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Plasmon excitations in two-dimensional atomic cluster systems

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ABSTRACT

Properties of plasmon excitations in two-dimensional (2D) atomic cluster systems are theoretically studied within an extended Hubbard model. The collective oscillation equations of charge, plasmon eigen-equations and the energy-absorption spectrum formula are presented. The calculated results show that different symmetries of plasmons exist in the cluster systems, and the symmetry of charge distribution in the plasmon resonance originate from the intrinsic symmetry of the corresponding eigen-plasmon modes, but not from the symmetry of applied external fields; however, the plasmon excitation with a certain polarization direction should be excited by the field in this direction, the dipole mode of plasmons can be excited by both uniform and non-uniform fields, but multipole ones cannot be excited by an uniform field. In addition, we show that for a given electron density, plasmon spectra are red-shifted with increasing size of the systems.

1. Introduction

In recent years, more and more researchers have paid close attention to plasmon properties in nano-structure systems because of their fundamental significance [1–12] and some potential applications [13–22] including optical imaging [16], single-molecule sensing and spectroscopy [17,18], photocatalytic reactions [19], nano-photonics and -electronics [20] and cancer therapy [22].

As the nanotechnology and scanning tunneling microscope (STM) are developed and improved rapidly, the studies of electromagnetic response of tiny cluster systems with few atoms have come true in experiment. Particularly, for microminiature metal and semiconductor particles [23–26], the collective electromagnetic response can be proceeded explicitly, owing to the exquisite control of the shape and size of atomic and molecular clusters. Recently, theoretical studies of plasmon excitation in the atomic clusters base on the random-phase approximation (RPA) [27–29] and time-dependent density functional theory (TDDFT) [10,12,30–36]. In these methods, the plasmon excitations are mostly calculated via the dipole response and other characteristic responses under applying an external field, and the excitations are determined by the corresponding response resonances. However, the modes of plasmons predicted in this way are dependent on the applied external fields. In the present paper, we apply an eigen-equation method based on the quantum response theory and random phase approximation to study the plasmon excitations in two-dimensional (2D) atomic cluster systems. In Ref. [12], the plasmon resonances are investigated by calculating the dipole-response function of 2D atomic cluster systems. In present work, we find that in 2D cluster systems there are not only dipole plasmons, but also multipole plasmons, and their mixtures. In fact, with the eigen-equation method, we can find out all types of plasmon modes in the systems. We also calculate energy absorption spectra for different applied external electric fields, and find that the external fields of different symmetry and direction excite different plasmon modes. The plasmons of dipole mode can be excited by both uniform and non-uniform fields, but the higher multipole plasmons cannot be excited by uniform field. Furthermore, the charge distributions are presented for different modes of plasmon excitations, which show different symmetry and polarization of the plasmon modes.

2. Model and theoretical approach

In this section, we will present the formulae for calculating plasmon excitation in 2D atomic cluster system, which is an $N_x \times N_y$ square lattice. For simplicity, an one-band external-field perturbed Hubbard model is employed, and the model hamiltonian is

$$H = -t\sum_{l\delta,\sigma}(d^{\dagger}_{l\sigma}d_{l+\delta\sigma} + h.\,c.\,) + \sum_{l,\sigma} eV^{ex}_{l}(t)d^{\dagger}_{l\sigma}d_{l\sigma} + \frac{U}{2}\sum_{l,\sigma} n_{l\sigma}n_{l-\sigma} + \frac{V}{2}\sum_{l\delta} n_l n_{l+\delta} \quad (1)$$

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where t is the tight-binding hopping matrix element which determines the width of the electronic band by $4t$, δ represents the nearest neighbor vector, $d^{\dagger}_{l\sigma}(d_{l'\sigma})$ is the creation(annihilation) operator in the Wannier representation, and $n_{l\sigma}=d^{\dagger}_{l\sigma}d_{l\sigma}$. $V^{ex}_{l}(t)$ is the perturbation external potential, U and V are the on-site and inter-site coulomb repulsions respectively. By using mean field approximation,

$$H = -t\sum_{l<l',\sigma}(d^{\dagger}_{l\sigma}d_{l'\sigma}+h.c.)+\sum_{l,\sigma}eV^{ex}_{l}(t)d^{\dagger}_{l\sigma}d_{l\sigma} + U\sum_{l,\sigma}\delta\langle n_{l-\sigma}(t)\rangle n_{l\sigma}+V\sum_{l\delta}\delta\langle n_{l+\delta}(t)\rangle n_{l}. \tag{2}$$

Where the deviation of average occupation $\delta\langle n_{l\sigma}(t)$ is induced by external field V^{ex}_{l}. Here, in the effective site-energy $U\langle n_{l\sigma}(t)\rangle = U\langle n_{l\sigma}\rangle_0 + U\delta\langle n_{l\sigma}(t)\rangle$, only the time-dependent part $U\delta\langle n_{l\sigma}(t)\rangle$ is considered, and the time-independent part $U\langle n_{l\sigma}\rangle_0 \approx U\langle n_{\sigma}\rangle_0$ is ignored, because it doesnot give rise to effects on the dynamics properties of the system. Furthermore, we do not consider the magnetic resolution, that is to say, the average occupation number $\langle n_{l\sigma}(t)\rangle = \langle n_{l}(t)\rangle/2$ is spin-independent, so we have

$$H = -t\sum_{l<l',\sigma}(d^{\dagger}_{l\sigma}d_{l'\sigma}+h.c.)+\sum_{l,\sigma}eV^{ex}_{l}(t)d^{\dagger}_{l\sigma}d_{l\sigma} + \sum_{l,\sigma}\left(\frac{U}{2}\delta\langle n_{l}(t)\rangle + V\sum_{\delta}\delta\langle n_{l+\delta}(t)\rangle\right)n_{l\sigma} \tag{3}$$

We will take the following transform in Eq. (3)

$$d_{l\sigma} = \sum_{n}\psi_{n}(l)c_{n\sigma} \tag{4}$$

where $\psi_n(l)$ is the eigenvector of the unperturbed tight-binding model, corresponding to eigenvalue E_n. The eigenvalue is

$$E_n = -2t\cos\left(\frac{n_x\pi}{N_x+1}\right)-2t\cos\left(\frac{n_y\pi}{N_y+1}\right), \tag{5}$$

and the eigenvector is

$$\psi_n(l) = \sqrt{\frac{4}{(N_x+1)(N_y+1)}}\sin\left(\frac{n_x\pi}{N_x+1}l_x\right)\sin\left(\frac{n_x\pi}{N_x+1}l_y\right) \tag{6}$$

where $n_x = 1, 2\ldots N_x$, $n_y = 1, 2\ldots N_y$, $l_x = 1, 2\ldots N_x$, and $l_y = 1, 2\ldots N_y$. Substituting Eq. (4) into Eq. (3), we have

$$H = \sum\varepsilon_n c^{\dagger}_{n\sigma}c_{n\sigma} + \sum_{l,\sigma}\left(eV^{ex}_{l}(t)+\frac{U}{2}\delta\langle n_{l}(t)\rangle + V\sum_{\delta}\delta\langle n_{l+\delta}(t)\rangle\right)\psi^{*}_{n}(l)\psi_{n}(l)c^{\dagger}_{n'\sigma}c_{n\sigma} \tag{7}$$

Based on the standard linear-response theory, the response of charge number to the time-dependent perturbation can be written as

$$\delta n_l(\omega) = \sum_{l'}\Pi(l,l',\omega)[V_{l'}(\omega)+V^{ex}_{l'}(\omega)] = \sum_{l'}\Pi(l,l',\omega)\left[eV^{ex}_{l'}(\omega)+\frac{U}{2}\delta\langle n_{l'}(\omega)\rangle + V\sum_{\delta}\delta\langle n_{l'+\delta}(\omega)\rangle\right], \tag{8}$$

where the Fourier transform with respect to time has been taken, and $\Pi(l,l',\omega)$ is the Lindhard function and can be calculated by

$$\Pi(l,l',\omega) = 2\sum_{mn}\frac{f(E_m)-f(E_n)}{E_m-E_n-\omega-i\gamma}\psi^{*}_{m}(l)\psi_{n}(l)\psi^{*}_{n}(l')\psi_{m}(l'). \tag{9}$$

The 2 appears in the front of Eq. (9) corresponds to two spins, and $f(E)$ are Fermi function. Therefore, the frequency-dependent response of charge number is

$$\delta n_l(\omega) - \sum_{l'}\Pi(l,l',\omega)\left(\frac{U}{2}\delta\langle n_{l'}(\omega)\rangle - \sum_{\delta}V\delta\langle n_{l'+\delta}(\omega)\rangle\right) = \sum_{l'}\Pi(l,l',\omega)eV^{ex}_{l'}(\omega) \tag{10}$$

For simplicity, Eq. (10) can be written as

$$\delta n_l(\omega) - \sum_{l'}\Pi(l,l',\omega)v_{l'l''}\delta\langle n_{l''}(\omega)\rangle = \sum_{l'}\Pi(l,l',\omega)[eV^{ex}_{l'}(\omega)] \tag{11}$$

with

$$v_{ll'}\begin{cases}\frac{U}{2}, & \text{when } l=l'\\ V, & \text{when } l' \text{ is the nearest neighbor of } l\end{cases} \tag{12}$$

The charge response is $\delta Q_l(\omega) = e\delta n_l(\omega)$, then

$$\delta Q_l(\omega) - \sum_{l'}\Pi(l,l',\omega)v_{l'l''}\delta Q_{l''} = e^2\sum_{l'}\Pi(l,l',\omega)[V^{ex}_{l'}(\omega)] \tag{13}$$

In order to give the eigen-oscillation equation, we make the external potential $V^{ex}_{l}(\omega)=0$, and have

$$\sum_{l'}\left[\delta_{ll'}-\sum_{l''}\Pi(l,l'',\omega)v_{l''l'}\right]\delta Q_{l'}=0 \tag{14}$$

According to eigen-equation (14), the plasmon excitation frequency ω can be calculated by

$$\Re(\omega) = \det\left[\delta_{ll'}-\sum_{l''}\Pi(l,l'',\omega)v_{l''l'}\right]=0 \tag{15}$$

It should be noted that Eq. (15) has no real solutions for the finite small imaginary part $i\gamma$. In the practical calculation, a small imaginary part $i\gamma$ is necessary, and the plasmon eigen frequency ω is obtained by $\mathrm{Re}[\Re(\omega)]=0$, with $\mathrm{Im}[\Re(\omega)]\sim 0$. This implies that spectrum function $A(\omega)=\mathrm{Im}[1/\Re(\omega)]$ will show a peak at the plasmon frequency ω. Here we want to point that the eigen resolution should be exactly real when $i\gamma = i0^{+}$, and $A(\omega)$ will give an infinite peak at plasmon frequency.

When a perturbation external field is applied to the system, the energy absorption can be calculated as

$$A_L(\omega) = \frac{1}{2}\mathrm{Re}\left\{\int\mathbf{E}(\mathbf{r},\omega)^{*}\cdot\mathbf{J}(\mathbf{r},\omega)d\mathbf{r}\right\} = -\frac{1}{2}\mathrm{Re}\left\{\int d\mathbf{r}[\nabla V(\mathbf{r},\omega)]^{*}\cdot\mathbf{J}(\mathbf{r},\omega)\right\} \tag{16}$$

where $\mathbf{J}(\mathbf{r},\omega)$ is the current density induced by external field in the system, and $\mathbf{E}(\mathbf{r},\omega)$ (or $V(\mathbf{r},\omega)$) is the total electric field. By some calculations, we can simplify Eq. (16) as

$$A_L(\omega) = -\frac{1}{2}\omega\,\mathrm{Im}\left\{\int d\mathbf{r}\rho^{in}(\mathbf{r},\omega)[V^{ex}(\mathbf{r},\omega)]^{*}\right\} \tag{17}$$

where $\rho^{in}(\mathbf{r},\omega)$ is charge density induced by the external field $V^{ex}(\mathbf{r},\omega)$ in the system.

For our tight-binding model, the absorption spectrum function can be written as

$$A_L(\omega) = -\frac{1}{2}\omega\,\mathrm{Im}\left\{\sum_{l}\delta Q_l(\omega)[V^{ex}_{l}(\omega)]^{*}\right\} \tag{18}$$

Here, we want to point that in present work we make a dynamical mean-field approximation, which is equivalent to the RPA, and ignore the exchange potential; however, calculations in Ref. [7] indicate that in comparison with the pure RPA the exchange term gives rise to only very slight shift in plasmon frequency. Therefore, we believe that