Effect of Electronic Coupling in the Optical Response of Plasmon–Exciton Systems

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We use time-dependent density functional theory (TDDFT) to explore the influence of electronic coupling in the optical response of quantum emitters (QEs) interacting with metallic nanoparticles (MNPs) that support plasmonic resonances. Our model system consists of a QE, with a HOMO–LUMO transition, placed at the center of a (sub)-nanometric gap nanoantenna formed by two spherical MNPs (Figure 1a). The TDDFT calculations address, without any *a priori* parameter, the dynamics of the electronic states of both the QE and the MNPs under external illumination, thus going beyond the electromagnetic interaction picture that is typically considered when describing the optical response of such narrow junctions.

Our study reveals the importance of the electronic coupling between the QE and the plasmonic gap nanoantenna for separations of the order of 1 nm. First, the electronic states localized at the MNPs hybridize with the states localized at the QE, which produces a drastic quenching of the LUMO state that standard classical models cannot capture. This *electronic quenching* strongly modifies the energy and width of the optical resonances of the coupled system (Figure 1b). Moreover, for subnanometric cavities, the presence of the QE triggers a net electron transfer between the two MNPs at low illumination frequencies [2,3]. The results in this work thus demonstrate that the electronic QE–MNPs coupling and charge-transfer processes between the emitter and the nanoantena play a crucial role in the optical response of (sub)-nanometric junctions.

References

[1] A. Babaze, *et al.*, Nano Lett., 19, 8466(2021)
[2] P. Song, *et al.*, J. Chem. Phys., 134, 74701 (2011)
[3] V. Kulkarni, *et al.*, ACS Photonics, 2, 987 (2015)

Figures

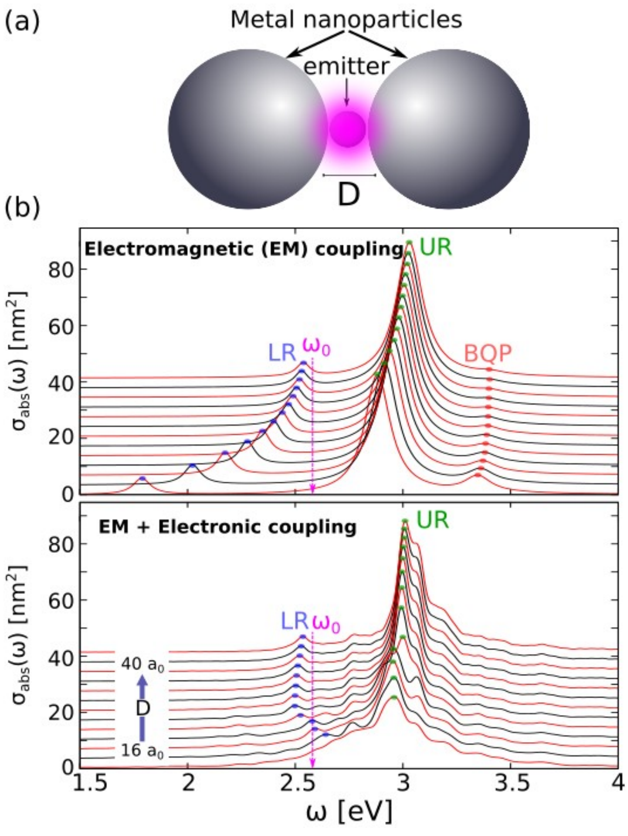

Figure 1: (a) *Sketch of the studied system, consisting of a QE placed at the nanogap of size D formed by two MNPs. (b) Absorption cross-section spectra of the coupled QE-MNPs system calculated within a classical model only accounting for the electromagnetic (EM) interaction (top) and within a TDDFT description that includes both the EM and the electronic coupling (bottom).*