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Invited Review

The simplest plasmonic molecules: Metal nanoparticle dimers and trimers

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ABSTRACT

This review discusses research on the plasmonic properties of small clusters of metal nanoparticles, with two and three particles. These are the simplest examples of 'plasmonic molecules'. Coupling between two particles leads to new surface plasmon resonances and to the creation of a hot spot of a strong electric field in the gap between the particles. Such a hot spot can be used to enhance Raman scattering or fluorescence, making plasmonic dimers useful for applications in spectroscopy and sensing. Trimers offer a richer spectrum of options for coupling between particles, which can be analyzed using group theory to obtain the plasmonic modes, in analogy to vibrational modes. Symmetry plays an important role in our understanding of the physics of plasmonic dimers and trimers, and new physical phenomena may appear when the symmetry of a dimer or a trimer is broken, including directional emission, Fano resonances, plane chirality and more. The review introduces some of these concepts, the basic physics behind them and their possible applications. Focus Point sections describing selected outstanding recent developments accompany the review.

Contents

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1. Introduction

Plasmonic molecules (PMs) are combinations of nanoscale metallic structures whose localized surface plasmon resonances (LSPR) interact to form new coupled excitations, similar to the way electrons interact in molecules to form bonds (Fig. 1). The ensuing concerted charge oscillations lead to enhanced electromagnetic fields that, due to the coupling between the particles, are spatially localized in so-called 'hot spots'. The shape and strength of hot spots depends on the geometrical arrangement of the nanoparticles, and can also be modified through other structural parameters, such as the materials, the size and the symmetry of the particles. PMs constitute one type of plasmonic antennas, and several recent reviews were devoted to the latter subject [1–4]. The goal of the current review is more modest and focused: to describe research on the simplest PMs, namely dimers and trimers of metal particles. Much research has been conducted in recent years on the properties of plasmonic dimers (PDs), both in theory and experiment, and there is also a growing bulk of work on plasmonic trimers (PTs). The review will start with a general but brief introduction to LSPR in metal nanoparticles. The discussion of PDs will allow us to introduce theoretical concepts related to the coupling of LSPR excitations, and show how these concepts can be probed experimentally. We will also discuss the utilization of PDs for applied research, including surface-enhanced Raman scattering (SERS) down to the single-molecule level, and various sensing applications. The presentation of PTs will benefit from the concepts already discussed in relation to PD, but new issues will become important, particularly symmetry considerations. We accompany some of the topics by Focus Point sections, each discussing in somewhat greater detail a particular research achievement.

2. LSPR in metal nanoparticles

Localized surface plasmons are collective oscillations of the conduction electrons of nanoparticles (typically made of noble metals [11–13]) that can be excited by light. The time-harmonic electric field of light accelerates the electrons and induces charge oscillations on the nanoparticle surface, while a restoring force is applied by the positively charged nuclei of the metal atoms [11,12]. For spherical nanoparticles, the resulting electromagnetic field and, consequently, the associated surface charge distribution, can be expanded in a series of spherical functions, where each term in the expansion represents a corresponding plasmonic normal mode [11]. Thus, plasmonic modes of an individual sphere are analogs to the electron states of an atom, which are described using the same basis set of spherical functions [14,15].

For nanoparticles that are significantly smaller than the wavelength of the excitation light, it is sufficient to account only for the leading dipolar term of the expansion ($l = 1$). The dipolar model is valid for $ka \ll 1$, where k is the scattering wave vector and a is the radius of a nanoparticle [12]. This condition holds approximately for silver nanoparticles of ca. 50 nm excited with visible light, which typify the systems discussed in the present review. In the dipolar limit a spherical nanoparticle has three dipolar plasmon normal modes represented by spherical functions of orders $m = -1, 0, 1$. Further, because the macroscopic electric field of light that the nanoparticle is subject to is uniform across the nanoparticle dimensions, the electrostatic approximation can be used, which renders the optical response of plasmonic nanoparticles in terms of the familiar expression for polarizability of a sphere [16]. It follows from this result that the plasmon resonance conditions are dictated by the frequency-dependent dielectric properties of the nanoparticle's material. Deviations from this simple picture may occur [17], but are beyond the current level of description.

When the nanoparticles are arranged into a cluster, or a 'plasmonic molecule', the plasmon states of the individual particles strongly interact to form the corresponding cluster states [18], in analogy to molecular orbitals built up by linear combinations of atomic orbitals. (In the case of dipolar states there are $3N$ cluster states, where N is the number of particles.) This analogy is exploited in the plasmon hybridization theory developed by Nordlander and co-workers, which provides an intuitive perspective on the mode structure of PMs [19,20]. Analogous to molecular orbitals, the plasmonic states can be designated as bonding or antibonding, depending on whether the induced charge is distributed in the low or high energy configuration. In addition, depending on the magnitude of their net dipole moment, the modes of the cluster can either appear in the plasmon spectrum collected for the plane-wave excitation (non-zero magnitude, "bright" modes) or be invisible in the dipolar limit (zero magnitude, "dark" modes).

When a PM is composed of more than two nanoparticles, both the energy and shape of its plasmon modes strongly depend on the exact arrangement of the particles. The plasmon mode structure is well-described evoking symmetry analysis based on group theory [21] – a standard tool in molecular spectroscopy [22–24]. The exact arrangement of the nanoparticles within a PM has an essential impact on the symmetry of the resulting plasmonic states. Symmetry-adapted linear combinations (SALCs) of individual particle states, derived with the aid of the irreducible representations of the relevant point group, are known to provide a good basis for understanding the physical states of a symmetric system. Symmetry breaking in plasmonic nanostructures can introduce effects that are not present in the symmetrical configurations. These effects, arising from coupling between otherwise uncoupled plasmon modes of the system, were explored, for example, with individual nanoshells [25], nanoparticle dimers [26] and trimers [27], nanocavities [28], and split-ring resonators [29]. Some of these effects will be discussed below.

3. Plasmonic dimers

3.1. Theoretical concepts

Continuing our discussion within the dipolar limit introduced above, we can introduce the plasmonic modes of a dimer. There are two sets of dipolar modes for a dimer; depending on the direction of the overall polarization (Fig. 2). The interaction between the dipoles, which increases as the distance between the particle decreases, dictates the energetic splitting of the pairs of modes. Plasmon hybridization theory shows how to classify the modes according to their angular momentum (or the order of the spherical functions describing them – see above) [20]. For polarization parallel to the dimer axis (azimuthal quantum number $m = 0$, longitudinal) the low-energy mode has its dipoles arranged parallel to each other (moving in phase with each other, or 'bonding'), while in the high-energy mode the dipoles are arranged tail-to-tail (moving out-of-phase with each other, or 'anti-bonding', see Fig. 2). Since only the former has a finite total dipole moment, it is bright while the latter is dark. For polarization perpendicular to the dimer axis (azimuthal quantum number $m = \pm 1$, transverse) the dipoles are anti-parallel in the low-energy mode (which is therefore dark), and parallel in the high-energy mode (which is bright). Obviously, the energy of the longitudinal bright mode is lower than that of the transverse mode.

The electromagnetic properties of dimers were calculated by multiple authors, using a variety of methods, analytical and