

Electronic Coupling and Optimal Gap Size between Two Metal Nanoparticles

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We study the electronic coupling between two silver nanoparticles using *ab initio* density functional theory for real atoms. We show that the electronic coupling depends on both the gap size of the dimer system and the relative orientation of the particles. As the two particles are separated from touching contact, the dimer undergoes a bond-breaking step, which also establishes the striking existence of an optimal gap size defined by a maximal static polarizability of the dimer. For some dimers, the electronic coupling before the bond breaking can be strong enough to give rise to a net magnetic moment of the dimer, even though the isolated particles are nonmagnetic. These findings may be instrumental in understanding and controlling the physical and chemical properties of closely packed nanoparticle aggregates.

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Nanoparticles have been the focus of intense recent interest because of their potential usage as building blocks for new functional materials and devices at the nanoscale. Many interesting phenomena have been observed when such particles are closely aggregated [1] and start to interact with each other. Examples include metal-insulator transitions in compressed nanoparticle superlattices [2] and enhanced local optical response of nanoparticle pairs, with the latter being an important aspect of surface-enhanced Raman spectroscopies (SERS) [3–7]. Therefore, a solid understanding of the interparticle coupling is of tremendous significance in both fundamental studies and applications of nanotechnology.

A nanoparticle dimer provides the simplest system to investigate how the interparticle coupling depends on the system geometry and how it affects the physical properties of the system. The majority of existing theoretical studies assumes a classical electromagnetic coupling between the particles [3–6]. It has led to the prediction of a monotonic increase of the static polarizability and local field enhancement with decreasing dimer gap size. However, at shorter distances, in particular, when nanoparticles are in touching contact [8–10], this treatment is bound to fail because the nanoparticles can also be coupled due to the overlap of wave functions from neighboring particles [11]. While recent studies focused on simplified models [12,13], a quantum mechanical treatment based on real atoms is crucial in order to accurately describe the touching contact limit.

In this Letter, we present the first comprehensive study of the electronic coupling between two metal nanoparticles using *ab initio* density functional theory with real atoms, and silver nanoparticles of varying sizes as prototype systems. We find that the coupling between the nanoparticles shows a strong dependence on the dimer gap size and relative orientation of the particles. When two particles are separated from touching contact, the dimer undergoes a

bond-breaking step, and the coupling strength crosses over from the strong to weak regime. This transition step also establishes the striking existence of an optimal gap size (OGS), defined by a maximum in the static polarizability of the dimer, an important finding in sharp contrast to the monotonic decrease predicted by classical theories. Moreover, depending on the particle size and their orientation, the electronic coupling before the bond breaking can be strong enough to give rise to a net magnetic moment of the dimer, even though the isolated particles are nonmagnetic. These findings may prove to be instrumental in understanding and controlling various physical and chemical properties of closely packed nanoparticle aggregates, as revealed by our discussions of their potential impact on SERS from nanoparticle arrays and quantum transport in related systems.

We choose silver nanoparticle dimers as our representative systems. We have studied four distinctive configurations of dimers, as illustrated in Fig. 1. These dimers are referred to as $(Ag_n)_2$ where n is the number of atoms within each particle. We have chosen $n = 14$ and 18, and two different orientations of the nanoparticles, namely, tip-tip ($t-t$) [Figs. 1(a) and 1(c)] and plane-plane ($p-p$) [Figs. 1(b) and 1(d)]. The calculation of the electronic structure and response was carried out using the finite difference pseudo-potential method in real space within the local spin-density approximation [14,15]. We used improved Troullier-Martins potential [16], generated from the $4d^{10}5s^15p^0$ configuration with core radii of 1.24 Å [17]. The exchange-correlation functional was chosen as that of Ceperley and Alder [18], parametrized by Perdew and Zunger [19]. For a given dimer, each of the particles is structurally relaxed so that the maximum magnitude of the force on any atom is smaller than 0.07 eV/Å [20].

The strength of the electronic coupling can be measured by the planar charge density λ at the center of the nanogap, defined by $\lambda = |q|/\Delta|_{\Delta \rightarrow 0}$, where q is the total charge in

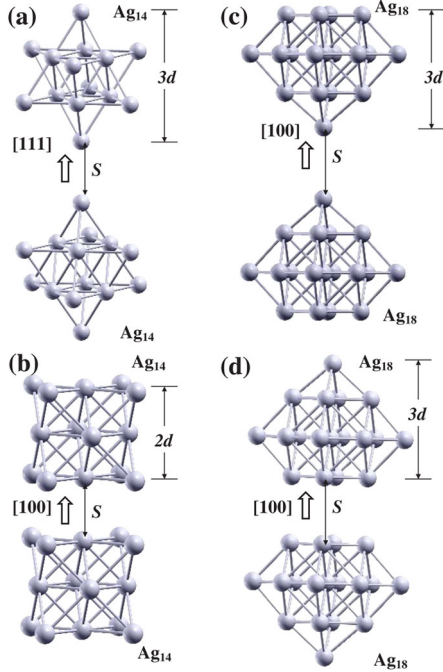


FIG. 1 (color online). Structures of dimers of silver nanoparticles. (a), (c) $(Ag_n)_2$ ($n = 14, 18$) with t - t orientation, (b), (d) $(Ag_n)_2$ ($n = 14, 18$) with p - p orientation. $d = 2.2$ Å for $(Ag_{14})_{2,t-t}$, 2.0 Å for $(Ag_{14})_{2,p-p}$, and 1.9 Å for $(Ag_{18})_2$ along both orientations. The dimer axis is along $[111]$ in the t - t and p - p orientations of $(Ag_{14})_2$.

the infinitely large slab shown in the inset of Fig. 2, and Δ is the thickness of the slab. Figure 2 shows λ as a function of the gap size S , which is measured in the units of the average layer thickness d of the nanoparticle throughout this Letter (see Fig. 1). For both particle sizes, the t - t orientation gives a significantly smaller charge density than the p - p orientation. This is because in the former case, only one atom at the tip of each nanoparticle directly faces each other; while in the latter, there are more than one atom. The weakest coupling in $(Ag_{14})_{2,t-t}$ among all four configurations results in its significant differences from others in various physical properties, as illustrated later.

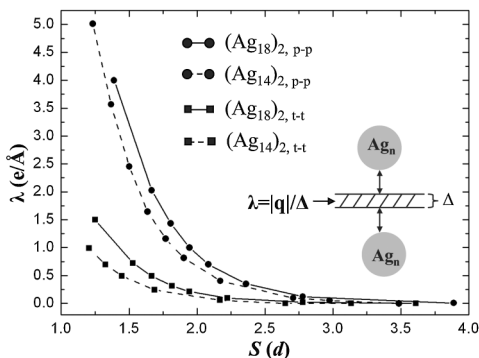


FIG. 2. Planar charge density λ in the nanogap of $(Ag_n)_2$ ($n = 14, 18$), for various gap sizes S in terms of the average layer thickness d of the corresponding nanoparticle.

Now we study the linear response of the dimers to an external electric field, which is expected to be strongly influenced by the coupling between the two nanoparticles. In our study, the response is measured by the static polarizability given by $\alpha_{zz} = \partial P_z(\vec{E})/\partial E_z|_{\vec{E}=0}$, where P_z is the dipole moment of the system along the dimer direction, and $\vec{E} = E_z \hat{e}_z$ is the external electric field [14,15]. We only consider the α_{zz} component because it is most sensitive to the dimer gap size among all the components. The polarizability was calculated using a finite field method, and the electric field was chosen to be sufficiently small so that the response is in the linear regime [21]. Surprisingly, the polarizability of a single Ag_{14} nanoparticle is almost identical along both the $[111]$ and $[100]$ directions, despite the anisotropic shape of the nanoparticles.

Figure 3(a) shows α_{zz} as a function of the gap size S , which displays a pronounced peak at the OGS for all four dimer configurations. However, unlike the isolated particle case, the orientation dependence becomes significant when the particles form a dimer: for the same particle size, the t - t orientation gives a significantly higher value of the maximum polarizability and a smaller OGS.

The physics behind this striking result, and the very existence of the OGS is as follows: a bond breaking occurs during the transition from strong to weak electronic coupling between the two nanoparticles as they become far

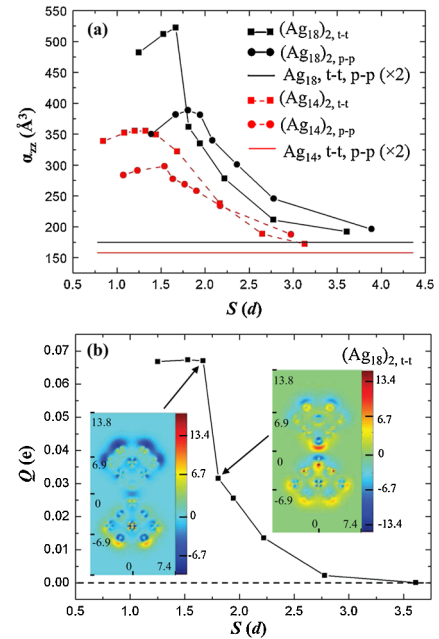


FIG. 3 (color online). (a) Static polarizability α_{zz} of $(Ag_n)_2$ ($n = 14, 18$) as a function of S . (b) Transferred charge Q from one nanoparticle to the other as a function of S in $(Ag_{18})_{2,t-t}$. The magnitude of the applied electric field is 0.013 eV/Å/e. Q is measured in units of e , the charge of an electron. Insets: spatial distributions of the induced charge density in the (100) lattice plane containing the dimer axes, at the OGS and right beyond it. The unit is Å for the spatial coordinates (left) and $e/\text{Å}^3$ for the color bar (right).

apart. Here, the bond refers to the channel for the charge flow between two nanoparticles. When two nanoparticles are very close to each other, a strong bond connecting them exists and charge can flow freely from one particle to the other. In this strong coupling regime, the trend of the polarized charge to recombine decreases with an increasing gap size S , leading to an increasing polarizability. When S continues to increase, the bond breaks down and the flow of charge is discounted, eventually to zero. For a dimer in this regime, the contribution of the classical electromagnetic coupling becomes dominating, leading to the monotonic decrease of the polarizability.

To demonstrate the above argument, we have calculated the transferred charge Q between the nanoparticles as a function of S , as shown in Fig. 3(b) for $(\text{Ag}_{18})_{2,t-t}$. As we can see, when S is smaller than the OGS, Q maintains a relatively constant value, while beyond the OGS, Q decreases sharply and eventually turns to zero. On the other hand, Q is clearly nonzero even at $2.5d$, indicating the remaining of a weak bond at this large gap size. The insets of Fig. 3(b) are the corresponding spatial distributions of the induced charge density in the (100) lattice plane containing the dimer axes, at the OGS and right beyond it. There is a dramatic redistribution of charge density when the gap size is beyond the OGS with appreciable amount of charges accumulating near the gap region, which is consistent with our argument that beyond the OGS, the charge ceases to flow between two nanoparticles. Dramatic charge redistributions were also seen in $(\text{Ag}_{18})_{2,p-p}$ and $(\text{Ag}_{14})_{2,p-p}$. A similar charge redistribution has been reported in a previous study based on the jellium model [12]. On the other hand, we found that unlike $(\text{Ag}_{14})_{2,p-p}$, the charge redistribution in $(\text{Ag}_{14})_{2,t-t}$ is always a gradual process. Such an orientation dependence is absent in the jellium model.

The electronic coupling not only affects the electronic but also the magnetic properties of the dimer. Figure 4(a) shows the net magnetic moment μ of the dimer as a function of the gap size S . The distinct feature of all the dimers except for $(\text{Ag}_{14})_{2,t-t}$, is the sudden occurrence of a net moment as the two nanoparticles approach each other, although both isolated Ag_{14} and Ag_{18} are nonmagnetic. We note that the net moment emerges at the OGS, beyond which the induced charge density dramatically redistributes.

To understand the appearance of the magnetic moment, we have plotted energy levels near the energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO gap) as a function of S for $(\text{Ag}_{14})_{2,p-p}$ in Fig. 4(b), and $(\text{Ag}_{14})_{2,t-t}$ in Fig. 4(c). When S is large, the HOMO is at least fourfold degenerate: two are from the spin degrees of freedom and the other two account for the number of identical particles. As the particles approach each other, the HOMO-LUMO gap decreases, and these energy levels split into different branches with the spin degeneracy intact. This splitting is

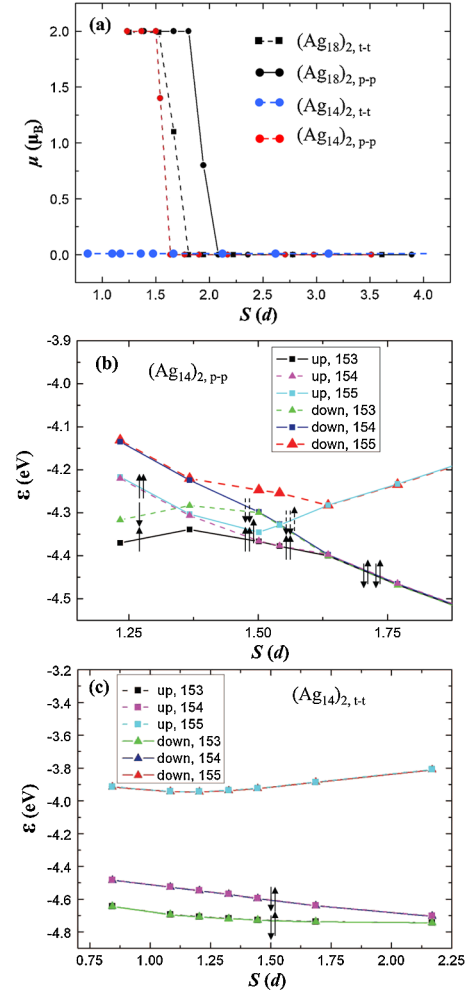


FIG. 4 (color online). (a) Net magnetic moment of $(\text{Ag}_n)_2$ ($n = 14, 18$) with various gap sizes S . (b) Energy levels around HOMO-LUMO gap of $(\text{Ag}_{14})_{2,p-p}$. (c) Energy levels around HOMO-LUMO gap of $(\text{Ag}_{14})_{2,t-t}$. In (b) and (c), a solid arrow pointing up (down) means a spin-up (down) level has an occupation of one, while a dotted arrow indicates a fractionally occupied level. The numbers following “up” and “down” in the legends of (b) and (c) index the electron energy levels.

due to the increased coupling between the two particles, corresponding to a bond formation process. When the gap size further decreases, the electronic coupling becomes even stronger, which splits the energy levels into spin-resolved levels, and the original HOMO and LUMO cross each other. In the end, there are three occupied spin-up levels and one occupied spin-down level, giving rise to a net magnetic moment of $2\mu_B$. The splitting into spin-resolved energy levels is in direct analogy with the Heitler-London model for diatomic molecules [22]. On the other hand, in the case of $(\text{Ag}_{14})_{2,t-t}$, although the HOMO splits into two branches because of the electronic coupling, it is never strong enough (see Fig. 2) to lift the spin degeneracy. This is why in this case, we observe no appearance of a net magnetic moment.

The simultaneous appearance of magnetic moment and the dramatic redistribution of induced charge density for $(\text{Ag}_{14})_{2,p-p}$ and $(\text{Ag}_{18})_2$ is not a coincidence. Let us consider a process in which the particles are pulled away from each other. Below and beyond the OGS, the HOMO-LUMO gap remains finite and the occupied wave function under external field changes adiabatically with the gap size S . Around the OGS, the HOMO and LUMO cross each other, which breaks the adiabaticity and changes the characteristic of the occupied wave function, leading to a dramatic change of the charge density. In the case of $(\text{Ag}_{14})_{2,t-t}$, because the HOMO and LUMO do not cross each other, such a dramatic redistribution is absent.

The bond breaking picture discussed above is expected to be enlightening in understanding various physical and chemical properties of closely packed nanoparticle aggregates. One example is SERS [3–7]. As demonstrated above, the electronic coupling can strongly affect the static polarizability of a dimer by modifying its energy spectrum. We expect similar effect on the dynamic polarization as well, which characterizes the optical response of the system. It can be generalized to the SERS when a molecule is trapped in the dimer gap. By changing the gap size, the electronic coupling between the molecule and the nanoparticles can be tuned to make the energy levels match the optical resonance condition for SERS.

The bond breaking also has important implications in transport phenomena. The fact that even at $S = 2.5d$ the electronic coupling is still relevant suggests that a nanowire can be stretched to more than its bulk lattice spacing yet still conducts. Indeed, there are experimental reports of similar phenomena for atomic chains [23–25]. In addition, the appearance of a net magnetic moment, and particularly the level crossing effect, points out a possible way to generate spin-polarized current in these nanostructures. This ramification will be the focus of a forthcoming work.

In summary, we have shown that the electronic coupling between two metal nanoparticles depends strongly on both the gap size and the relative orientation of the nanoparticles. As the gap size increases from touching contact, the dimer undergoes a bond-breaking step, which establishes the striking existence of an OGS for static polarizability. Moreover, depending on the particle size and orientation, the electronic coupling before the bond breaking can be strong enough to give rise to a net magnetic moment of the dimer, even though the isolated particles are nonmagnetic. These findings may prove to be instrumental in understanding and controlling the physical and chemical properties of closely packed nanoparticle aggregates.

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