

Quantum Effects in Extreme Nanocavity-Enhanced Molecular Spectroscopy

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The optical response of nanoscale systems has been successfully described during the last years by implementing a variety of classical and semiclassical methods to solve Maxwell's equations. However, optical resonators as well as the matter to be tested in them have evolved to reach extreme field confinement conditions, a situation which pushes optical spectroscopy and microscopy towards non-standard regimes of light-matter interaction giving rise to strongly coupled systems and nonlinear optical response. Under these conditions, one needs to go beyond classical optical response formalisms, and adopt a variety of quantum approaches to describe light-matter interaction.

We apply different quantum theories to describe the optical response of a canonical nanosystem constituted by a plasmonic nanoantenna and a molecular emitter. By doing so, we are able to interpret a variety of results obtained in field-enhanced molecular spectroscopy experiments. First, we describe the non-local optical response of an emitter in close proximity to a plasmonic nanoantenna with the use of Time-Dependent Density Functional Theory (TDDFT). This calculation serves as a reference result to identify the limitations of the standard Surface Response Formalism (SRF), based on Feibelman parameters, to capture non-locality in situations of extreme field-confinement [1]. We introduce here the novel *dispersive* SRF, which is shown to successfully address nonlocality in those extreme field confinement conditions [2] (see Fig. 1 where the concept of *dispersive* SRF is depicted).

Next, we address light emission from single organic molecules at the gap of a tunneling cavity, forming a picocavity (see schematics of the configuration in Fig. 1(b)), where one needs to describe the electronic transition density of the molecule as well as the picocavity field confinement with the implementation of Density Functional Theory (DFT) methods [3]. The calculation of the electronic transition density and the picocavity field allow for correctly interpreting Purcell factors and Lamb shifts of the light emitted by the molecule, obtained with Ångström-scale resolution [4].

Last, we focus on the quantization of the cavity-photons in plasmonic resonators interacting with molecular emitters by adopting a cavity-Quantum Electrodynamics approach, which serves to capture non-linear signals from molecular vibrations [5] as well as correlations of light emitted from strongly coupled molecular excitons to plasmonic fields [6], as obtained in Hanbury Brown–Twiss (HBT) interferometry (see schematics in Fig. 1(c)).

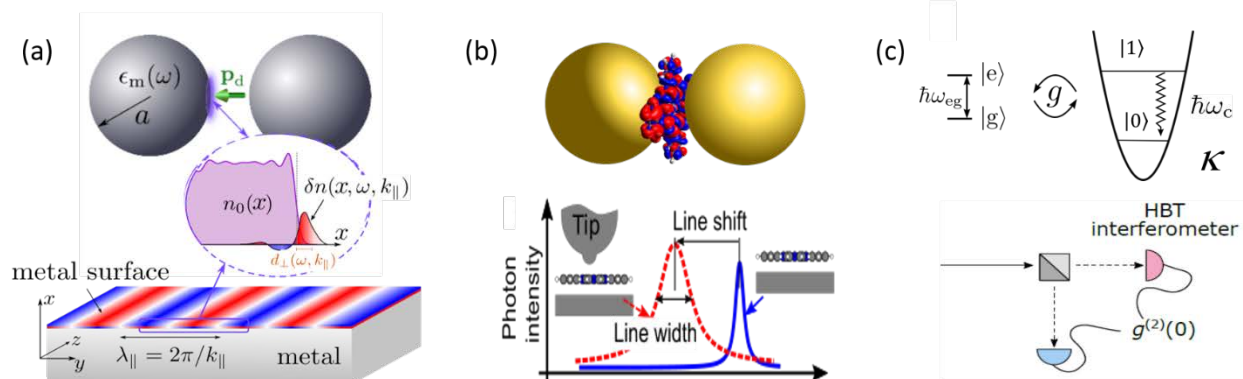


Fig. 1 (a) Schematics of the dispersive SRF, which adopts a frequency, ω , and parallel momentum, k_{\parallel} , dependency of the Feibelman parameters, $d_{\perp}(\omega, k_{\parallel})$ to address nonlocality involving extreme plasmonic fields acting on an emitter of electric dipole momentum p_d . (b) An organic molecular emitter in an inhomogeneous plasmonic field formed by a tip on a surface experiences Purcell effect and Lamb shift, resolved by the scanning tip at the Ångström scale. (c) A cavity-QED approach of plasmonic fields of energy $\hbar\omega_c$, strongly coupled to an excitonic transition of energy $\hbar\omega_{eg}$, reveals rich photon emission correlations, $g^{(2)}(0)$, in HBT interferometry.

References

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