A plasmonic nanogap is an ideal platform to explore and test quantum effects in the optical response of nanoscale structures. As the separation between interfaces in a nanogap becomes below nanometric distances, the optical response of the system enters a strong nonlocal regime where the quantum nature inherent to the coherent oscillation of interacting electrons becomes apparent. We have developed full quantum mechanical calculations within time-dependent density functional theory (TDDFT) to address nonlocal effects in plasmonic gaps [1]. By doing so, we have identified a tunneling regime for separation distances of the interfaces below 0.5 nm, which totally modifies the spectral fingerprints of the cavity. Quantum tunneling screens plasmonic modes localized at the cavity and establishes charge transfer across the gap producing lower energy modes of the optical response. Furthermore, we consider the presence of an emitter in the nanogap, as depicted in the Fig., under the strong coupling regime where hybrid plexcitonic modes are produced. At very close distances from the metal interfaces, resonant electron transfer (RET) from the excited state of the emitter into the continuum of metallic states occurs (see scheme of states in the Fig.), producing a quenching of the plexcitonic fingerprint [2], an effect intrinsically different to the classical quenching of emission by classical interaction with surface plasmons.

Once the plexcitonic response obtained within classical and quantum approaches are proven to be consistent, we incorporate RET into the classical optoelectronic description of the cavity-emitter system by including the electron transfer rates as an extra broadening of the response of the emitter. As observed in the spectra of the Fig., the spectral fingerprint of the emitter is lost for short distances to the interfaces. The results presented here emphasize the importance of quantum effects in the coupling between plasmons and single emitters.