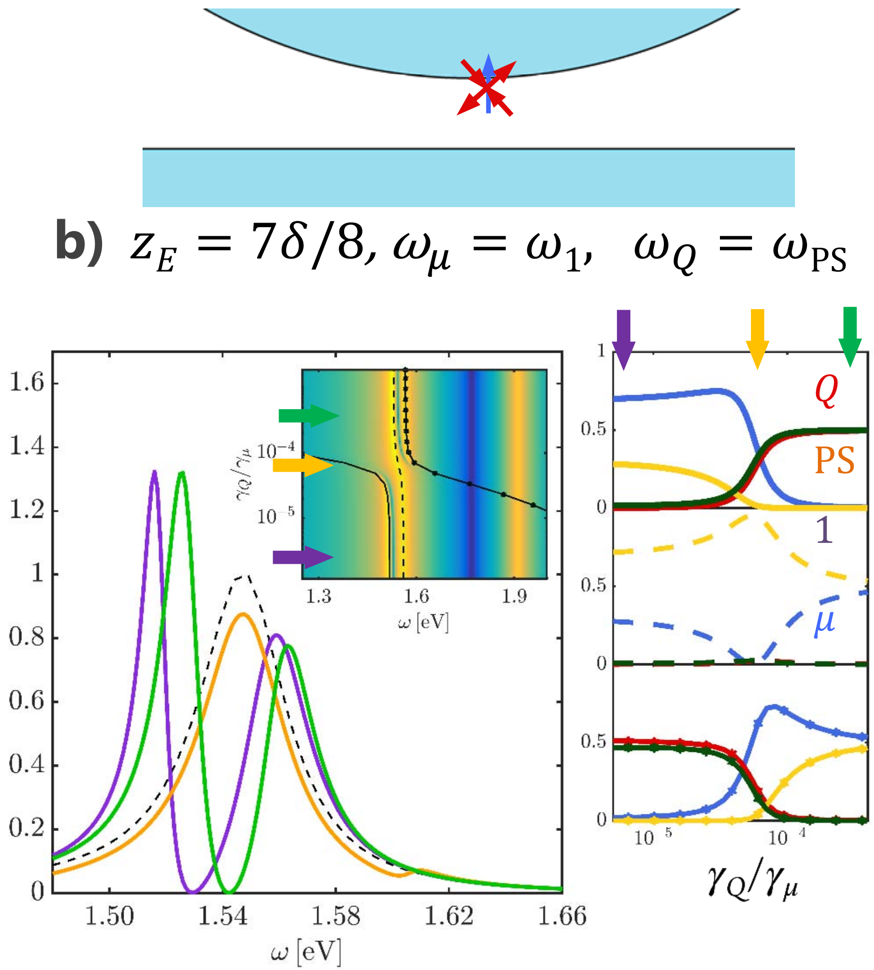


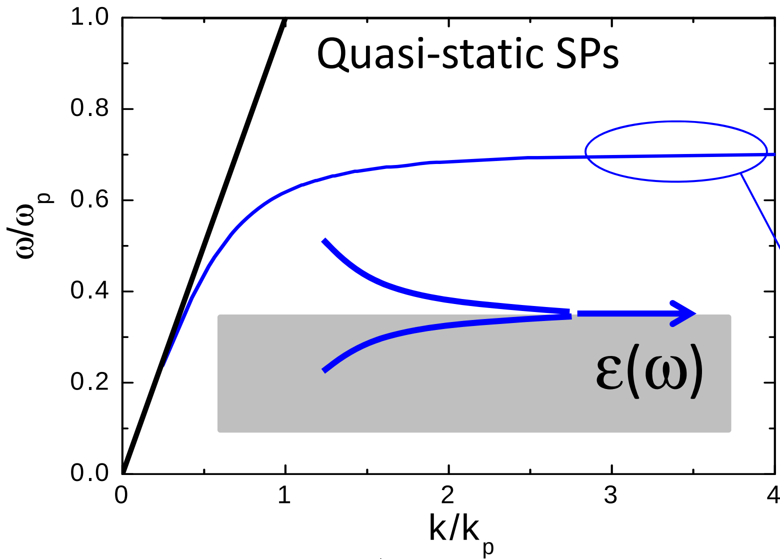
a) $z_E = \delta/2, \omega_\mu = \omega_1, \quad \omega_Q = \omega_1$

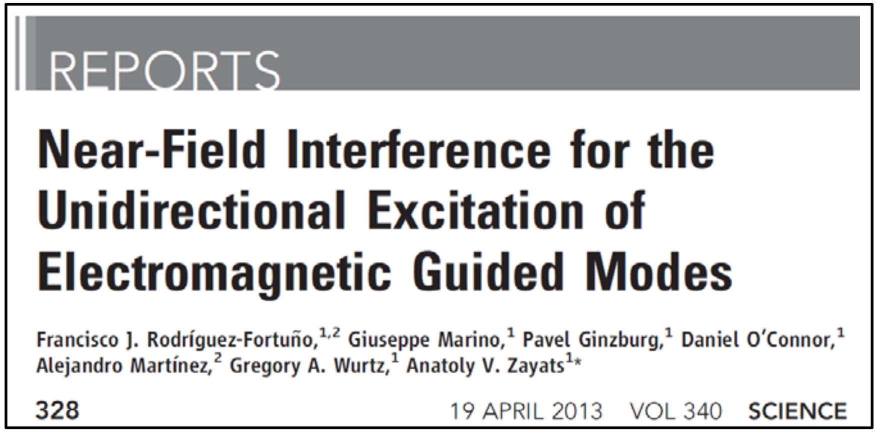


b) $z_E = 7\delta/8, \omega_\mu = \omega_1, \quad \omega_Q = \omega_{PS}$

A. Cuartero-González et al., ACS Photonics 5, 3415 (2018).

Surface plasmon chirality





REPORTS

Near-Field Interference for the Unidirectional Excitation of Electromagnetic Guided Modes

Francisco J. Rodríguez-Fortuño,[1,2] Giuseppe Marino,[1] Pavel Ginzburg,[1] Daniel O'Connor,[1] Alejandro Martínez,[2] Gregory A. Wurtz,[1] Anatoly V. Zayats[1]*

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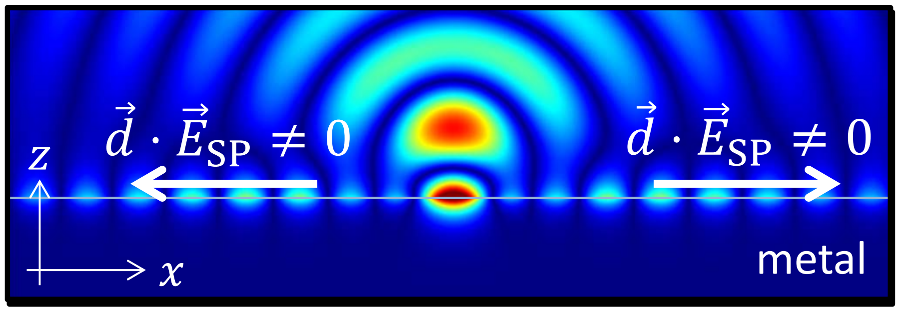
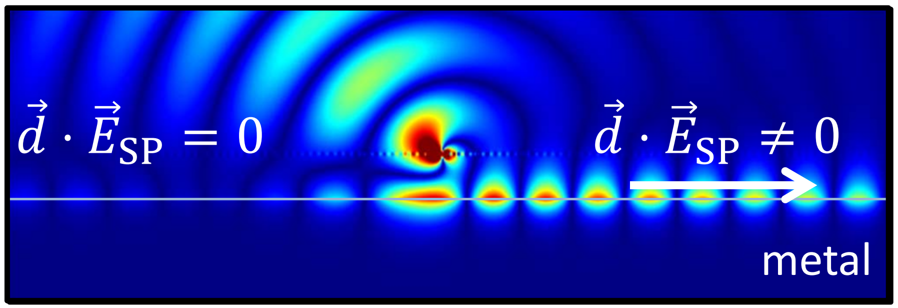
$$\vec{E}_{SP} = \begin{pmatrix} \mp i \\ 1 \end{pmatrix} E_0 e^{\pm ikx} e^{-ky}$$

$$\vec{d} = d\hat{z}$$



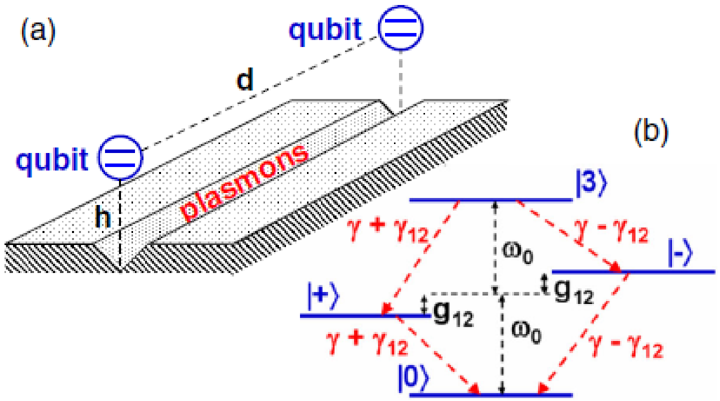
$$\vec{d} = d(\hat{x} + i\hat{z})/\sqrt{2}$$



Circularly polarized dipole sources allow the directional excitation of tightly confined SPs.

Coherent and dissipative coupling between QE

González Tudela et al. PRL 106, 020501 (2011)

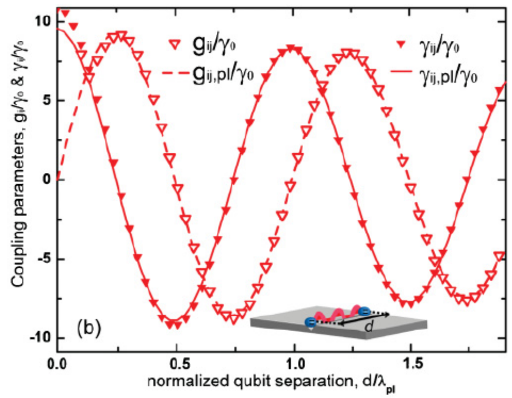


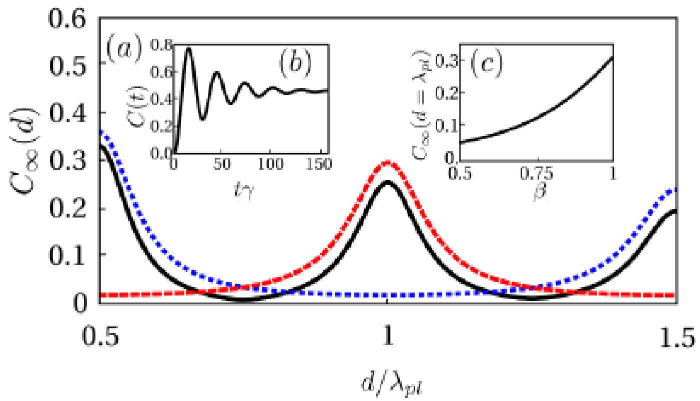
General master equation:

$$\partial_t \rho = \frac{i}{\hbar}[\rho, H] + \sum_{i,j=1,2} \frac{\gamma_{ij}}{2}(2\sigma_i \rho \sigma_j^\dagger - \sigma_i^\dagger \sigma_j \rho - \rho \sigma_i^\dagger \sigma_j),$$

$$H = \hbar\omega_0 \sum_{i=1,2} \sigma_i^\dagger \sigma_i + g_{12}(\sigma_1^\dagger \sigma_2 + \sigma_2^\dagger \sigma_1).$$

$$\gamma_{ij} = \frac{2\omega_0^2}{\hbar\varepsilon_0 c^2} \mathbf{d}_i^* \,\mathrm{Im}\mathbf{G}(\mathbf{r}_i, \mathbf{r}_j, \omega_0)\, \mathbf{d}_j,\; g_{ij} = \frac{\omega_0^2}{\hbar\varepsilon_0 c^2} \mathbf{d}_i^* \,\mathrm{Re}\mathbf{G}(\mathbf{r}_i, \mathbf{r}_j, \omega_0)\, \mathbf{d}_j.$$





Surface plasmons allow tuning the balance between QEs coherent and dissipative coupling.

Chiral quantum optics

Chiral quantum optics

Peter Lodahl[1], Sahand Mahmoodian[1], Søren Stobbe[1], Arno Rauschenbeutel[2], Philipp Schneeweiss[2], Jürgen Volz[2], Hannes Pichler[3,4] & Peter Zoller[3,4]

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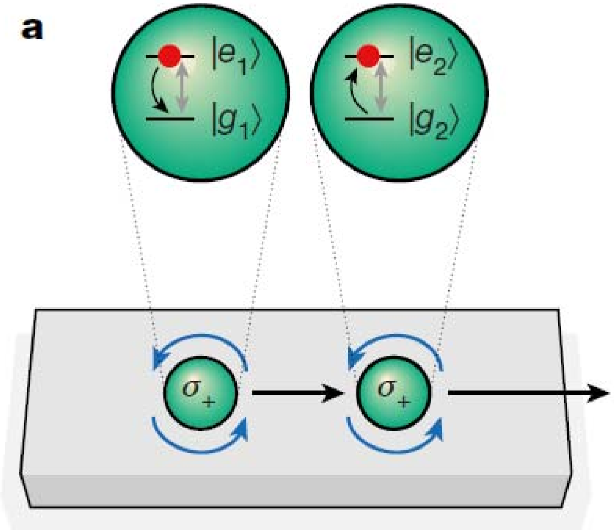


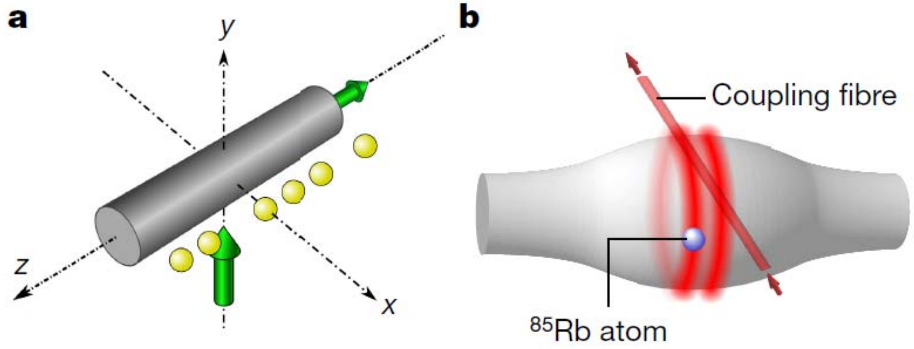


Figure 3 | Nanophotonic devices used for chiral coupling between light and quantum emitters.

Chiral one-photon devices: non-reciprocal quantum networks, topological effects

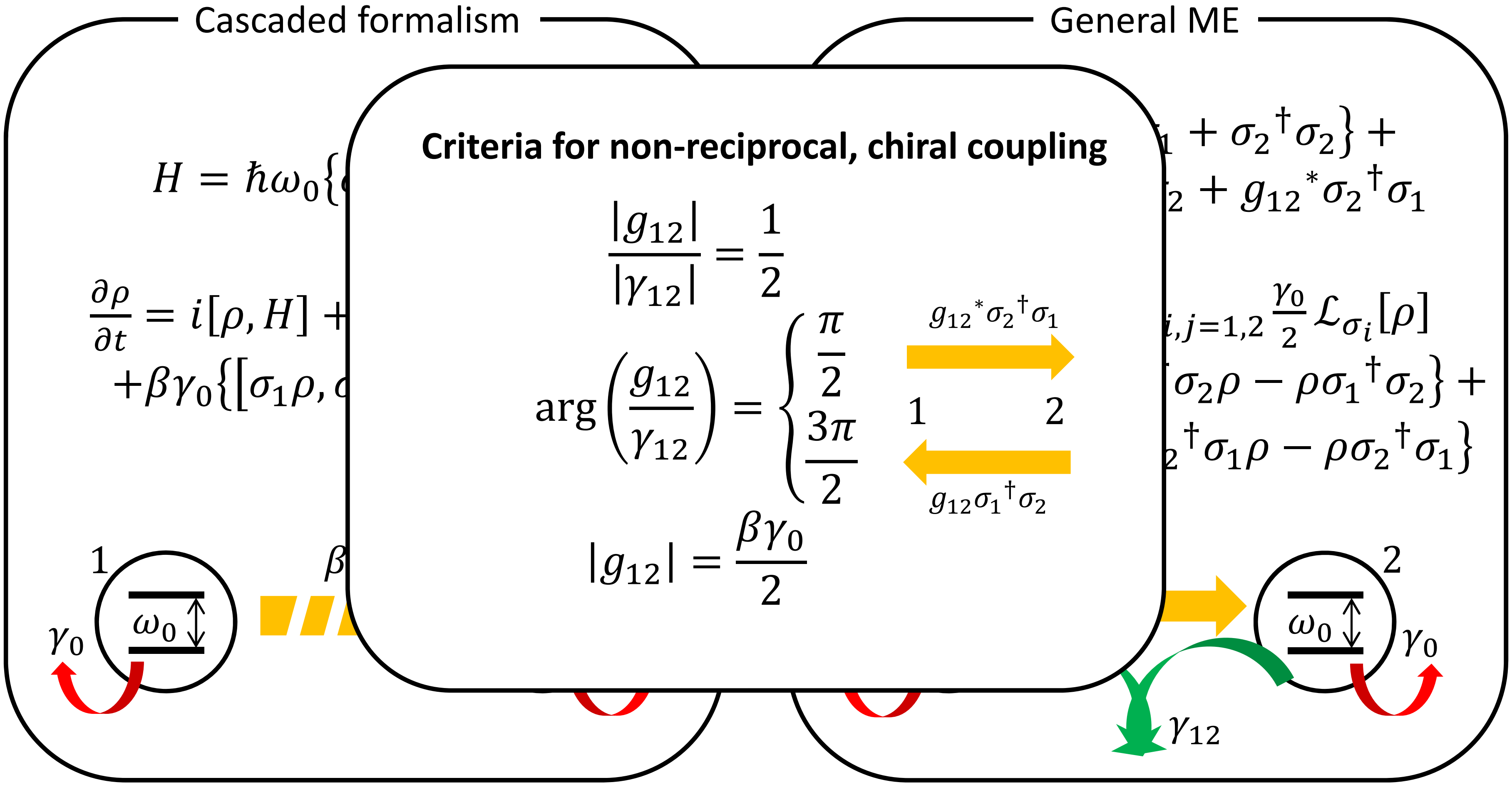
BOX 3

Master equation for a cascaded quantum system

J. C. López-Carreño et al. PRL 115 196402 (2015).

Dissipative coupling behind the cascaded formalism for neighbouring QEs.

Master equation mapping (two identical 2LSs)



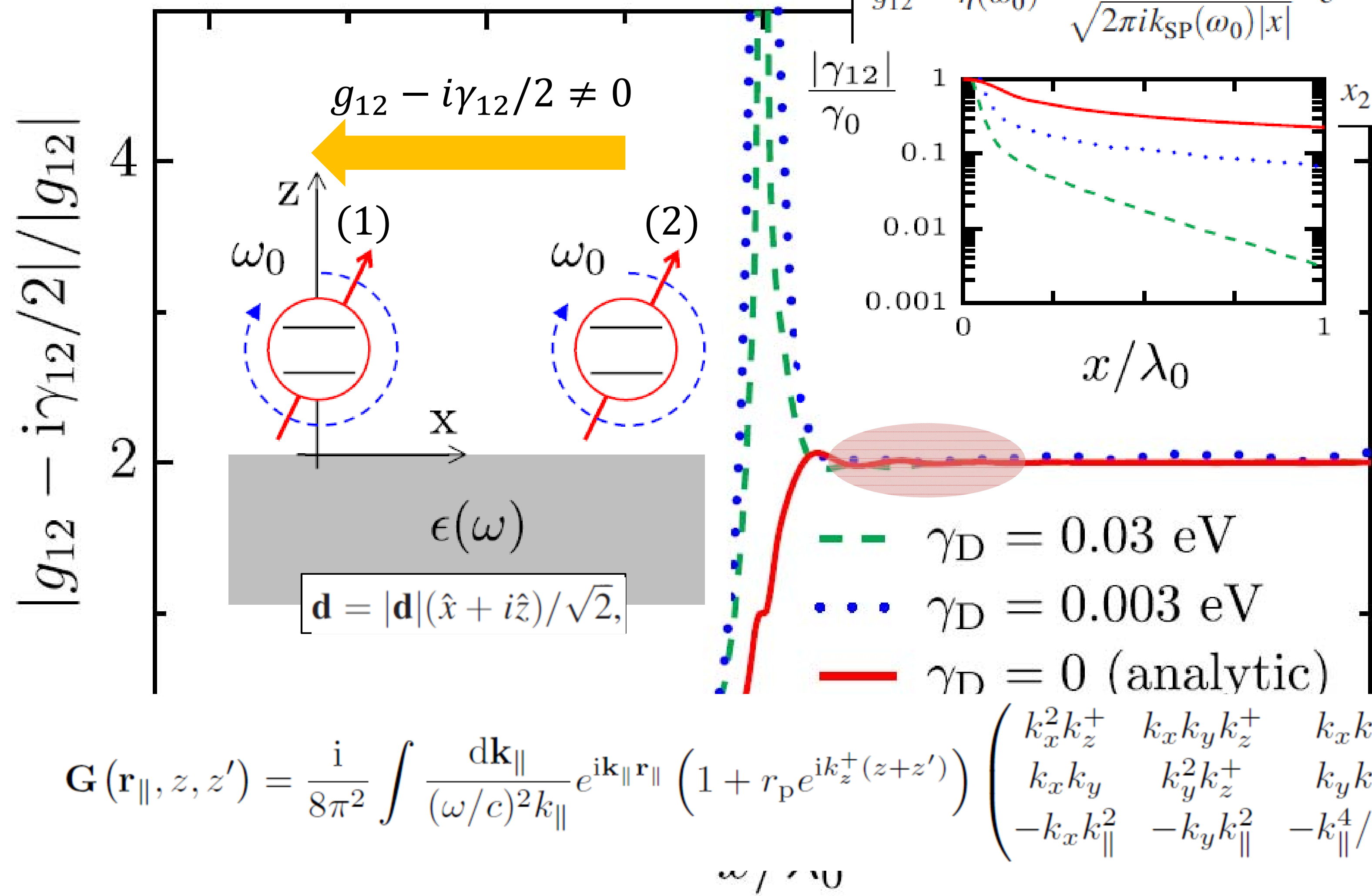
Non-reciprocal conditions: A. Metelman et al., Phys. Rev. X 5,021025 (2015).

Simplest plasmonic platform

Plasmon-pole, z<<λ_0, $\omega_0 \rightarrow \omega_{SP}$:

$$g_{12} = \eta(\omega_0) \frac{e^{-2\sqrt{k_{SP}(\omega_0)^2 - (\omega_0/c)^2} z}}{\sqrt{2\pi i k_{SP}(\omega_0)|x|}} e^{i k_{SP}(\omega_0) x} = g_{21}^*,$$

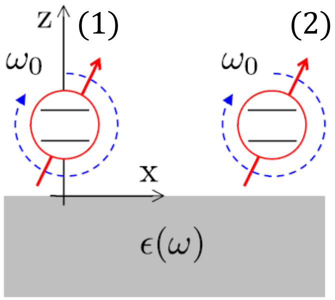
$x_2 - x_1$)



$$\mathbf{G}(\mathbf{r}_\parallel, z, z') = \frac{\mathrm{i}}{8\pi^2} \int \frac{d\mathbf{k}_\parallel}{(\omega/c)^2 k_\parallel} e^{\mathrm{i}\mathbf{k}_\parallel \mathbf{r}_\parallel} \left(1 + r_p e^{\mathrm{i}k_z^+(z+z')}\right) \begin{pmatrix} k_x^2 k_z^+ & k_x k_y k_z^+ & k_x k_\parallel^2 \\ k_x k_y & k_y^2 k_z^+ & k_y k_\parallel^2 \\ -k_x k_\parallel^2 & -k_y k_\parallel^2 & -k_\parallel^4/k_z^+ \end{pmatrix}$$

Deviations from the analytical prediction at small |x| and rapid decay of γ_{12}: chirality at the nanoscale

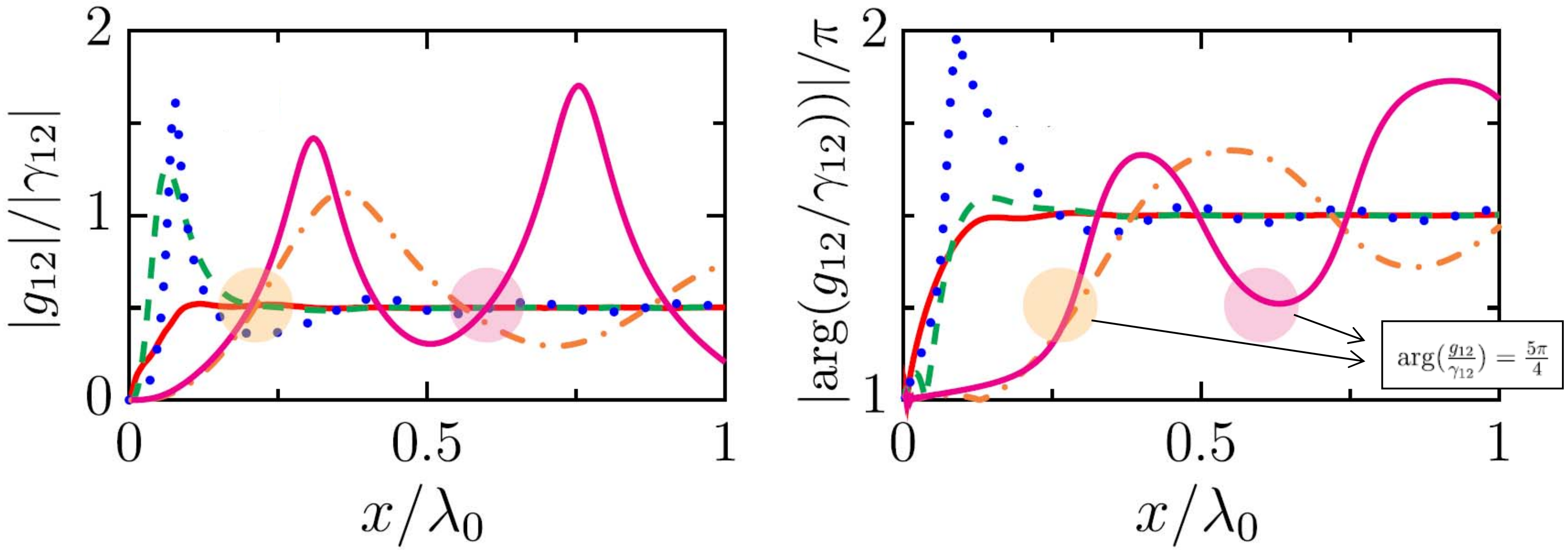
Simplest plasmonic platform



Increasing z, the Dyadic Green´s function is no longer governed by the plasmon pole: **Deviations from the chiral conditions.**

$$\mathbf{G}\left(\mathbf{r}_\parallel, z, z'\right) = \frac{\mathrm{i}}{8\pi^2}\int \frac{\mathrm{d}\mathbf{k}_\parallel}{(\omega/c)^2 k_\parallel} e^{\mathrm{i}\mathbf{k}_\parallel \mathbf{r}_\parallel}\left(1 + r_\mathrm{p} e^{ik_z^+(z+z')}\right)\begin{pmatrix} k_x^2 k_z^+ & k_x k_y k_z^+ & k_x k_\parallel^2 \\ k_x k_y & k_y^2 k_z^+ & k_y k_\parallel^2 \\ -k_x k_\parallel^2 & -k_y k_\parallel^2 & -k_\parallel^4/k_z^+ \end{pmatrix}$$

z=5 nm, 30 nm, 60 nm, 150 nm, 300 nm



Quasichiral regime: amplitude conditions are met, phase conditions are not (shaded areas).

Incoherent pumping and emission spectrum

Weak incoherent pumping of the two QEs:

$$\frac{\partial \rho}{\partial t} = i[\rho, H] + \frac{\gamma_0}{2}\{\mathcal{L}_{\sigma_1}[\rho] + \mathcal{L}_{\sigma_2}[\rho]\} + \frac{\gamma_{12}}{2}\{2\sigma_1\rho{\sigma_2}^\dagger - {\sigma_1}^\dagger\sigma_2\rho - \rho{\sigma_1}^\dagger\sigma_2\} +$$
$$+\frac{{\gamma_{12}}^*}{2}\{2\sigma_2\rho{\sigma_1}^\dagger - {\sigma_2}^\dagger\sigma_1\rho - \rho{\sigma_2}^\dagger\sigma_1\} + \boxed{\frac{P_0}{2}\{\mathcal{L}_{\sigma_1}[\rho] + \mathcal{L}_{\sigma_2}[\rho]\}^\dagger}$$

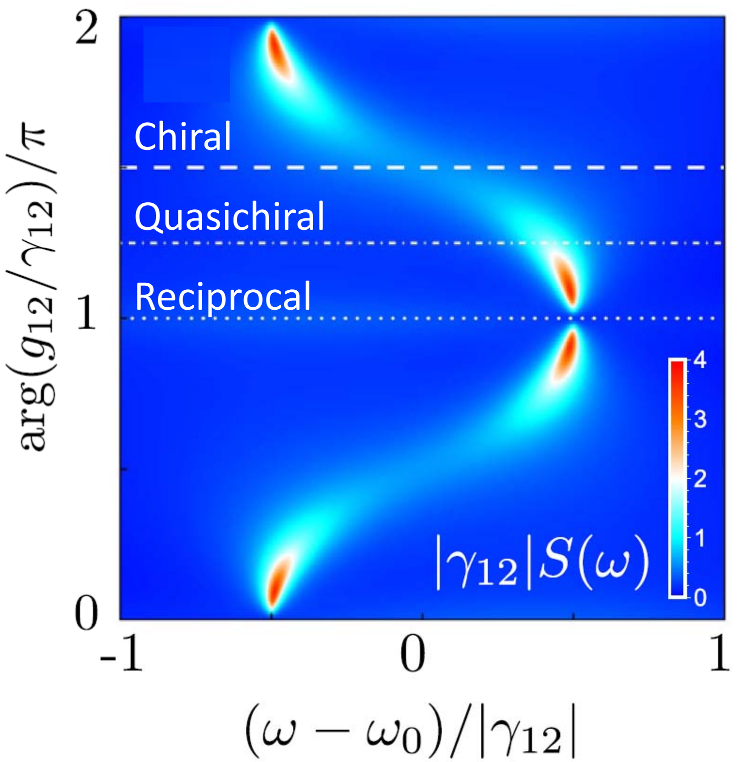
Using the Quantum Regression Theorem, analytical evaluation of the emission spectrum:

$$S(\omega) = \frac{1}{\pi\langle\xi^\dagger\xi\rangle} \lim_{t\to\infty} \mathrm{Re}\left\{\int_0^\infty d\tau \langle\xi^\dagger(t)\xi(t+\tau)\rangle e^{i\omega\tau}\right\}$$

with $\xi = \sigma_1 + \sigma_2$.

We explore the quasichiral regime, in which:

$$\frac{|g_{12}|}{|\gamma_{12}|} = \frac{1}{2}, \; |g_{12}| = \frac{\gamma_0}{2}$$



Sharp features emerge in quasichiral emission spectra

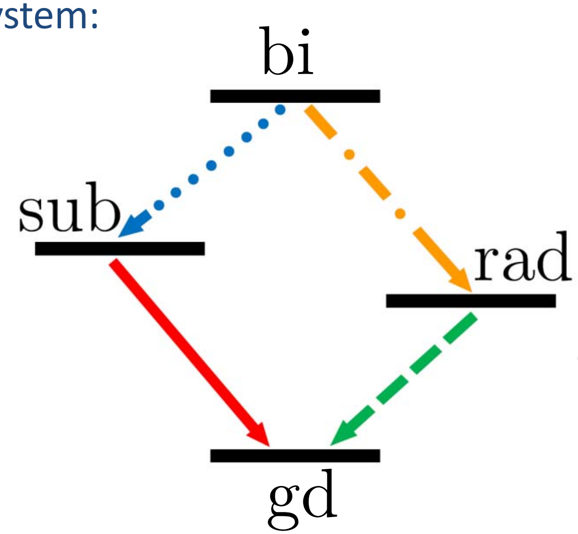
Incoherent pumping and emission spectrum

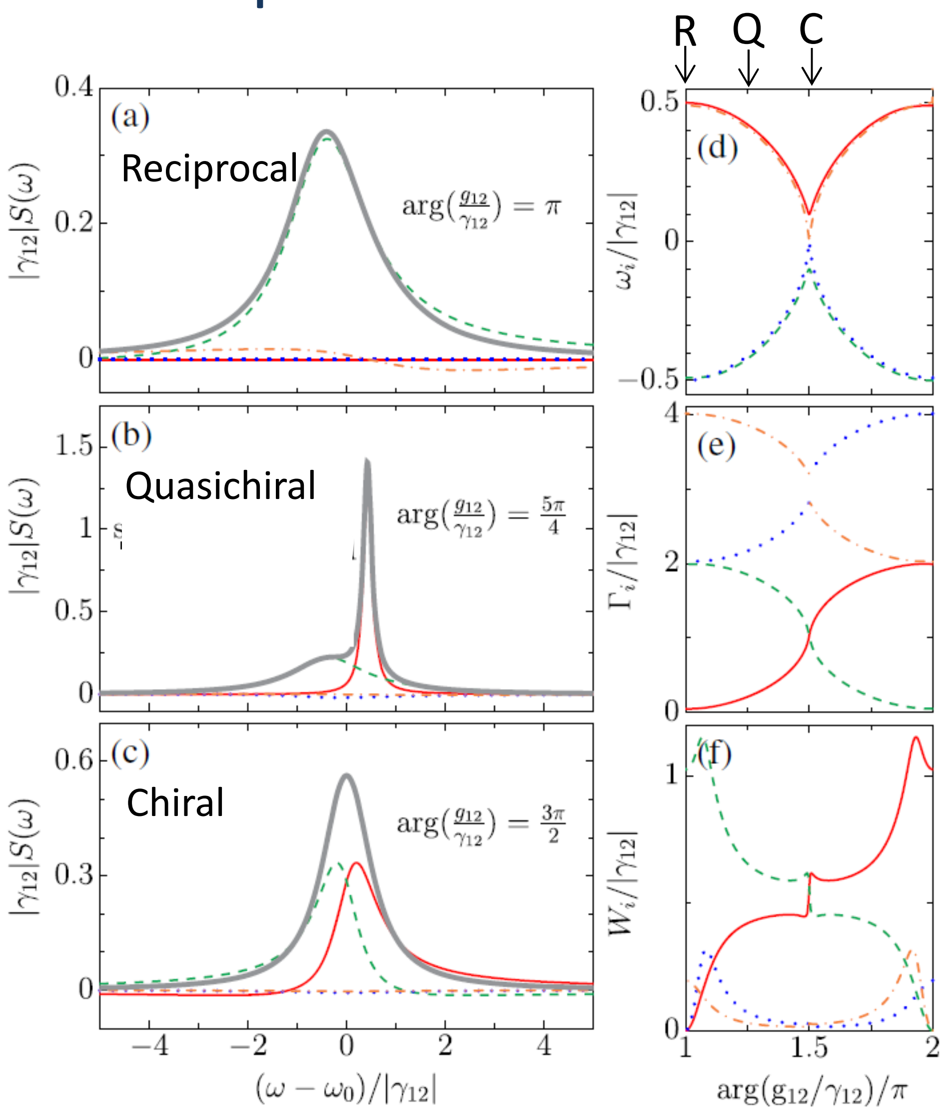
Analytical expression for the spectrum:

$$S(\omega) = \sum_{i=1}^{4} S_i(\omega) = \frac{1}{\pi} \sum_{i=1}^{4} \frac{\frac{\Gamma_i}{2} L_i + (\omega - \omega_i) K_i}{(\omega - \omega_i)^2 + \left(\frac{\Gamma_i}{2}\right)^2}$$

with $W_i = \sqrt{{L_i}^2 + {K_i}^2}$.

The index labels the four transitions in the system:

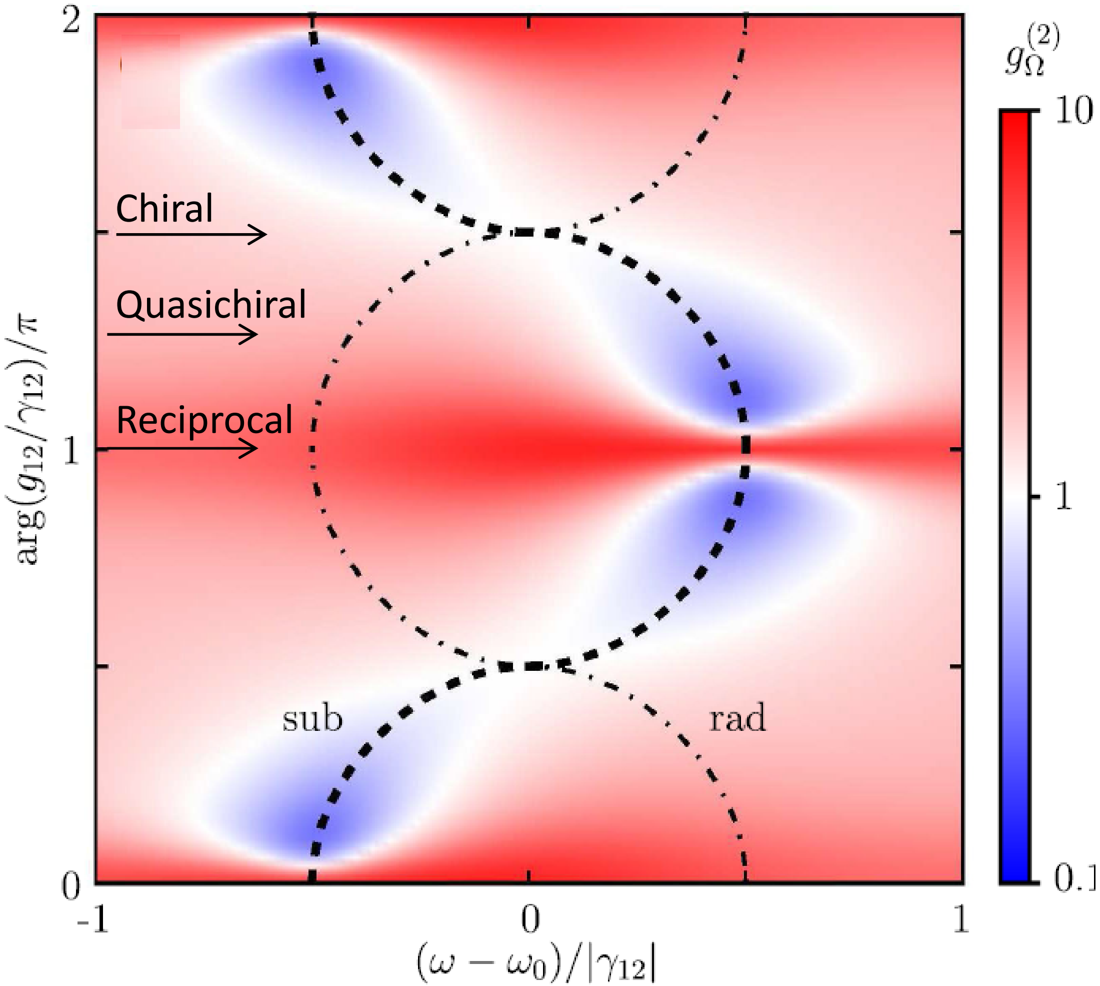




C. Downing et al., Phys. Rev. Lett. 122, 057401 (2019)

Quasichiral photon correlations

$$\frac{|g_{12}|}{|\gamma_{12}|} = \frac{1}{2}, \ |g_{12}| = \frac{\gamma_0}{2}$$

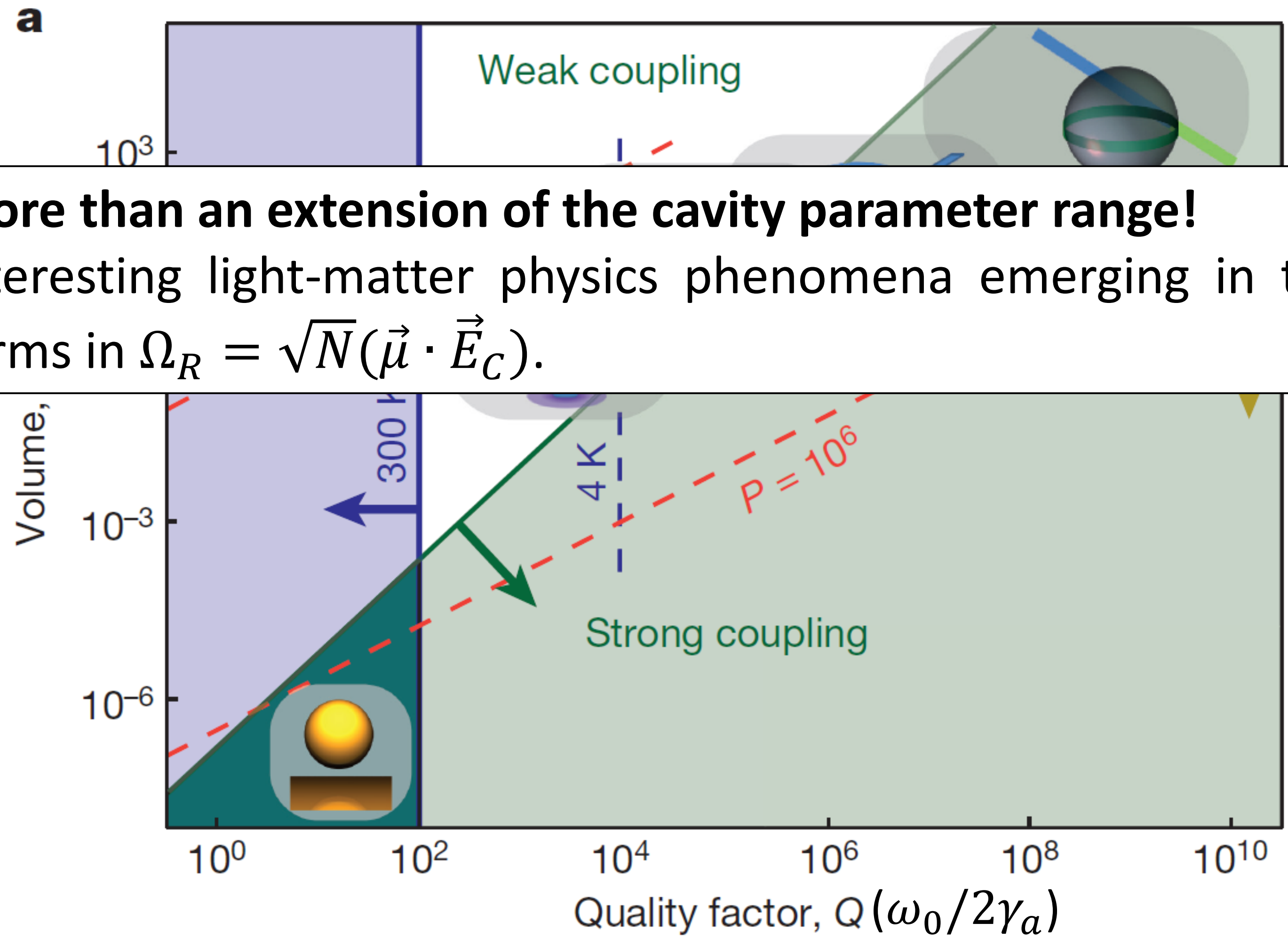


Frequency-filtered second order correlation function [PRL 109, 183601 (2012)] with a detector spectral window $\Omega = \gamma_{12}/5$.

Photon antibunching occurs only in the quasichiral configurations.

C. Downing et al., Phys. Rev. Lett. 122, 057401 (2019)

Plasmonic nanocavities:



More than an extension of the cavity parameter range!

Interesting light-matter physics phenomena emerging in the different terms in $\Omega_R = \sqrt{N}(\vec{\mu} \cdot \vec{E}_C)$.

Chikkarady et al. Nature 7, 535 (2016)

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Thank you!

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