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# Plasmon Excitations in Spin-Polarized Iron Atomic Chains: A Time-Dependent Density Functional Theory Study

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**Abstract.** By using the time-dependent density functional theory calculations, we study the plasmon excitations in Fe atomic chains with different numbers of atom and different Fe-Fe separations, which are now possible to fabricate experimentally. Because of the Fe valence  $3d$  orbitals and the spin polarization, the excitations along the chain (longitudinal (L) mode) and perpendicular to the chain (transverse (T) modes) are found to be largely different from those in noble metal and alkali metal atomic chains. First, the strength of dipole response becomes weaker due to the more localized Fe  $3d$  states; Second, the L mode is mixed with some multipole contribution; Third, the end mode of the T modes is absent.

## 1. Introduction

Plasmons are due to collective oscillations of free electrons in metallic materials [1] that can be localized at the surface or found in the bulk of a material. A localized surface plasmon resonance (LSPR) can be excited by the electromagnetic field of light and enhances the field locally by orders of magnitude. This concept has become increasingly important in nanotechnology nowadays because of the prospect of plasmon manipulation and potential applications in many fields, such as chemical detection [2], sensing and spectroscopy [3]. The underlying physical mechanism is that the frequency of LSPR is sensitive to the size, shape, and surrounding environment of the nanostructure. The nature of LSPR in nanostructures larger than 10 nm can be understood by electrodynamic models, such as the Mie theory [4]. However, for nanostructures made of only tens of atoms, their LSPR properties are neither exactly the same as the Mie plasmon in a classical metal sphere nor like the compressional bulk plasmon [5]. This significant difference is due to the fact that the electronic properties of small nanostructures are determined by the discrete energy levels instead of the continuous energy bands [6]. As a consequence, the nature of plasmon excitations in small nanostructures (or quantum plasmon) needs a full quantum mechanical description. So far, quantum plasmon excitations in single linear atomic chains have received extensive experimental and theoretical investigations [6-10], which are used as model systems for fundamental science and for potential device applications [10]. For instance, by using time-dependent density functional theory (TDDFT) calculation Lian et al. [6] studied the possibility of plasmon excitations in linear Au atomic chains with different lengths. By using a real-space and real-time TDDFT method Yuan and co-workers [7,8] studied the plasmon resonances in linear atomic chains consisting of alkali and noble metal atoms. An important finding is that when the excitation is perpendicular to the chain the transverse (T) mode will split into a central (TC) mode and an end (TE) mode and the latter one is a pure quantum effect. They also found that in the case of Ag atomic chains the  $d$  electrons will decrease the intensity and frequency of the T modes but do not affect much the longitudinal (L) modes where the excitation is along the chain. Wang et al [11] used



TDDFT calculations to investigate the plasmon excitations in Na double atomic chains and the effect of inter-chain coupling.

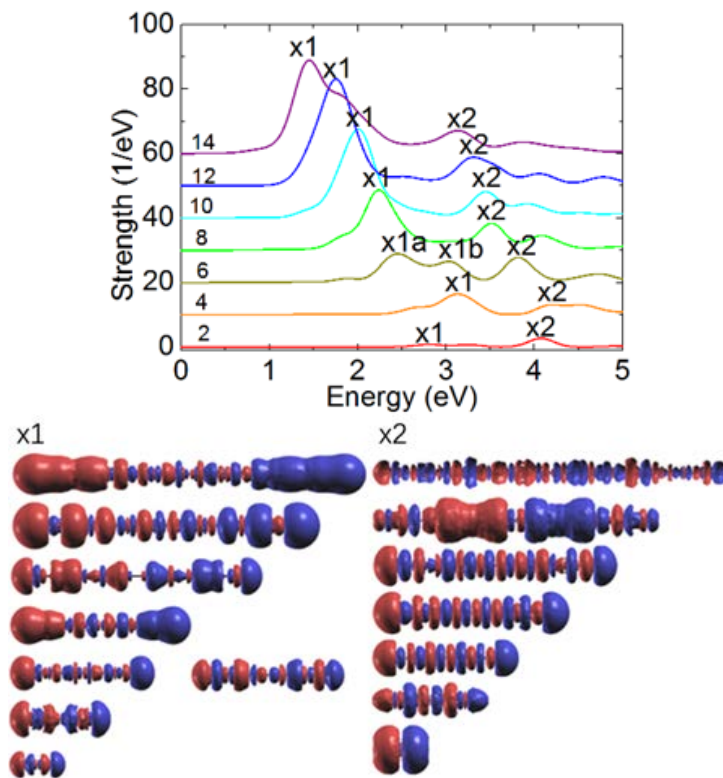
Recently, small transition metal nanostructures, such as Fe atomic chains and islands, were successfully fabricated on graphene surface by chemical vapor deposition method [12]. Fe has very different electronic properties compared to alkali and noble metals, where the partially occupied  $3d$  orbitals and the spin polarization dominate its electronic properties. How these differences affect the plasmon excitations in Fe nanostructures is still an open problem. In this work, we investigate the quantum plasmon excitations in linear Fe atomic chains with different numbers of atom and Fe-Fe spacings by using a TDDFT method implemented in real space and real time [13]. The results are analysed and discussed in terms of the dipole response and in comparisons to the alkali and noble metal atomic chains.

## 2. Computation

The linear Fe atomic chains considered consist of 2 -14 Fe atoms. The optimized Fe-Fe spacing is  $2.35\text{\AA}$  given by the density functional theory (DFT) calculation in the local density approximation (LDA). We also considered other different Fe-Fe spacings from  $2.35$  to  $3.29\text{\AA}$  which cover the experimentally measured atomic spacing of  $\sim 2.65\text{\AA}$  [12] to see the effect. We adopt a real-space and real-time TDDFT program Octopus [13] to carry out calculations of electronic excitations. The Fe ion is described by norm-conserving pseudopotentials. The electron exchange and correlation are treated by the LDA and the adiabatic LDA (ALDA) for the ground-state and excited-state calculations, respectively. The ALDA has been shown to work well for some excitations, such as those under a strong laser pulse and strong-field ionization [14] which are similar to the plasmon excitations investigated in this work. A grid in real space which is defined by assigning a sphere around each atom with a radius of  $6\text{\AA}$  and a uniform mesh grid of  $0.15\text{\AA}$  is adopted to describe the wavefunction and charge density. To obtain the dipole response which is related to the photoabsorption spectrum, the system is impulse from its initial ground state with a very short delta-function-like perturbation, and then the time-dependent Kohn-Sham equation is evolved in real space and real time for a period of time which is set to be 20000 time steps with each being  $0.0015\hbar/\text{eV}$  long. After the real-time propagation, the photoabsorption spectrum is extracted by Fourier transforming the time-dependent dipole strength. Additionally, a 3D image of the frequency-resolved induced density (FRID) distribution is obtained for each resonance in the spectrum by Fourier transforming the time series of the total induced charge density at each resonance frequency for every real-space mesh grid.

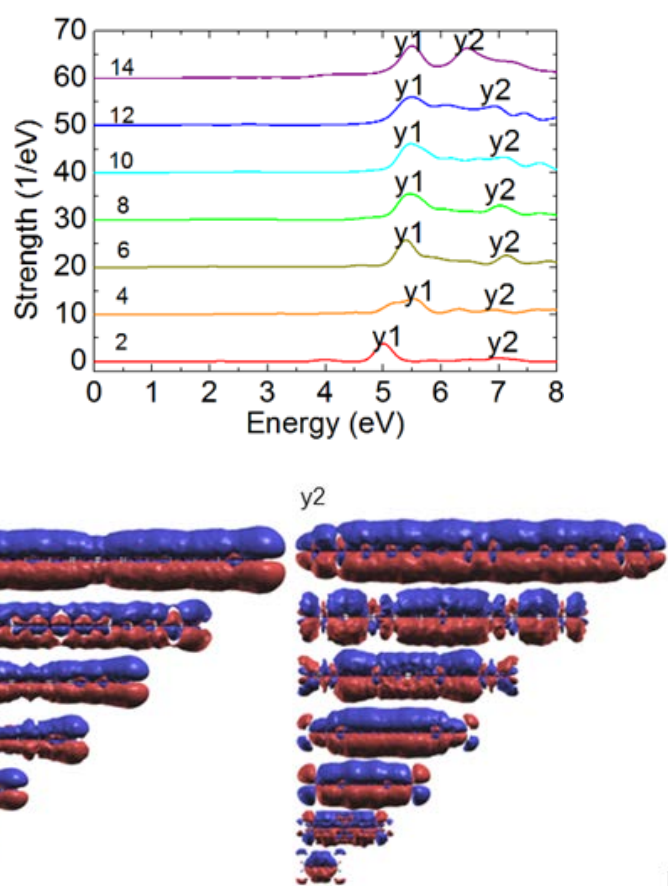
## 3. Results and Discussion

First let us look at the plasmon excitations in the Fe atomic chains with the Fe-Fe spacing being  $2.35\text{\AA}$ . When the excitation is along the chain ( $x$ -axis), the total strength of dipole response (spin-up + spin-down) and the corresponding FRIDs are shown in figure 1. Because of the spin polarization the individual dipole response of the spin-up or spin-down electron density can have negative peaks in the spectra due to the interactions between the two spin components. While the total strength of dipole response is always positive. From figure 1 one can see that when the chain is very short (2, 4, 6 atoms) the dipole response is irregular. As the chain gets longer ( $\geq 8$ ) the response becomes regular, showing a stable plasmon behaviour. There are two major resonances ( $x1$  and  $x2$ ) in the spectra: The strength of the lower-energy resonance ( $x1$ ) increases with the number of atom increasing, while the other ( $x2$ ) keeps almost unchanged. From the FRIDs we can see clearly that the  $x1$  resonance is a longitudinal plasmon mode while the higher-energy  $x2$  is basically a multipole resonance. With the increase of the number of atom, both the  $x1$  and  $x2$  resonances redshift because of the decreased energy gaps between the occupied and unoccupied states. One thing to note is that here the L mode is combined with some multipole contribution around the middle of the chain, which is different from alkali and noble metal atomic chains and can be understood by considering the more localized  $s$ - $d$  hybridization.

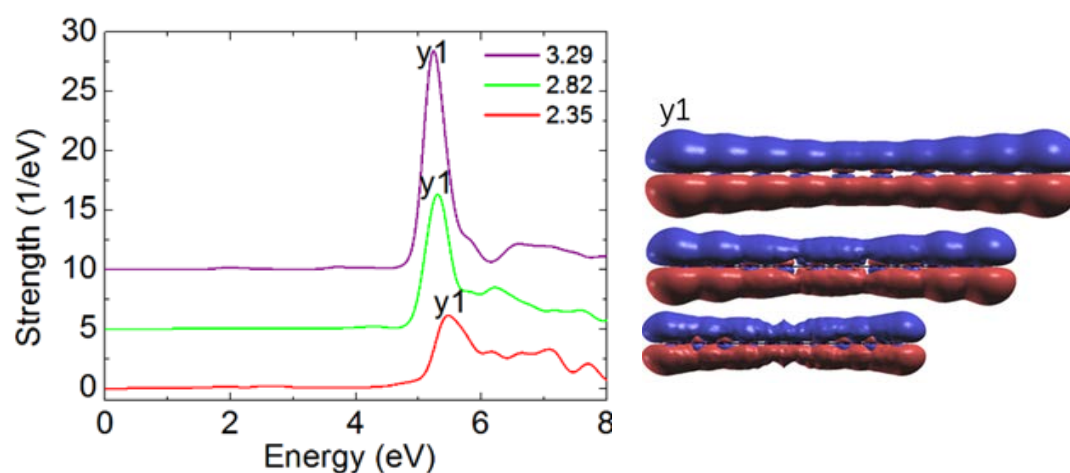


**Figure 1.** The optical absorption spectra of the Fe atomic chains with different numbers of atom under an excitation along the chain (left panel) and the corresponding FRIDs for the two major peaks (right panel).

When the excitation is perpendicular to the chain (y-axis), the results of dipole response and FRIDs are given in figure 2. Similar to the alkali and noble metal atomic chains [6-8], the strength and frequency of the transverse (T) modes are not sensitive to the number of atom. This is because the polarization is perpendicular to the chain and each atom is basically responding separately to the excitation. Here, a significant difference from the alkali and noble metal atomic chains is the absence of the so-called end (TE) mode which is separated from the central (TC) mode, and is shown to be a pure quantum effect [6-8]. From the FRIDs in figure 2 one can see that here the T modes look like a combination of the TC and TE modes. Since the separation of the TC and TE modes may be affected by the Fe-Fe spacing, we perform further calculations using different Fe-Fe spacings for the chain consisting of 10 Fe atoms. The results are shown in figure 3. One can see that for the three different Fe-Fe spacings there is only one major peak in the spectra whose FRIDs show a nature of combination of TC and TE modes. Our results indicate that the so-called TE plasmon mode appearing in alkali and noble metal atomic chains is not a general behaviour for all one-dimensional metallic systems. Its existence depends on the electronic properties of the material itself.



**Figure 2.** The optical absorption spectra of the Fe atomic chains with different numbers of atom under an excitation perpendicular to the chain (left panel) and the corresponding FRIDs for the two major peaks (right panel).



**Figure 3.** The optical absorption spectra of the Fe<sub>10</sub> atomic chain with different Fe-Fe spacings indicated in the legend, and the corresponding FRIDs of the major peak.

#### 4. Acknowledgment

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