Novel Electronic and Magnetic Properties of a Metal Nanoparticle Dimer

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Summary: A collaboration between two CMSN programs, one on strongly-correlated systems (Eguiluz) and the other on nanomaterials for energy (Zhang) —PCSCS and NANO, respectively— has been devoted to the study of the electronic, magnetic, and optical properties of coupled metal nanoparticles. They have shown [1,2] that the electronic coupling and magnetic moment of a silver nanoparticle dimer *can be easily tuned by applying an external electric field*. For a given interparticle separation, the electronic coupling becomes tunable as soon as the system crosses over to the nonlinear dielectric-response regime. Remarkably, *the non-linear regime sets in for rather weak electric fields* —for which the nanoparticles in the dimer, if isolated, respond linearly. This effect represents a signature of the unique electronic environment in the dimer gap. In the crossover to the non-linear regime, the HOMO-LUMO gap of the dimer is closed by Stark shifts, and this is accompanied by the emergence of a net magnetic moment —from two nonmagnetic clusters. These findings, obtained within density-functional theory, exhibit the delicate coupling between the electronic and magnetic degrees of freedom, and point to new approaches to gain multifunctionality of nanoparticle aggregates.

The explosive current interest in nanosystems is traced to the fact that the physical and chemical properties of these systems often are significantly different from those of both individual atoms and bulk matter. The hope —and challenge— is that those properties may be tuned to maximize fundamental insights and/or technological impact. This situation can be visualized from the fact that the energy levels of nanosystems lie in between the discrete, well-separated energy levels of atoms and the continuous spectra of extended, condensed-matter systems. Thus, one expects that "tuning" the energy levels may lead to unique manifestations of an interplay between electronic, magnetic (spin), and vibrational degrees of freedom, on a spatial scale inherent to matter at the nanoscale. Examples include metal-insulator transitions in compressed nanoparticle superlattices [3] and enhanced local optical response of nanoparticle pairs, the latter being an important ingredient of surface-enhanced Raman spectroscopy [4,5].

We have demonstrated [2] the existence of a critical value of the separation *S* between two nanoparticles (e.g., those in Fig. 1; see also the inset in Fig.2), which we refer to as "optimal gap size" (OGS), for which the (linear) polarizability of the dimer is maximized. The OGS was traced to maximal overlap between orbitals from both nanoparticles, as they approach each other. Such maximum in the polarizability *vs. S* can be extremely sharp for appropriate dimer geometries. This is the case for the (Ag₁₈)_{2t-t} dimer shown in Fig. 1 (our nomenclature will be defined shortly), for which the OGS occurs for S=1.67*d*, where *d* is average interlayer

thickness d of the nanoparticle (see Fig. 1). This discovery has led to suggestions about tunability of certain electronic properties [2].

Now the presence of an external electric field introduces a new energy scale, the Stark shift of the HOMO-LUMO gap. Tuning this shift (and thus the gap), the magnetic (spin) degrees of freedom may display unusual properties due to changes in occupancies of states with either spin projection. Moreover, the very concept of the OGS and related properties of the polarizability, suggests that a subtle interplay between electronic and spin degrees of freedom may result by tuning the strength of the electric field. The surprise is not that we have found that such interplay is actually realized, but rather that the same is achievable for field



Fig. 1. Atomic configurations of $(Ag_{18})_2$, nanoparticle dimers with tip-tip (left) and planeplane (right) orientations. In both cases the dimer axis is along [100], and d = 1.9Å.

strengths that are actually quite weak—i.e., weak enough that in the absence of the dimer gap (isolated nanoparticles) the system would respond linearly.

We have considered [1,2] silver nanoparticle dimers made up of identical 18-atom and 14-atom Ag clusters, respectively, and have allowed for two different orientations (Fig. 1): tip-tip (t-t) and plane-plane (p-p). The dimers are referred to as $(Ag_n)_2$, where *n* is the number of atoms in each nanoparticle —which is a fragment of bulk silver in the face-centered cubic structure. The coordinates of each individual cluster have been relaxed. Our density-functional theory calculations were performed within the local spin-density approximation. The Kohn-Sham (KS) equation *was solved in the presence of a static, uniform electric field*, directed along the dimer axis, using a higher-order finite-difference real-space method [6], which is ideally suited for finite systems. In the brief outline presented herein, we will refer only to the case of the $(Ag_{18})_{2t-t}$ dimer, for which our findings are the most striking. A full discussion of the role played by cluster orientation, by dimer-axis orientation (along [100] and [111]), and by the number of particles in the clusters, is presented in [1,2].

In order to characterize the dielectric response of the system, we study the ratio P/E, where P is the calculated dipole moment (Fig. 2). Of course, in the linear response regime, P/E is independent of E. Thus, as a reference, we first studied the isolated Ag₁₈ nanoparticle and found that its dipole moment exhibits a linear response up to $E_L \sim 0.25 \text{ eV}/(\text{Å/e})$. This field strength provides a natural scale of field strength, in the present context. Now the physics of the response in the dimer depends on the interplay between two variables: The gap size S and the field strength E. We illustrate the role of both variables in Fig.2:

First, in Fig. 2a P/E is shown vs. E. The key issues are as follows: (i) for S=1.67, which as noted above, corresponds to the OGS, the P/E curve is indeed independent of E; *thus, the corresponding response is linear*; (ii) however, as we increase the value of S beyond

this threshold (three such values are considered), the system switches abruptly to the non-linear regime, in which P/E clearly depends strongly on the value of E, even for very weak E-values —much weaker than E_L defined above! (The "saturation" of the P/E curves for large E-values is explained in [1] as resulting from increased Columb interaction effects, coupled with vanishing of the level-crossing effects discussed below.)

Second, in Fig. 2b P/E is shown vs. S, for three values of E. It is apparent that when the clusters are in the so-called 'strongcoupling" (strong orbitaloverlap) regime, which corresponds to S<OGS, the ratio P/E is independent of the field strength ---the system responds linearly. However, as soon as S grows beyond the OGS, the *P/E curve depends strongly* on the value of E; so much so that for large S the polarizability does not approach the "expected" independent-neutral clusters limit, which is only obeyed by the linear-response curve in Fig. 2b. [In fact, it is





Fig. 2. For $(Ag_{18})_{2t-t}$: (a) The ratio *P/E vs.* field strength *E* for increasing dimer gap size *S* (in units of *d*, see Fig. 1), starting from *S*=1.67 (= OGS). (b) The ratio *P/E vs. S*, for several values of *E*; note that for weak field strengths such as *E* = 0.026 and 0.052 eV/(Å/e) *the response is strikingly non-linear for S*>OGS.

instructive to note that for the present case of $(Ag_{18})_{2t-t}$ the response is so intrinsically nonlinear for *S*>OGS, that the result labeled as "linear response" in Fig. 2b —corresponding to the weakest possible value of *E* consistent with our numerical accuracy for the solution of the KS equation— was obtained via a "constrained" calculation in which the occupation numbers for each spin projection were kept fixed to their values for *S*<OGS! Otherwise, the behavior represented by the non-linear results in Fig. 2b is unavoidable, and the limit of the polarizability of twice that of the isolated clusters is not realized.]

In summary, from Fig. 2 we have that for $(Ag_{18})_{2t-t}$ the switch over to the non-linear regime is very sharp, and beyond S=1.67 the response becomes nonlinear for the smallest field we can use in our numerical study. The physical picture behind this result is the impact of the electronic coupling (orbital overlap) on the HOMO-LUMO gap of the dimer. The response of the dimer to an electric field is controlled by the parameter $E \cdot S/\Delta\varepsilon$, where $\Delta\varepsilon$ is the HOMO-LUMO gap (in the absence of the field), and $E \cdot S$ is a measure of the applied voltage; a large value of $E \cdot S/\Delta\varepsilon$ favors the nonlinear regime. For well-separated nanoparticles, the electronic coupling between them causes the formation of bonding and antibonding orbitals and reduces the HOMO-LUMO gap of the combined system. For the case of $(Ag_{18})_{2t-t}$, the HOMO-LUMO gap closes at the critical separation S=1.67. Therefore the system responds nonlinearly beyond S=1.67 even for a very weak electric field (much smaller than E_L). The onset of the non-linear response signals a significant change in the energy spectrum, and this may lead to novel emerging properties. Here we focus on *electric-field induced magnetic* properties of the dimer. Figure 3a shows the net magnetic moment of $(Ag_{18})_{2t-t}$ as a function of *E* for two separations beyond the OGS, S=1.95 and S=2.23 —which, as discussed above, correspond to the non-linear dielectric-response regime. Remarkably, the net magnetic moment changes as a function of the applied field, going from zero at *E*=0 to 2 µB at *E*=0.26 eV/(A/e). As a reference, Fig. 3a also shows the magnetic moment for *S*=1.39, for which the dimer is in the linear regime, for the values of *E* in question. As expected, when the dimer is in the linear regime (*S*=1.39), the net magnetic moment remains constant for all *E*.



Fig. 3. For $(Ag_{18})_{2t-t}$: (a) Net magnetic moment as function of the applied electric field, for S=1.39, 1.95, and 2.23 (in units of *d*). (b) Energy levels around the HOMO-LUMO gap (labeled by the numbers to the right of the legend) as function of *E* for S=1.95. An arrow pointing up (down) indicates that a spin up (down) level is occupied.

The above result for the magnetic moment is closely tied to the Stark-shifted HOMO-LUMO gap. Figure 3b shows the dependence of the energy levels around the HOMO on the applied electric field strength, for S = 1.95. Now at E = 0, the HOMO-LUMO gap is finite and the occupation numbers for the spin-up and spin-down states are the same, yielding a vanishing magnetic moment. When *E* increases, the HOMO-LUMO gap decreases *and the energy levels* split into spin-resolved levels. Eventually, the HOMO and LUMO cross each other and

exchange their spin indices, leading to a net magnetic moment of 2 μ_B . This physics can be easily visualized in terms of the cartoon presented to the right, which pertains to similar physics realized on going from the weak-coupling limit (large S) to the large-coupling limit (S<OGS): The HOMO and HUMO levels aproach each other, eventually crossing each other, followed by exchange of spin indices. The result is the formation of a magnetic from non-magnetic building moment blocks.



The shift of the energy levels of the dimer, and therefore the decrease of the HOMO-LUMO gap, can have important manifestations in many physical and chemical properties of the system

—such as the charge transfer between the nanoparticles. The importance of the HOMO-LUMO gap and the electronic coupling have been pointed out in the electron transport in single conjugated organic molecules [7] and in the charge transfer process between two Si quantum dots. [8] Our results show that these phenomena may be fine-tuned by varying the electric field. In addition, given the similarity between nanoparticles and molecules, our results may also have important implications in quantum transport in molecular devices.[9] When the molecule is in touching contact (strong overlap) with the leads, the usual linear-response assumption must be taken with great caution, as a tiny bias voltage may lead to the nonlinear behavior discused herein.

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