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Research paper

Nanoparticle heterodimers: The role of size and interparticle gap distance on the optical response

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ABSTRACT

Composite plasmonic nanostructures with controlled size, shape and relative arrangement is a subject of significant current research interest. Much of this is stimulated by the prospects by generating enormous near-field enhancements of the surface and interparticle gap regions for potential applications in surface-enhanced spectroscopies. In this manuscript, using time-dependent density functional theory (TDDFT) calculations, we investigate how the optical response in size matched homodimers and size mismatched heterodimers composed of Aluminum modify while varying the size and interparticle gap distances in the sub-nanometer range. Both systems show interesting optical response evolution. In particular, the size mismatched heterodimers show even more complex optical response evolution due to a symmetry-breaking in the system.

1. Introduction

The collective and coherent oscillation of free electrons in metallic nanoparticles (NPs), known as plasmons [1–5], have been widely studied and pursued in various applications spanning from molecular sensing to light manipulation [6–22]. Recent reports have strongly proved that various parameters such as shape, size and chemical composition of the individual NPs can be employed to modify the plasmonic features. Recently, more flexibility in plasmon modification has demonstrated the use of composite NPs. This is because when two or more NPs placed next to each other at a close distance, their plasmons couple to form hybridized modes [23]. This facilitates tuning the plasmonic features such as its intensity and frequency at the desired energy range of the electromagnetic spectrum via red- or blue-shifts. Moreover, it has been shown that when the gap distance shrinks to nanometer or sub-nanometer length-scales, quantum effects such as the nonlocal screening and electron tunelling [24–27,31,28–30] emerges that enables new functionalities that can be used to control plasmon devices.

Since the original work of Nelayah [32] and Bosman [33], a variety of composite nanostructures have been demonstrated, including nanorods (NRs) [34,35], nanocubes [36–38], nanowires [39,40] and ordered NP arrays [41,42]. Among these composite nanostructures, size matched NP pairs known as homodimers are the most investigated system. In this structure, the plasmon coupling increases with decreased interparticle gap distance yielding continuously red-shifted hybridized plasmons until the emergence of electron tunnelling leading to blue-shifting charge transfer plasmons. This structure is of huge interest in various surface-enhanced spectroscopies due to the enormously enhanced local field regions known as "hot-spots" forming in the interparticle gap region. On the other hand, size and shape variations of NPs that occur commonly within typical synthesis techniques accommodates enough structural differences to result in frequent occurrences of size mismatched NP pairs known as heterodimers, though these dimers have reported being more challenging to characterize than the homodimers and give rise to new optical features not seen in homodimers [43].

In this work, with the help of our TDDFT calculations, we investigate how the optical response in homodimers and heterodimers made of Aluminum evolve as a function of the NP size and interparticle gap distance. In the past few years, Aluminum nanostructures have drawn significant attention due to their enthralling optical response in the visible and ultra-violet region of the spectrum [44–50]. TDDFT provides the adequate framework to tackle the optical response of plasmonic nanostructures since it takes into account the quantum behavior of the electrons in their interaction with light. For example, in a pioneering study, Zuloaga and co-workers [51] used TDDFT to perform a fully quantum mechanical calculation of the linear response of plasmonic dimers. Other groups extended this study to treat both linear and nonlinear effects in a variety of gap configurations [52–58,63].

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2. Computational aspects

In the present work, the absorption spectra are calculated using Casida's linear response formalism in the frequency domain [67] as implemented in Turbomole software [64–66]. We use the BP-86 generalized gradient approximation (GGA) to the exchange and correlation energy and a triple-zeta plus polarization (TZP) basis set. The multipole accelerated resolution of identity method is used for the Coulomb term and quadrature grids of m3 quality are employed. It should be emphasized that the use of semi-local xc-functionals for computing the optical properties of simple metals like aluminum yields quantitatively correct results [58–62]. This is mainly because it contains only *sp* electrons and misses the computationally difficult *d* electrons. We found that BP-86 GGA xc-functional together with the resolution of identity method speeds up our TDDFT calculations significantly. The optical spectra are computed by solving the following eigenvalue equation,

$$\Omega F_I = \omega_I^2 F_I \tag{1}$$

where Ω is a matrix consisting of products of occupied-virtual Kohn-Sham orbitals and the eigenvalues ω_I^2 correspond to squared excitation energies while the oscillator strengths are extracted from the eigenvectors F_I. The number of dipole-allowed transitions (roots) should be high enough to cover the desired range in the absorption spectrum. We found 1500 roots is adequate to cover the spectrum up to an energy of 4.5 eV. All absorption spectra are broadened by a Gaussian smearing of width $\sigma = 0.1$ eV.

3. Results and discussion

We consider the symmetric NPs with face-centered cubic structure, composed of a central atom and successive shells with increasing distance from this center. No constraints are imposed during the structural relaxations of the NPs. Before discussing the optical response of dimers, let us start by briefly discussing the optical response of a series of individual NPs with sizes ranging from 5 to 15 Å in the energy range of 1–4.5 eV, see Fig. 1. One observes that the optical response of the smallest NP (5 Å) exhibits a series of narrow peaks but does not show any dominant peak. Upon increasing the NP size to 12.5 and 15 Å, the optical response changes drastically: the peaks become flattened. A smoother optical response with larger NP sizes is not unexpected because a large number of electrons in the system will transform the system gradually towards a bulk-like system. To illustrate the nature of plasmon coupling occurring in the dimers, we present the results for gap distances that are continuously reducing from large to small gap distances of 8–3 Å. It is worthwhile to mention that although the NPs employed in this work are smaller than those used in realistic experimental conditions, it still allows us to perform a qualitative study of plasmon coupling and gaining key information regarding the quantum effects. In several recent experiments and theoretical studies, it has been shown that when two plasmonic NPs placed next to each other forming a NP dimer, the plasmons of the individual NPs interact, resulting in coupled plasmon modes with energies that can be strongly red- or blue-shifted relative to the plasmons of the individual NPs. The interaction energy of a NP dimer can be written using a simple equation of the form, $V \propto P_1P_2/D^3$, where P_1 and P_2 are the magnitudes of the dipole moments [68].

To understand the plasmon coupling in dimers, we start by analyzing the optical response of homodimers made of NPs with size of 15 Å via gap distance variations from 8 to 3 Å (see Fig. 2). It should be recalled that the homodimers retain a higher symmetry in comparison to heterodimers and one expects this will have significant implications in the absorption spectra. Note that the 15 Å individual NP exhibits multiple peaks in the spectrum, though flattened. Interestingly, when the interparticle gap distances reduced to 8 or 6 Å, there appears a strong plasmon in the visible region (between 2.5 and 3.0 eV) of the electromagnetic spectrum. It is evident from Fig. 2 that for a gap distance of 5 Å, due to the increased electron tunelling, there appear dramatic modifications in the plasmon characteristics in the form of extraordinarily large plasmon energy-shifts. This is because as the gap distances between two NPs get shorter, the potential barrier becomes narrower, leading to the electron tunnelling that extremely modifies the optical response. We note that small sizes of NPs used in this study should be taken into account when deriving quantitative conclusions about the onset of quantum effects. We believe that for a dimer consisting of bigger NPs, realistic for experimental studies, the overlap of the electronic wavefunctions could increase to give rise to an earlier onset of quantum effects.

Let us now focus our attention on various heterodimers. One may expects that the heterodimers give rise to new optical features not seen in homodimers [43]. To this aim, we present the spectral evolution of two different heterodimers: a slightly size mismatched one (see Fig. 3) and a heavily size mismatched one (see Fig. 4). It is intriguing to see how the optical response get modified in comparison to that of the homodimer. Let us first start with a heterodimer composed of 15 and 12.5 Å NPs, see Fig. 3. Note that both the individual NPs exhibit multiple peaks in the spectrum but largely flattened. As the gap distances reduce to 8 or 6 Å, there

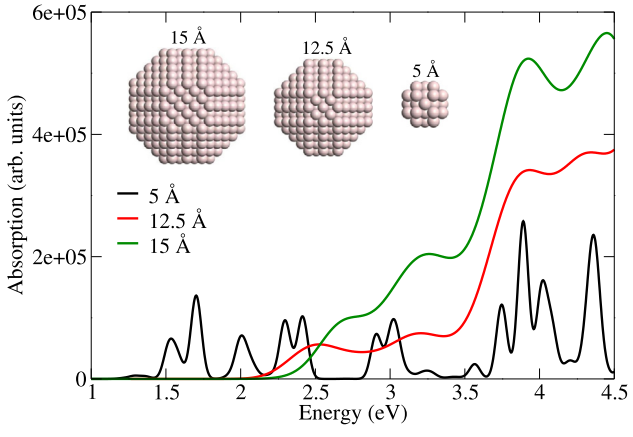

Fig. 1. The absorption spectra of Aluminum NPs of different sizes computed using TDDFT.

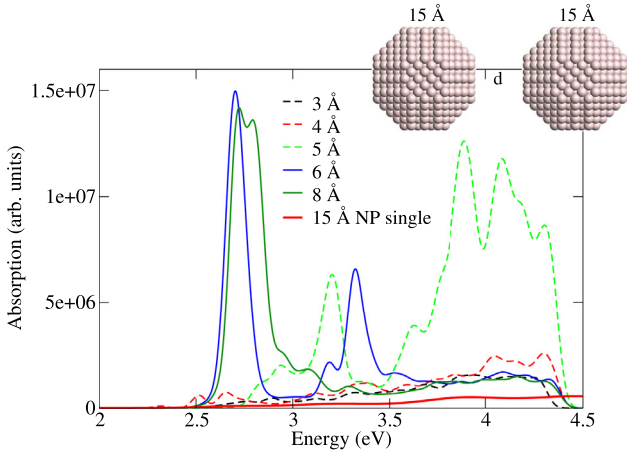

Fig. 2. The absorption spectra evolution of size matched Aluminum homodimers made of NPs of 15 Å size as a function of *d* (in units of Å).