A time-dependent density functional theory investigation of plasmon resonances of linear Au atomic chains*

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We report theoretical studies on the plasmon resonances in linear Au atomic chains by using *ab initio* time-dependent density functional theory. The dipole responses are investigated each as a function of chain length. They converge into a single resonance in the longitudinal mode but split into two transverse modes. As the chain length increases, the longitudinal plasmon mode is redshifted in energy while the transverse modes shift in the opposite direction (blueshifts). In addition, the energy gap between the two transverse modes reduces with chain length increasing. We find that there are unique characteristics, different from those of other metallic chains. These characteristics are crucial to atomic-scale engineering of single-molecule sensing, optical spectroscopy, and so on.

Keywords: plasmon resonance, time-dependent density functional theory, longitudinal plasmon mode, transverse plasmon mode

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1. Introduction

The collective oscillations in metallic nanostructures are referred to as localized surface plasmon resonances (LSPRs)[1−7] and lead to dynamic charge accumulation, a field enhancement near their surfaces. The LSPRs exhibit unusual properties in energy, frequency, resonant mode, and optical spectroscopy. These properties, which are highly sensitive to the size and shape, are very useful for many interesting applications in optical nano-sensor,[1,2] surface-enhanced spectroscopy,[8−10] catalytic reaction,[11] and biomedical treatment.[12] Previous work has demonstrated that LSPRs occur in a wide variety of nanostructures including nanocage, nanostar, nanocrescent, nanorice nanobar, nanodisk, nanoring, and triangular nanoparticle.[13−20] The LSPRs of Au nanostructures have been studied because of the favourable bulk dielectric properties.[21−28] Such structures have been fabricated using electron beam and colloidal lithography[29] to explore their electronic properties experimentally. Usually, most studies are motivated by the possibilities for sensor miniaturization offered by atomic-scale plasmon localization combined with efficient microspectroscopy. And most experiments performed so far have focused only on the structures in a 10–100 nm size range where the LSPRs can be qualitatively understood by electrondynamic model like the Mie theory.[30]

In the present paper, we focus on collective excitations of artificial linear atomic chains assembled with a scanning tunnelling microscope (STM).[23] The LSPR properties of linear atomic chains have been extensively investigated by various experiments and theories,[23−28] both as a model system for fundamental studies and as potential conducing wires for device applications. Nilius *et al.*[31] first demonstrated the formation of one-dimensional band structure out of individual atomic state as the chain length increases atom by atom. In particular, the collective oscillations of gold linear atomic chains have received significant attention in recent years as a result of their potential applications in nanotechnologies. For example, the electronic density oscillations have been observed in Au atomic chains on a NiAl surface via the manipulating of single atom with STM and the subsequent imaging of one-dimensional electronic density oscillations along their length.[23] Wei *et al.*[24] have reported experimental and theoretical studies on the plasmon resonances of finite one-dimensional Au

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chains excited by evanescent light waves with polarization parallel to the chains. Recently, the plasmon resonances of closely coupled Au nanosphere chains have been calculated by Harris *et al.*[28] by using the T-matrix method. These studies focused only on the properties of LSPRs behaviour classically while no explanations were given on how the collective excitation in atomic dimension is induced from their electronic structures.

We calculate the plasmon excitations of linear Au atomic chains. Using *ab initio* description of the valence electrons, the optical spectra are calculated by using the time-dependent density functional theory (TDDFT). The TDDFT has been proved to be accurate and widely used in techniques dealing with the electronic excitations. This technology has been successfully used to calculate linear[32,33] and non-linear harmonic spectra,[34,35] laser induced fragmentation,[36] *etc.* In the current work, the evolution of absorption spectrum clearly demonstrates the integration of its oscillator strength, which starts from a single atom and accumulates atom by atom. The polarization is simulated by applying an impulse in the direction along or perpendicular to a chain. And the corresponding plasmon modes are longitudinal or transverse respectively. In addition, the factors influencing collectivity of electron oscillations are observed, and the local atomic confinement and the global quantization imposed by the geometric boundary of the system are found. Meanwhile, the excitation spectrum which changes with variable interatomic distance is also studied.

2. Method

All calculations have been carried out by a real-space and real-time TDDFT code, OCTOPUS.[37] The theoretical foundation of the TDDFT calculation has been presented elsewhere.[33,38] Here, we only summarize the essentials of TDDFT method used in this work. The photoabsorption spectrum is calculated by using the formalism developed by Casida.[39] The system is excited from its initial ground state with a delta electric field causing the potential $v(\boldsymbol{r},t) = -K_0\gamma\delta(t)$, where $\gamma = x, y, z$ denotes the polarization direction and K_0 is the amplitude of the perturbation. Then we obtain the dipole strength function by averaging over the three spatial coordinates. There are two methods that can be used: linear response method and the method of propagation for the time-dependent Kohn–Sham (KS) equation in real space. However, the time-propagation scheme is faster for large systems and yields more information about the real-time dynamics of the electrons. The results in this paper are mainly based on the calculation for the propagation of the time-dependent KS equation. The main parameters in the OCTOPUS calculations are as follows. The simulation zone is determined by assigning a 6.0-Å diameter sphere around each atom and the electronic wave functions are represented on a uniform mesh grid of 0.3 Å. The real-time propagation of electronic wave pack evolves for 50 fs in total with a time step of 0.003 fs. The local-density approximation (LDA) is used as an approximation to the exchange-correlation functional, and the frozen-core approximation together with norm-conserving pseudopotentials is used to describe the ionic environment of the electronic system. In Figs. 1 and 2, the interatomic distance is taken to be 2.89 Å, chosen from the experimental configuration of atom chains on the NiAl (001) surface.[23] The optical spectra obtained with linear-response calculation present the same spectral feature.

3. Results and discussion

The evolution of dipole strength as a function of the chain length, which is measured by the number of Au atoms, is shown in Fig. 1. The present work is consistent with the foundation of Refs. [26] and [27] in the existence of a longitudinal (L) and two transverse (T) plasmon resonances, transverse end mode (TE) and transverse centre mode (TC) in metallic chains. Figures 1(a) and 1(b) correspond to the L and T polarizations of dipole excitations. For a single Au atom (the bottom curve), one resonance peak at 5.45 eV is observed, which consists of the 6s $\rightarrow$ 6p transition predominantly. The dipole response (the second curve from the bottom) exhibits a longitudinal mode at 3.69 eV and a transverse one at 6.25 eV. As the number of the Au atoms increases one by one, the evolutions are different substantially between the longitudinal mode and the transverse mode. The energy of the L mode decreases gradually from 3.10 eV in the Au3 chain to 1.01 eV in the Au14. This redshift in energy was found in Ref. [28] by using the T-matrix code. The intensity of the L mode increases linearly with the increase of atom number as found in Ref. [28]. The redshift of the resonance frequency results mainly from the reduction of energy

gap. Meanwhile, that the intensity of the L mode increases linearly can be understood to be due to the accumulation of electrons as more electrons participate in the collective oscillations. As shown in Fig. 1, the multiple excitations ($n = 2$ and $n = 3$) of the L mode are discernible for longer chains, for example, at the 2.51 eV and 3.70 eV in energy (the topmost curve).

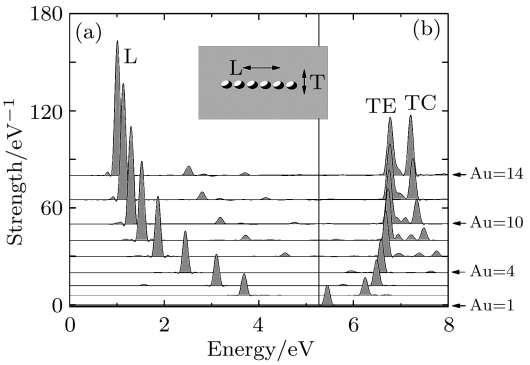


Fig. 1. Dipole responses (optical absorption) of linear Au chains, each as a function of Au atom number, to an impulse excitation with momentum increment $\delta k = 0.05$/Å polarized in (a) the longitudinal direction and (b) the transverse direction. The series of spectra correspond, counting up from the bottom, to $n = 1$, 2, 3, 4, 6, 8, 10, 12, and 14.

Figure 1(b) shows the evolution of the T mode. The transverse peak of the chain at 6.68 eV has a blueshift and splits into three branches in Au6 with a low-energy resonance at 7.00 eV, 7.39 eV and a high-energy band at 7.76 eV. This phenomenon of splitting peak for T mode is consistent with other studies.[26−28] It can be understood that the interaction between the electrons hybridizes into bonding and antibonding combinations that are shifted to a lower energy and a higher energy, respectively.

Figure 2 shows the energies and the oscillator strengths of the two T modes, each as a function of number of Au atoms. For chains shorter than six atoms, it is obvious that the spectra are dominated by the low-energy mode, the end mode. From Au_6, the high-energy mode (central mode) increases in intensity and develops into a dominant resonance, which is separated from the end mode by a finite-energy gap. With the number further increasing, the intensity of the end mode becomes saturated with an oscillation strength of about 6 electrons, while the strength of the central mode grows almost linearly with the length. The finite-energy gap suggests that the two modes degenerate neither in energy nor in character.

The energy splitting in transverse plasmon resonance can be explained as follows. One is the electron potential, which is dependent on the position of the atoms along the chain, which is the highest at the two

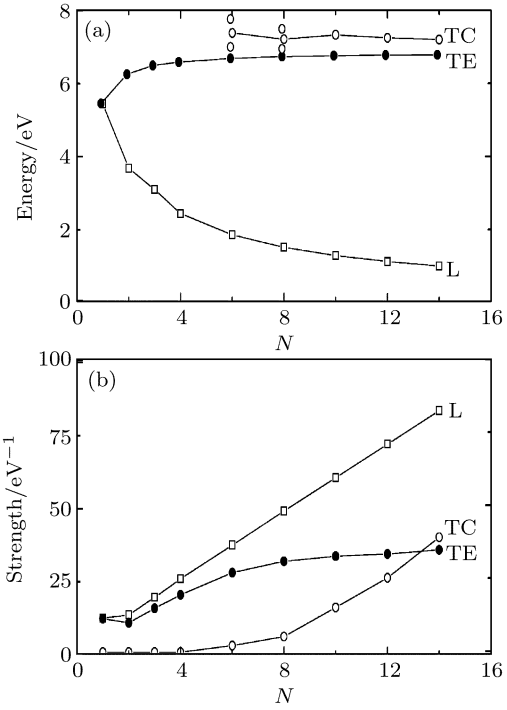


Fig. 2. (a) Excitation energies and (b) dipole strengths, each as a function of the number of atoms N, for the three resonance modes shown in Fig. 1. They are marked with L, TE and TC as discussed in the text.

ends and lower in the middle of the chain. The other is electron-electron interaction, which is different between the end atom and the central atom due to the dangling bond at the end. The former is responsible for the energy splitting, while the latter would determine mainly the collectivity and the strength of the end mode. Both quantities are dependent on the interatomic spacing d. The splitting should diminish with distance increasing and completely disappear in the large d limit, where the plasmons of the chains will become degenerate with dipole resonances of noninteracting atoms. To further study the formation of end mode, we check the calculations for Au10 by using variable interatomic distance. The results are shown in Fig. 3, where the dipole strength is plotted with varying distances by increasing the value of d up to 4 Å. As expected, the dipole response depends on interatomic distance. The end and the central modes appear in all calculations. They are both approaching the dipole resonance of the free Au atom at 5.45 eV, as a function of d. It is apparent that both modes are redshifted in energy and the energy gap between them reduces from 0.58 eV at 2.89 Å to 0.47 eV at 3.09 Å. The trend in the evolution of the transverse excita-

tions shown in Fig. 3 is in accordance with the qualitative analysis. Similar analyses for Na and K chains were carried out in previous studies.[26,27] Quantitatively, the frequencies and the strengths of Au chains differ substantially from those of the Na (K) chains, especially for the two T modes. The energy splitting ΔE between the TC and the TE modes is almost the same as those for both K and Na chains.[28] However, for Au chains, the ΔE between the TC and TE modes is 043 eV for Au_{14}, which is larger than 0.28 eV for Na_{14} or 0.29 eV K_{14}. This seems to suggest that the energy gap is dependent mostly on the local confinement within the atomic cores and the interatomic interactions, although it is difficult to measure their relative contributions in the present calculations. It would be valuable to find out how the two modes evolve in energy and intensity each as a function of d and how they merge into the free atomic resonance in the large enough d. However, the rapid increase in the number of grids with d increasing needs very high computation level which is beyond our reach now. Meanwhile, local-density approximation also becomes deficient at large d, where nonlocal van der Waals interaction is expected to be introduced to handle the interatomic interaction.

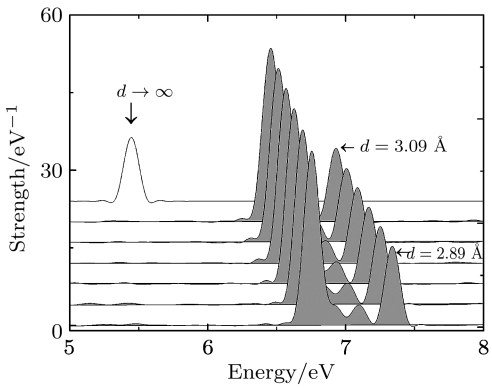


Fig. 3. Dipole responses (optical absorption) of Au10, each as a function of the interatomic distance d. The series of spectra corresponds, counting up from the bottom, to d from 2.89 Å to 3.09 Å with an increment of 0.04 Å.

To gain an insight into potential application to the chain plasmon resonances and their mediate processes, we control atomic plasmon in energy and space, for example, using atomic manipulation according to an STM experiment. The plasmon resonances, attaching a single atom at different positions of the chain, are extensively calculated to probe the electron potential effects. Figure 4 shows a comparison of the dipole strength between Au10 chain and Ag–Au10 chain which is formed by attaching a single silver atom at one end of Au10. The distance of Ag–Au is still 2.89 Å. The results are contrary to ones in Fig. 4(a) of Ref. [26], where the end mode decreases in intensity and splits into a high-energy mode at 4.5 eV. For Ag–Au10 chain, the intensity of end mode decreases at 6.76 eV and the mode splits into a low-energy mode at 6.00 eV. This can be explained as the fact that Au atom has stronger electronic potential than Na and the electronic potential of silver atom is intermediate between the two. Both of the central modes increase in intensity due to the fact that one more atom is added to the chain. Above all, our results show a redshift for Ag–Au10 chain as compared with Au10 chain. This difference suggests that the sensitivity and the tenability of collective excitation of the chain are dependent on both the atom position in the chain and the environment. Therefore, although all metallic chains have general characteristics obtained on Na chains, there are individual characteristics which are crucial to atomic-scale engineering of single-molecule sensing, optical spectroscopy, and so on.

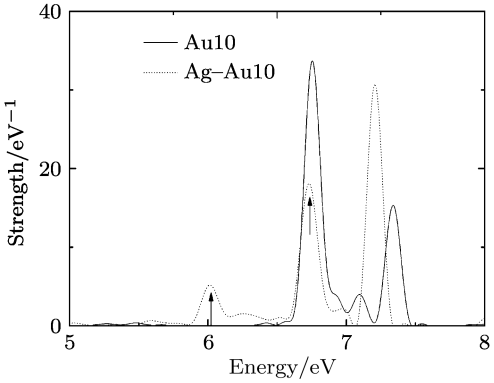


Fig. 4. Dipole strengths of Au10 atom chain (solid curve) and Ag–Au10 chain (dot curve) formed by attaching a single silver atom at Au10 one end.

4. Conclusions

We investigate the electronic excitations in linear atomic chains of Au using the time-dependent density-functional theory. The plasmon resonance of the linear atom chain presents a longitudinal mode, whose frequency depends on its length. In addition, there are two transverse plasmon modes, end mode and central mode, whose density resonances are localized at the two ends and in the central region of the chain, respectively. The plasmon resonances of the linear atom chains should offer unique and profound applications in atom-scale engineering of optical spectroscopy and associated dynamical processes. In particular, the

splitting of transverse mode makes it possible to selectively induce charge excitations in different spaces, selectively control the charge localization and transport, local field enhancement and chemical reactions, and plasmon-medium interaction at the atomic scale. We hope that our results presented here will be directly compared with experimental measurements in the near future.

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