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DAMPING RATES OF DISSIOATIVE PROCESSES IN METAL PLASMONIC NANOPARTICLE

Krystyna KOLWAS

Group of Optical Characterisation of Micro- and Nanoobjects, Institute of Physics, Warsaw, 02-668, Poland

Krystyna.Kolwast@ifpan.edu.pl

Abstract

The scope of the present report is the closer look at the dynamics of damping processes in MNP in order to answer the question which plasmonic quantities are damped as such data do not result from the classical EM considerations. The model is based on the link between the classical EM description of plasmonic properties of MNP and the quantum picture in which MNPs are treated as "quasi-atoms" or quasi-particles (PQPs). The energy level structure with the zero energy level state for non-excited plasmon allows studying the system dynamics accounting for dissipative processes.

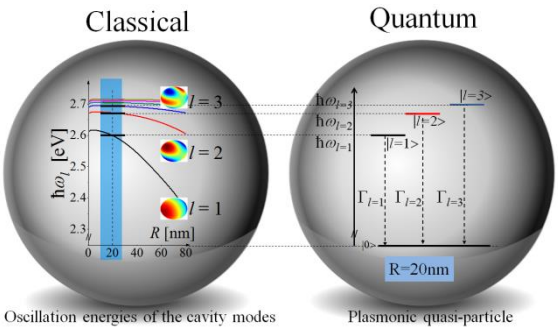

Figure 1 The starting scheme for modelling which relates the oscillation energies of LSP modes to the energy levels of quantum plasmonic quasi-particle

The evolution of the reduced density matrix of quantum open systems is ruled by the master equation in the Lindblad form which enables us to distinguish between damping processes of populations and coherences of multipolar plasmon oscillatory states and to establish the intrinsic relations between the rates of these processes. The size dependence of the rates of dephasing of the collective electron motion and of damping of populations are given for gold and silver MNPs on the base of the established classical-quantum relations of damping channels.

1 Introduction

Plasmonic properties of nanoscale structures lay the groundwork for many future technologies, applications and materials. Plasmonics is based on the excitations of surface plasmons understood as surface charge density oscillations, which form the standing waves of Localised Surface Plasmons (LSP) in the case of finite-size nanostructures. In spherical metal nanoparticles (MNPs) the basic properties of LSPs can be controlled by their radius and manifest in the scattering, absorption or extinction spectra in form of the maxima with size-dependent spectral position, spectral width and intensity. The maxima in the spectra reflect the resonant character of LSP excitations resulting from the size-dependent intrinsic properties of MNP [1]. Such spectra can be predicted by the classical Mie scattering theory when calculated for consecutive chosen radii. However, Mie scattering theory gives no direct information about the size-dependence of the pick position in the spectra.

2 Classical oscillation eneries and damping rates of plasmonic cavity modes versus MNP radius

The dynamics of plasmon excitations is described by the important intrinsic functions of MNP's size such as resonant frequencies of the cavity modes and damping rates of such modes. The excitation of LSP is a resonance process which takes place when the frequency of the incoming light ω fits a self-frequency (-ies) of a plasmonic resonator $\omega_l(R)$ (of the cavity modes), where l, $l = 1,2,3,..$.

Therefore, the key issue is to find the intrinsic properties of a plasmonic cavity i.e. the size-dependent self frequencies of plasmon modes $\omega_l(R)$ but also the damping rates $\Gamma_l(R)$ of the oscillations. Such parameters characterise the plasmonic MNPs and can be found by looking for solutions of the self-consistent Maxwell equations in absence of the incoming light field in connection with the continuity relations at the sphere boundary [1]. The resulting dispersion relations for surface-localized fields define the complex, discrete eigenvalues $\hbar(\omega_l(R) - i\Gamma_l(R)/2)$. So the dynamics of surface localized EM fields: $E(r = R) = \exp(i\omega_l - \Gamma_l/2)t)$ is unambiguously determined by the material properties of the MNP of a given size and its dielectric environment. Found in absence of the illuminating radiation, $\omega_l(R)$ and $\Gamma_l(R)$ inherently characterize an MNP of the radius R in the same way as the energy levels and the inverse of lifetimes characterize an atom or a molecule. In both cases, these quantities manifest in the spectra, when the systems are illuminated.

3 Quantum modeling of the plasmonic quasi-particle (PQP) decay dynamics

Let us ascribe [2] the oscillation energies $\hbar\omega_l(R)$ of the classical modes to the discrete energy levels, which are distinct from the zero-energy non-oscillatory level by the energies $\hbar\omega_l(R)$ (Fig. 1). The corresponding states of the

plasmonic systems S in the Hilbert space are $|l>$ with l = 1,2,3.... The only possible transitions are those with the absorption or emission of a photon with the energy $\hbar\omega_l$. Such transitions occur between the state $|l>$ and the non-oscillatory state $|0>$.

3.1 The density matrix and quantum master equation

To describe the state of the plasmonic system S we use the density matrix which is convenient in describing the quantum systems in mixed states and in time-dependent problems. The diagonal elements of the density matrix correspond to the probabilities $p_n = N_n/N$ of occupying a quantum states $|n>$, so they describe the relative populations of these states. The complex off-diagonal elements of the density matrix in the basis $|n>$, $|0>$ contain time-dependent phase factors that describe the evolution of the coherent superposition of the states.

As no physical system is absolutely isolated from its surroundings, the plasmonic system S has to be considered as an open quantum system which is a subsystem of a larger combined quantum system $S+E$, where E represents the environment to which the open system S is coupled. Following the main assumption of the basic theory of open quantum systems [3], the environment is assumed to be a large system with an infinite number of degrees of freedom. The interaction of the open system S with the environment causes an irreversible behavior of the open system S and leads to decoherence (randomization of phases) and dissipation of energy into the surroundings.

The dynamics of open systems in the case of Markov processes can be described by a quantum Markovian master equation in Lindblad form [3]:

$$\frac{\partial \rho^S(t)}{\partial t} = -\frac{i}{\hbar}\left[H, \rho^S(t)\right] - D[\rho^S(t)] \qquad (1)$$

where $\rho^S(t)$ is the reduced density matrix of the system S, and $D[\rho^S(t)]$ is the so-called dissipator:

$$D[\rho^S] = \frac{1}{2}\sum_\alpha \left(L_\alpha^\dagger L_\alpha \rho^S + \rho^S L_\alpha^\dagger L_\alpha - 2L_\alpha \rho^S L_\alpha^\dagger\right) \qquad (2)$$

Summation over α extends over all processes of coupling with the environment. The dissipator $D[\rho^S]$ describes the environmental influence on the system. The `jump' operators L_k describe a random evolution of the system which suddenly (at the time scale of the evolution) changes under the influence of the environment.

The first term on the right-hand side describes of eq. (1) the unitary evolution of the system S under the action of a Hamiltonian H.

3.2 Two-level system plasmonic system S_l

The simplest quantum system is a two-level system whose Hilbert space is spanned by two states, an excited state $|l>$ and a ground state $|0>$. The system S is then a sum of S_l of independent, open subsystems: $S = \sum_{l=1,2..} S_l$. Such description is a good approximation for many level systems, provided that the transitions to other than the ground state levels can be neglected so there is no coupling between the modes. Each system S_l is coupled to the environment independently. and all assumptions about the coupling of the S to the environment remain fulfilled for subsystems S_l. The form of the Lindblad equation guarantees, that also dynamics of each matrix operator $\rho^{S_l}(t)$, $\rho^S(t) = \sum_l \rho^{S_l}(t)$ is governed by the equation in the Lindblad form.

The Hamiltonian of a two-level system H_l, $H = \sum_l H_l$. Quantum properties of the cavity mode l are carried by the annihilation a_l and creation a_l^+ mode "amplitudes" (annihilation and creation operators of photons), which satisfy: $[a_l, a_l^+] = a_l a_l^+ - a_l a_l^+ = 1$. The Hamiltonian of the mode l: $H_F = 1/2\hbar\omega_l(a_l a_l^+ + a_l a_l^+) = \hbar\omega_l(a_l a_l^+ + 1/2)$. Dropping the zero-point energy $\hbar\omega/2$ from the Hamiltonian by redefining the zero of energy, we introduce the Hamiltonian H_l for the plasmonic QA in the form: $H_l = \hbar\omega_l\sigma_+\sigma_-$, where and σ_- and σ_+ and are the energy lowering (resulting in photon creation) and energy rising operators (resulting in photon annihilation) in the PQP system).

3.3 Dissipative processes

An excited plasmon, similarly as an excited atom, decays to the state of lower energy spontaneously emitting a photon. In the theory of open quantum systems, such decay is assumed to be due to the coupling of the system to the environment, which introduces radiative losses due to the spontaneous decay (coupling to the EM vacuum fluctuating fields) and heat losses due to the inevitable collisions of electrons in a metal (coupling to a heat-bath in a thermal equilibrium state with an infinite number of degrees of freedom). Dynamics of both coupling processes is assumed to be much faster than those of the open system S_l, so the dynamics of S_l (andthose of S) is Markovian. The jump operators describing these processes are:

$$L_{s,l} = \sqrt{\Gamma_l^s}\sigma_-, \quad L_{col,l} = \sqrt{\Gamma_l^{col}}\sigma_- \qquad (3)$$

where $\Gamma_l^s = \Gamma_l^r$ is the rate of radiative, spontaneous decay and $\Gamma_l^{col} = \Gamma_l^{nr}$ is the rate of nonraditive, collisional losses resulting in absorption and heat production.

3.4 Free evolution of populations and coherences

After algebra involving 2x2 matrices, the Lindblad master equation including radiative and nonradiative dissipation processes one can find the evolution of populations of the excited end ground state $\rho_{ll}(t), \rho_{00}(t)$ and of coherences $\rho_{l0}(t) = \rho_{00}^*(t)$ in the form:

$$\begin{aligned}
\rho_{ll}(t) &= \rho_{ll}(t_0)\exp\left(-\Gamma_l(t-t_0)\right), \\
\rho_{00}(t) &= \rho_{ll}(t_0)\left(1-\exp\left(-\Gamma_l(t-t_0)\right)\right)+\rho_{00}(t_0), \\
\rho_{0l}(t) &= \rho_{0l}(t_0)\exp\left(-i\omega_l-\Gamma_l/2)(t-t_0)\right), \\
\rho_{l0}(t) &= \rho_{l0}(t_0)\exp\left(i\omega_l-\Gamma_l/2\right)(t-t_0).
\end{aligned} \tag{4}$$

where $\Gamma_l = \Gamma_l^r + \Gamma_l^{nr}$.

3.5 Conclusions:

The dephasing of coherences: $\Gamma_l^{coh} = 1/2\Gamma_l$ is twice as slower as damping of populations: $\Gamma_l^{pop} = \Gamma_l$.

The rates of population damping Γ_l^{pop} and Γ_l^{coh} depend on the size of a MNP. For gold and silver nanoparticles these rates can be accessed from our classical model based on the dispersion relation considerations [4]. In gold MNP of several nanometers the damping rates Γ_l^{pop} and Γ_l^{coh} are larger than those in silver, however in larger MNPs of tens of nanometers this relation changes.

4 References

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