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Quadrupole plasmon excitations in finite-size atomic chain systems

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ABSTRACT

The existence and the nature of a new mode of electronic collective excitations (quadrupole plasmons) in confined one-dimensional electronic systems, used to mimic finite-size linear metal atomic chains, have been predicted by an eigen-equation method. The eigen-equation based on the time-dependent density-functional theory is presented for calculating the collective excitations in confined systems. With this method, all modes of collective excitations in the 1D systems can be found out. These modes include dipole plasmons and quadrupole plasmons. The dipole plasmon mode corresponds to the antisymmetric oscillation of induced charge, and can be shown as a resonance of the dipole response. In the quadrupole plasmon modes, the induced charge distribution is symmetric, and the dipole response vanishes. The motion of the electrons in the quadrupole modes is similar to the vibration of atoms in the breathing mode of phonons. This type of plasmon can be shown as a resonance of the quadrupole response, and has to be excited by a non-uniform field.

1. Introduction

Plasmon properties in nano-structure systems have attracted more and more physics researcher's attentions, due to their fundamental significance [1–11] and potential applications [12–21]. Nanostructures sustain localized plasmon resonances within their confining boundaries, leading to dynamic charge accumulation and strong enhancement of field near their surfaces. Such plasmon oscillations and the decay at surfaces are responsible for the novel applications in optical imaging [15], single-molecule sensing and spectroscopy [16,17], photocatalytic reactions [18], nano-photonics and -electronics [19] and cancer therapy [21].

Recent scanning tunneling microscope observations showed development of one-dimensional (1D) band structure when the numbers of atoms in Au chains on NiAl(110) exceed 10 [22]. This arouses the research interest on the plasmon excitation in 1D electronic systems of a few atoms. Many subsequent theoretical calculation [7–11,23–25] confirmed the presence of the collective plasmon mode in the confined one-dimensional electronic systems of a few atoms. Collective excitations in few-atom systems have been investigated both experimentally [26–30] and theoretically [31–34] in last decades. However, recent theoretical studies of plasmon excitations are mostly done via calculating the dipole response [8–11] and other characteristic responses [23–25] by applying an external field, and the excitations are shown as the corresponding response resonances. One may wonder whether the modes predicted in this way are dependent on the applied external fields. The answer is clearly yes. It has been shown in Ref. [9] that a longitudinal field induces longitudinal-mode plasmon resonance, and a transverse field induces a transverse resonance. Therefore, finding a proper theoretical approach to calculate plasmon spectra is essential for further studies of plasmons in confined electronic systems. An eigen-equation approach was ever introduced for confined condensed-matter systems with a spherical shape in Refs. [31–33], and the plasmon multipolarities were studied. In present work, we attempt to present an eigen-equation of plasma collective-oscillation in confined systems, and find all plasmon excitations of the systems by solving the equation. Consequently, we found a new mode of electronic collective excitations, quadrupole plasmons, in the confined 1D electronic systems. In the 1D systems, the dipole plasmon mode corresponds to the antisymmetric charge oscillation and can be shown as a resonance of the dipole response [8–11]. Distinct from the dipole plasmon, the quadrupole plasmon corresponds to the symmetric charge oscillation and the dipole response vanishing, but can be shown as a resonance of the quadrupole response. The motion of the electrons in the quadrupole modes is similar to the vibration of atoms in the breathing mode of phonons. Our calculations are made based on the two models: the one-dimensional electron gas and one-dimensional tight-binding models. Refs. [8,9] and present work have shown that the longitudinal dipole-plasmon resonances in linear atomic chains predicted by using a confined 1D electron gas model are qualitatively in agreement with the

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calculations made by ab initio time-dependent density functional theory. We believe that the new mode of collective excitations exists in the atomic chain systems in Refs. [8–11,23–25].

2. Theoretical approach

Based on the time-dependent density-functional theory (TDDFT), the induced charge density [35] can be written as

$$\rho(\mathbf{r},\omega)=\int d\mathbf{r}'\Pi(\mathbf{r},\mathbf{r}',\omega)V(\mathbf{r}',\omega), \tag{1}$$

Here we have transformed the time-domain into the frequency-domain. Where the Kohn–Sham response function, i.e., the density–density response function of non-interacting electrons with unperturbed density, ρ_0, defined by

$$\Pi(\mathbf{r},\mathbf{r}',\omega)=\frac{\delta\rho[V](\mathbf{r},\omega)}{\delta V(\mathbf{r}',\omega)}\Big|_{V[\rho_0]}. \tag{2}$$

where the frequency dependent charge density $\rho[V](r,\omega)$ is a functional of the potential V, and $V[\rho_0]$ is a functional of the unperturbed density ρ_0. In Eq. (1), the perturbation potential is

$$V(\mathbf{r},\omega)=V^{ex}(\mathbf{r},\omega)+V^{in}(\mathbf{r},\omega), \tag{3}$$

where $V^{ex}(\mathbf{r},\omega)$ is the external potential, and

$$V^{in}(\mathbf{r},\omega)=\frac{1}{4\pi\varepsilon_0}\int d\mathbf{r}'\frac{\rho(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}+\int d\mathbf{r}'K_{xc}(\mathbf{r},\mathbf{r}',\omega)\rho(\mathbf{r}',\omega) \tag{4}$$

is the induced potential. The time-dependent xc kernel is defined by $K_{xc}(\mathbf{r},\mathbf{r}',\omega)=\delta V^{xc}[\rho](\mathbf{r},\omega)/\delta\rho(\mathbf{r}',\omega)$. In fact, the density–density response function defined in Eq. (2) is the random-phase approximation (RPA) Lindhard function:

$$\Pi(\mathbf{r},\mathbf{r}',\omega)=2e^2\sum_{mn}\frac{f(E_m)-f(E_n)}{E_m-E_n-\omega-i\gamma}\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')\psi_m(\mathbf{r}'), \tag{5}$$

where $f(E_n)$ is the Fermi-function, $\psi_n(\mathbf{r})$ is the energy eigen-function of electrons in the unperturbed system, and E_n is the eigen-energy. In this paper only zero temperature case is considered, so $f(E_n)=\theta(E_F-E_n)$, where E_F is the Fermi energy. The unperturbed eigen-states can be obtained using local density functional theory. Substituting Eq. (5) in Eq. (1), we have

$$\rho(\mathbf{r},\omega)=2e^2\sum_{mn}\frac{f(E_m)-f(E_n)}{E_m-E_n-\omega-i\gamma}\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})[V_{n,m}^{ex}(\omega)+V_{nm}^{in}(\omega)], \tag{6}$$

where $V_{nm}^{X}(\omega)=\int d\mathbf{r}V^{X}(\mathbf{r},\omega)\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})$. Combining Eq. (6) with Eq. (4), we can obtain the self-consistent equation for $V^{in}(\mathbf{r},\omega)$:

$$V^{in}(\mathbf{r},\omega)=2e^2\sum_{mn}\frac{f(E_m)-f(E_n)}{E_m-E_n-\omega-i\gamma}\int d\mathbf{r}'K(\mathbf{r},\mathbf{r}',\omega)\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')[V_{n,m}^{ex}(\omega)+V_{nm}^{in}(\omega)], \tag{7}$$

where $K(\mathbf{r},\mathbf{r}',\omega)=1/4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|+K_{xc}(\mathbf{r},\mathbf{r}',\omega)$. Multiplying Eq. (7) by $\psi_{m'}^*(\mathbf{r})\psi_{n'}(\mathbf{r})$ and integrating over the space yield

$$\sum_{mn}[\delta_{m'n',nm}-M_{m'n',mn}(\omega)]V_{nm}^{in}(\omega)=\sum_{mn}M_{m'n',mn}(\omega)V_{n,m}^{ex}(\omega), \tag{8}$$

with

$$M_{m'n',mn}(\omega)=2e^2\frac{f(E_m)-f(E_n)}{E_m-E_n-\omega-i\gamma}\int d\mathbf{r}\int d\mathbf{r}'\psi_{m'}^*(\mathbf{r})\psi_{n'}(\mathbf{r})K(\mathbf{r},\mathbf{r}',\omega)\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}').$$

Now one can calculate the collective charge-oscillation (Eq. (6)) by solving Eq. (8). Setting $V_{n,m}^{ex}(\omega)=0$, Eq. (8) becomes

$$\sum_{mn}[\delta_{m'n',nm}-M_{m'n',mn}(\omega)]V_{nm}^{in}(\omega)=0. \tag{9}$$

This is the plasmon eigen-equation we derived, it can be extensively used to study the excitation problems in condensed matter system, and compared with the RPA, it is more suitable to calculate the plasmon excitation with the electromagnetic interaction. So the eigen-equation can be generally applied to confined electronic systems with the Coulomb interactions and other multi-interaction. Furthermore,with the equation all the plasmons of a system may be found and are not dependent on the applied external fields. It is worth to point out that using the symmetry of $V_{nm}^{in}(\omega)$ and $M_{m'n',mn}(\omega)$, the number of equations in Eqs. (8) and (9) may be reduced. Usually, the eigen-states of a confined system may be expressed by real wave-functions, and in this case the number of equations in Eqs. (8) and (9) can be further reduced.

According to eigen-equation (9), the plasmon excitation energy $\hbar\omega$ can be determined by $A(\omega)=\det[\delta_{m'n',nm}-M_{m'n',mn}(\omega)]=0$. However, $A(\omega)$ is a plural value due to the finite small imaginary part $i\gamma$. In the practical calculation a small imaginary part $i\gamma$ is necessary since the electrons always suffer some scattering, so the eigen-plasmon excitation energy $\hbar\omega$ is obtained by $\mathrm{Re}[A(\omega)]=0$ with $\mathrm{Im}[A(\omega)]\sim 0$. Equivalently, here we use $\mathrm{Im}[1/A(\omega)]$ to give a real plasmon energy that $\mathrm{Im}[1/A(\omega)]$ show a finite peak at the plasmon energy $\hbar\omega$. This eigen-equation method not only let us find out all the plasmon modes of a system, but also greatly reduces the amount of computation in comparison with the original TDDFT.

3. Results and discussion

3.1. Quasi-one-dimensional electron gas model

First we study the plasmon excitation in a quasi-one-dimensional electron gas (Q1DEG) confined within a quantum well with length of $(N+1)a$ and width of $2a$, which is used to mimic a finite-size atomic chain as shown in Fig. 1, where a is the virtual lattice constant and taken as 0.35 nm in our calculation. For this model, the unperturbed wave-function is $(\sqrt{2/(N+1)a^2})\sin(n\pi x/(N+1)a)\sin(\pi y/2a)$. With this model an atomic chain of N atoms is mimicked. The similar model was employed by Gao and Yuan [7] to study the plasmon excitation of a atomic chains. Their calculations indicate that in comparison with the pure RPA the exchange term $K_{xc}(\mathbf{r},\mathbf{r}',\omega)$ gives rise to only very slight shift in plasmon frequency. In present work, we are just interested in the qualitative investigation of the plasmon excitation, in particularly finding out all of the collective excitation in the confined systems. Therefore, we will ignore exchange term $K_{xc}(\mathbf{r},\mathbf{r}',\omega)$ to simplify our calculation.

Our calculation shows that some plasmon eigen-modes corresponding to the peaks of dipole absorption spectra induced by a local uniform field such as $V^{ext}(x,t)=-xE_0e^{-i\omega t}$ [7], but for other eigen-modes there is not appearance of the absorption-peak. In Fig. 2(a) we show an eigen-mode by a peak of the spectrum function $\mathrm{Im}[1/A(\omega)]$ at frequency $\omega\approx 0.3058$, and in Fig. 2(b) one can find that this frequency is the zero-point of $\mathrm{Re}[A(\omega)]$, where the numbers of atoms $N=12$, and the numbers of electrons $N_e=12$. The energy (frequency) is normalized by $\pi^2\hbar^2/2m_ea^2$, and m_e is the mass of electrons. In addition, taking $V^{ext}(x,t)=-xE_0e^{-i\omega t}$ as in Ref. [7], we calculate the dipole response function (absorption spectrum) $P(\omega)=\omega\int x\,\mathrm{Im}[\rho(r,\omega)]\,dx\,dy$ by using Eqs. (6) and

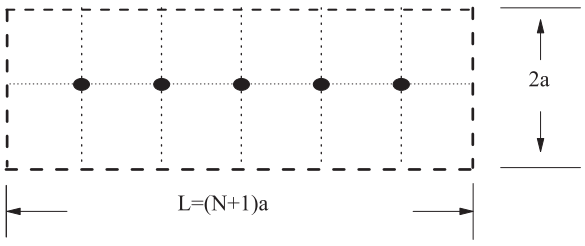

Fig. 1. A schematic demonstration of the considered system.