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Quantum spin transport through magnetic superatom dimer (Cs_8V - Cs_8V)

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Theoretical studies of the spin transport through a magnetic superatom dimer (Cs_8V)-(Cs_8V) have been carried out within a density functional theory combined with nonequilibrium Green's-function formalism. It is shown that the electronic transport is sensitive to the binding site as well as the contact distance between the dimer and the electrode, and that the conductance at zero bias exhibits an oscillatory behavior as a function of the contact distance. The conductance in ferromagnetic state shows an unusually high spin polarization that exceeds 80% at large separations. The I - V curve shows negative differential resistance for specific contact distances, whose origin lies in the shift of frontier energy levels as well as the charged state of the superatom, under external bias. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4763461>]

I. INTRODUCTION

An exciting development in the field of clusters and nanostructures is the finding that the electronic states in small symmetric clusters of metallic elements are grouped into electronic shells that can be labeled by the principal and angular momentum quantum numbers ($1s$, $1p$, $1d$, $2s$, $1f$, etc.) reminiscent of electronic shells in atoms.¹ The electronic, magnetic, and chemical features of clusters are found to be governed by the shell occupation. In particular, clusters with filled electronic shells are found to be more stable as seen via the mass spectra of clusters generated in beams and clusters with large gaps between the filled and unfilled shells show inertness in reactivity. These analogies have given rise to the conceptual basis that selected clusters could be classified as superatoms.^{2,3} Unlike atoms, the electronic shells in superatoms, however, span over multiple atoms and are intimately coupled to the atomic structure. The partial filling of electronic states often lead to species with lowest spin multiplicity (doublet for odd electron and singlet for even electron systems) as the cluster can break orbital degeneracy through structural deformations thus lowering the energy via Jahn-Teller distortions over exchange coupling.⁴ One way to stabilize magnetic species is to implant transition metal atoms in the cluster to generate mixed species where the localized d -states of the transition metal form the higher occupied molecular orbitals (HOMO). Such mixed clusters can possess high spin moments as the localized atomic states with large exchange coupling become occupied with unpaired electrons following the Hund's rule. In addition, the deeper shells of diffuse orbitals, if filled, can stabilize the magnetic species through superatomic shell closure. We recently demonstrated this intriguing finding via studies on a Cs_8V cluster⁵ that had a filled shell sequence $1s$, $1p$ with 8 electrons and a shell of five unpaired higher occupied d -states, mostly localized on V, leading to a spin magnetic moment of $5 \mu_B$. Preliminary calculation of the spin transport through such an assembly

showed that the superatom-dimer could be a highly efficient spin polarizer leading to an almost 100% spin polarization.⁶ These studies were based on a single location of the superatom dimer on the lead surface.

In this work, we present a detailed investigation of the transport properties through superatomic dimers to examine other features offered by such a device. Ordinary molecular devices⁷ are known to exhibit a wide range of interesting phenomena including negative differential resistance (NDR),^{8,9} rectification,¹⁰ and current switching.¹¹ These features are desirable for applications in processors, molecular switches, logic cell, and memory devices.¹² We wanted to examine if a superatomic molecular device could also exhibit these features. To examine this, we have carried out transport studies by positioning the superatomic motif at various locations on a gold surface and allowing various superatom-electrode separations. Note that since each superatom contains delocalized superatomic orbitals and localized d -orbitals, the formation of bonds in superatomic molecules proceeds mainly by the overlap of diffuse orbitals providing a gas of nearly free electrons for conduction. The V d -orbitals, breeding the magnetic character, are localized, and can polarize the electron gas without introducing strong spin-orbit interactions. Such a combination is ideal to maintain spin coherence over longer distances. Through investigations of different molecular conformations corresponding to possible contact geometries and variations in the contact distance of the superatom, we show that the device can not only act as a strong spin polarizer but also that variations in the superatom-electrode separation change the coupling between the superatom and the electrode and can lead to NDR at selected bias voltages. We would like to add that while there have been previous works on the oscillatory conductance in clusters, the transport through magnetic clusters and in particular, magnetic superatomic species, has not been previously studied. As we will show, an analysis of the shift of frontier energy levels along with the change in charge state of the superatom under external bias provides a microscopic mechanism for the oscillatory conductance and NDR behavior.

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II. CALCULATION METHOD

The theoretical investigations of the transport were carried out in two steps. We first examined the ground state of a $\text{Cs}_8\text{V}-\text{Cs}_8\text{V}$ dimer attached to a gold surface by carrying out molecular orbital calculations and placing the dimer at various locations on a $\text{Au}(001)$ surface. For each orientation of the Au surface, the atoms were allowed to relax in the direction of forces till the Au forces dropped below a threshold value of $0.05 \text{ eV/\AA}$. The cluster was then sandwiched between two Au electrodes placed symmetrically on both sides. The electronic transport was monitored using the Keldysh nonequilibrium Green's-function formalism (NEGF) within a self-consistent density functional theory. The exchange correlation effects were incorporated using generalized gradient approximation using the form proposed by Perdew-Burke-Ernzerhof.¹³ Double-zeta basis sets with polarization functions were used on Cs and V atoms, while a single-zeta basis set was used for Au. The actual calculations were carried out using the set of codes as implemented in the Atomistix ToolKit.¹⁴⁻¹⁷

The spin current was calculated by the nonequilibrium Green's function approach based on the Landauer-Büttiker formula¹⁸

$$I_\sigma = \frac{e}{h} \int_{\mu_L}^{\mu_R} T_\sigma(E, V_b) [f_l(E - \mu_L) - f_r(E - \mu_R)] dE.$$

Here, $\mu_{L,R}$ are the chemical potential for left-electrode (L) and right-electrode (R), respectively. For a given bias voltage, V_b , $[\mu_L(V_b), \mu_R(V_b)]$ represents the energy region that contributes to the current integral and is usually referred to as the bias window. In the presence of external bias, the electrochemical potential in the left/right electrode ($\mu_L(V_b)$, $\mu_R(V_b)$) is shifted to $\mu_L(V_b) = \mu_L(0) + eV_b/2$ and $\mu_R(V_b) = \mu_R(0) - eV_b/2$. Here, $\mu_L(0) = \mu_R(0) = E_F$ (Fermi level) and is set to zero, so the bias window corresponds to the range $[-V_b/2, +V_b/2]$.^{19,20}

III. RESULTS AND DISCUSSION

We first determine the energetic favorable adsorption geometry of $(\text{Cs}_8\text{V})_2$ superatoms on a $\text{Au}(001)$ surface. Three different adsorption sites including hollow, bridge, and atop sites were monitored. The cluster dimer was oriented perpendicular to the surface and the atoms of the cluster and surface were held in separately relaxed positions. For each location, we calculated the binding energy of the cluster to the surface using the equation

$$\Delta E = E_{\text{Tot}}(\text{Au}(001)) + E_{\text{Tot}}(\text{Cs}_8\text{V}-\text{Cs}_8\text{V}) - E_{\text{Tot}}(\text{Au}(001) + \text{Cs}_8\text{V}). \quad (1)$$

The calculated binding energy (ΔE) of $(\text{Cs}_8\text{V})-(\text{Cs}_8\text{V})$ to $\text{Au}(001)$ surface is 4.33, 4.22, and 4.07 eV for hollow, bridge, and atop sites, respectively. This indicates that the superatom dimer $(\text{Cs}_8\text{V})-(\text{Cs}_8\text{V})$ prefers to bind at a hollow site on the $\text{Au}(001)$ surface.

To examine the transport properties, the $(\text{Cs}_8\text{V})-(\text{Cs}_8\text{V})$ was sandwiched between two $\text{Au}(001)$ leads. The assembly is schematically shown in Fig. 1 and can be broadly divided into

FIG. 1. Schematic plot of the two-probe system involving superatom dimer and electrodes. Red and purple circles of the superatom represent V and Cs atoms, respectively.

three regions. The left electrode of Au, the central scattering region, and the right electrode of gold. The magnetic superatom $(\text{Cs}_8\text{V})-(\text{Cs}_8\text{V})$ complex was positioned such that the Cs sites are located at the hollow sites of $\text{Au}(001)$ electrodes that extend to reservoirs at $\pm\infty$. To ensure that there is no interaction between the periodic images, a vacuum layer (about $15 \text{ \AA}$) is included in the electrode cell in the x and y direction. In this work, four Au layers were chosen for the electrode cell in the z direction. In addition, multiple atomic layers in the left and right electrodes, which act as surface-atom layers, are chosen to screen the perturbation effect of the cluster on the potential beyond the scattering region.

The superatom-electrode distance is an important parameter for the transport. As mentioned before, the contact distance was determined by calculating the equilibrium separation between the $(\text{Cs}_8\text{V})-(\text{Cs}_8\text{V})$ superatom complex and the corresponding gold surface via the total-energy calculations. To this end, a four-layer slab with a (5×5) unit cell was chosen to model the $\text{Au}(100)$ surfaces, and one $(\text{Cs}_8\text{V})-(\text{Cs}_8\text{V})$ superatom dimer with one cesium binding to gold surface was placed above the hollow surface site, which, we found to be the most energetically favorable. The vertical distance between the cesium atom and the slab was then varied and the total energy of the whole adatom-slab system was monitored. The calculated total energy of the superatom $(\text{Cs}_8\text{V})-(\text{Cs}_8\text{V})$ -adsorbate gold slab as a function of the Cs-slab vertical distance is shown in Fig. 2, where the zero point of the energy has been chosen with respect to the optimal distance. This figure

FIG. 2. The total energy of the magnetic superatom Cs_8V -adsorbate gold slab as a function of the Cs-slab vertical distance. The zero point of the energy has been chosen with respect to the optimal distance.

FIG. 3. (a) The distance dependence of the equilibrium conductance (G - d curve), (b) transmission coefficient $T_\sigma(E, V_b)$ vs energy E . The inset of (a) is the conductance polarization [$P = (G_\uparrow - G_\downarrow)/(G_\uparrow + G_\downarrow)$] as a function of the distance.

shows that the energetically optimal superatom-surface vertical distance is 2.885 Å, corresponding to the nearest-neighbor distance $d_{\text{Cs-Au}}$ of 3.533 Å.

The calculated conductances at zero bias ($\partial I / \partial V|_{V=0}$) of this two-probe system as a function of the distance are shown in Fig. 3. Note that the conductance at zero bias exhibits an oscillatory behavior in both spin states. As the distance decreases from 4.059 Å to 1.558 Å, the conductance first increases and reaches a local maximum at 3.011 Å in FM state (0.70369 G_0) and at 2.703 Å in AFM state (0.40358 G_0), then decreases and local minimums appear at 2.258 Å in both configurations. The conductance begins to increase as the distances decrease further in both cases. While similar oscillatory behavior of the equilibrium conductance has previously been found in non-magnetic systems,^{21–23} but here, different spin states lead to separate oscillatory variation.

It is interesting to recall that the total energy of the system shows an equilibrium distance of 2.885 Å with the corresponding conductance of 0.55115 G_0 in FM state and 0.35846 G_0 in AFM state. The above results, however, show that an optimal binding (maximum binding) does not necessarily cor-

FIG. 4. (a) The HOMO and LUMO level of spin-down in FM state as a function of the distance; (b) the transferred charge as a function of the distance in the FM state, the negative value represents the case where the electrons are transferred from the superatom to the electrode.

respond to the highest conductance. This is rooted in the fact that apart from bonding, the conductance is governed by other factors. These include the localization of the electronic orbitals of the superatom and nature of orbitals in electrodes, and the location and broadening of the electron levels of the superatomic molecule due to interaction with gold.²⁴ Another important parameter is the charge transfer between the superatom and the gold electrodes and a combination of these features can move the maximum in conductance to a different location than the maximal binding. More specifically, at 1.558 Å, the conductance FM/AFM ratio is largest and about 2. As the distance is increased to 3.758 Å, the ratio drops to 1.02. This progression is rooted in the variations in the electron distributing at Fermi level, leading to different conductance at zero bias. These can be seen from the transmission coefficients $T_\sigma(E, V_b)$ at zero bias (top and middle of Fig. 3(b)), which shows at 1.558 Å, there is a large difference between FM and AFM states, resulting in the largest ratio. As the distance increases to 3.758 Å, the contributions of the FM and AFM states at the Fermi level are almost the same.

FIG. 5. Spin currents of the model system with the distances $d_{\text{Cs-Au}(001)}$ as: (a) 2.5578 Å, (b) 3.2085 Å, (c) 3.5548 Å, and (d) 4.0585 Å.

Another important quantity is the polarization of the electron gas. The inset of Fig. 3(a) shows the conductance polarization $[P = (G_{\uparrow} - G_{\downarrow})/(G_{\uparrow} + G_{\downarrow})]$ as a function of distance. Note that it also displays oscillatory behavior. The polarization in FM state exceeds 80% when the distance reaches 2.258 Å, indicating that the magnetic superatom Cs_8V could be used as a highly efficient spin polarizer.⁶ Since the spin orbit coupling is significantly reduced, the spin could maintain coherence over a longer distance. Due to a little central asymmetry of the $\text{Cs}_8\text{V-Cs}_8\text{V}$ supermolecule when it is contacted to the Au electrode, the electrons distributions of the spin-up and spin-down channel in AFM state are not perfect symmetric through the whole energy region, even though the total magnetic moment is zero, which can be seen clearly from the bottom of Fig. 3(b). Meanwhile, it is the electrons around Fermi level that determine the transport properties, and this asymmetry around Fermi level leads to a small current polarization even in AFM state.

To gain further insight into this oscillatory behavior of the conductance as a function of distance, we probed the nature of

electronic orbitals contributing to the conduction. Figure 4(a) shows the variation of the electronic levels corresponding to frontier molecular orbitals. The Fermi level of the gold electrode is set to zero, and we show the HOMO and the lowest unoccupied molecular orbital (LUMO) levels. When the distance increases, both the HOMO and LUMO levels initially go up. But after 2.808 Å, the LUMO level drops down and the HOMO-LUMO gap is reduced to 0.3 eV at 3.011 Å, resulting in a local maximum of the conductance.

Another quantity controlling the transport is the charge transfer from the electrodes to the superatom dimer. To this end, the charge on the superatom dimer was calculated by adding the charge at the individual sites of the cluster. The calculated total transferred charge is presented in Fig. 4(b). Note that it decreases as the distance is increased. This trend is different from the trend shown by the overall conductance indicating that the observed behavior is not dominated by the charge transfer and that variations in the frontier energy levels and the strength of the coupling play a more dominant role.²⁴

FIG. 6. (a) The transferred charge for spin-down at different bias voltages in FM state, the positive value represents that electrons are transferred from the electrode to the superatom; (b) the spin-down projected energy spectrum of the superatom as a function of bias voltage in FM state, the region between the solid curves is the bias window. Here $d_{\text{Cs-Au}(001)}$ is 3.5548 Å.

We next examine the effect of the bias voltage on the current in the system. These studies were carried out at various superatom-electrode distances and here we present results for four representative cases corresponding to $d_{\text{Cs-Au}(001)}$ of 2.558 Å, 3.209 Å, 3.555 Å, and 4.059 Å. Figure 5 shows the current-voltage (I - V) curves for these distances. From these figures, we see that there exists a linear region at small bias voltage for all distances. However, the value of the current under the same bias depends on the distance, and the current decreases with increasing distance. For all applied bias voltages, the current monotonically increases with voltage for the AFM state. On the other hand, when the superatom-electrode distance attains to a certain value, the system exhibits a NDR for the FM state in the spin-down channel. Further this behavior is accentuated at larger distances. The peak-to-valley ratio is 1.05, 1.05, and 1.14 for $d_{\text{Cs-Au}(001)}$ of 3.209 Å, 3.555 Å, and 4.059 Å, respectively. As is well known, NDR has many applications including high-speed switch, memory, and amplifier.²⁵ However, our calculations

show that the existence of NDR is closely linked to the superatom-electrode separation.

In order to further probe the origin of the NDR in spin-down channel, we have calculated the spin-down transferred charge at different bias voltages (Fig. 6(a)) where the positive value represents that electrons are transferred from the electrode to the superatom, and the spin-down projected energy spectrum of the superatom Cs_8V as a function of bias voltage (Fig. 6(b)) in the FM state for $d_{\text{Cs-Au}(001)}$ 3.555 Å. One notes several features: (1) As the bias increases, the transferred charge reaches maximum at 0.24 V, and then decreases with increasing bias leading to the NDR; (2) after 0.24 V, with increasing bias, the HOMO-LUMO gap increases, and as a result, the current decreases and NDR appears; (3) the current reaches minimum at 0.3 V and after 0.3 V, more energy levels shift into the bias window, and the current increases. Note that while the NDR has been found in many devices,^{8,9,26,27} the microscopic origin here is different from previous cases where the molecules are strongly coupled with the electrode. In present work, the variation of the contact distance between the superatom and the electrodes results in a change in the charge state of the superatom under external bias, which along with the shift of frontier energy levels leads to NDR. We have now examined other magnetic superatomic clusters at large contact distance between the superatom and the electrodes, and observed a similar NDR behavior, indicating that the present finding is common to weak coupling nanodevice.

IV. CONCLUSIONS

In conclusion, we have investigated the spin-polarized transport through a magnetic superatom dimer (Cs_8V)-(Cs_8V) using first-principles calculations combined with NEGF approach. Our results indicate that the calculated equilibrium conductance of this two-probe system shows an oscillatory behavior in both spin channels that is linked to the coupling strength as well as the shift of energy levels. A high spin polarized conductance in FM state is also found, and it increases when the distance becomes large, exceeding 80% when the distance reaches to 2.258 Å, indicating that the magnetic superatom Cs_8V could be used as a highly efficient spin polarizer. We also show that the variation of the contact distance between the superatom and the electrodes under bias leads to NDR.

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¹W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, *Phys. Rev. Lett.* **52**, 2141 (1984).

²S. N. Khanna and P. Jena, *Phys. Rev. B* **51**, 13705 (1995).

³A. W. Castleman and S. N. Khanna, *J. Phys. Chem. C* **113**, 2664 (2009).

⁴S. N. Khanna, B. K. Rao, P. Jena, and J. L. Martins, in *Physics and Chemistry of Small Clusters*, edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987), p. 435.

- ⁵J. U. Reveles, P. A. Clayborne, A. C. Reber, S. N. Khanna, K. Pradhan, P. Sen, and M. R. Pederson, *Nat. Chem.* **1**, 310 (2009).
- ⁶H. He, R. Pandey, J. U. Reveles, S. N. Khanna, and S. P. Karna, *Appl. Phys. Lett.* **95**, 192104 (2009).
- ⁷V. P. Georgiev and J. E. McGrady, *J. Am. Chem. Soc.* **133**, 12590 (2011).
- ⁸T. Kostyrko and B. R. Bulka, *Phys. Rev. B* **79**, 075310 (2009).
- ⁹R. Pati, M. McClain, and A. Bandyopadhyay, *Phys. Rev. Lett.* **100**, 246801 (2008).
- ¹⁰Y. Min, K. L. Yao, H. H. Fu, Z. L. Liu, and Q. Li, *J. Chem. Phys.* **132**, 214703 (2010).
- ¹¹C. Xia, H. Liu, and C. Fang, *Adv. Mater. Res.* **152**, 839 (2011).
- ¹²R. H. Mathews, J. P. Sage, T. Sollner, S. D. Calawa, C. Chen, L. J. Mahoney, P. A. Maki, and K. M. Molvar, *Proc. IEEE* **87**(4), 596 (1999).
- ¹³J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ¹⁴See www.Atomistix.com for Atomistic ToolKit version 2008.02.0, Atomistix A/S.
- ¹⁵M. Brandbyge, J. L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, *Phys. Rev. B* **65**, 165401 (2002).
- ¹⁶J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Unquera, P. Ordejón, and D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002).
- ¹⁷J. Taylor, H. Guo, and J. Wang, *Phys. Rev. B* **63**, 245407 (2001).
- ¹⁸B. G. Wang, J. Wang, and H. Guo, *J. Phys. Soc. Jpn.* **70**, 2645 (2001).
- ¹⁹J. Taylor, M. Brandbyge, and K. Stokbro, *Phys. Rev. Lett.* **89**, 138301 (2002).
- ²⁰S. Datta, W. Tian, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, *Phys. Rev. Lett.* **79**, 2530 (1997).
- ²¹Z. X. Dai, X. Q. Shi, X. H. Zheng, X. L. Wang, and Z. Zeng, *Phys. Rev. B* **75**, 155402 (2007).
- ²²Z. X. Dai, X. H. Zheng, X. Q. Shi, and Z. Zeng, *Phys. Rev. B* **72**, 205408 (2005).
- ²³N. D. Lang and P. Avouris, *Phys. Rev. Lett.* **84**, 358 (2000).
- ²⁴J. L. Li, Z. Z. Zhao, C. Yu, H. B. Wang, and J. W. Zhao, *J. Comput. Chem.* **33**, 666 (2012).
- ²⁵B. A. Mantoosh and P. S. Weiss, *Proc. IEEE* **91**, 1785 (2003).
- ²⁶Z. Q. Fan and K. Q. Chen, *Appl. Phys. Lett.* **96**, 053509 (2010).
- ²⁷M. Qiu, Z. H. Zhang, X. Q. Deng, and J. B. Pan, *Appl. Phys. Lett.* **97**, 242109 (2010).