Quadrupole plasmon excitations in confined one-dimensional systems

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Abstract – A new mode of electronic collective excitations (quadrupole plasmon) in confined one-dimensional electronic systems is predicted herein 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 may be found out. These modes include dipole plasmons and quadrupole plasmons. The dipole plasmon mode corresponds to the antisymmetric oscillation of the 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 plasmons can be shown as a resonance of the quadrupole response, and has to be excited by a nonuniform field.

Plasmon properties in nano-structure systems have attracted more and more the physics researchers’ attention, due to their fundamental significance [1–11] and potential applications [12–21]. Different from the bulk and surface-plasmon waves, nanostructures sustain localized plasmon resonances within their confining boundaries, leading to dynamic charge accumulation and field strong enhancement near their surfaces. Such plasmon oscillations and 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].

Collective excitations in few-atom systems have been shown both experimentally [22–28] and theoretically [29–35] in a voluminous literature. Recent scanning tunneling microscope observations showed the development of a one-dimensional (1D) band structure when the number of atoms in the Au chains on NiAl(110) exceeds 10 [36], which further triggered the research interest on the plasmon excitation in 1D electronic systems of a few atoms. Many subsequent theoretical calculations [7–11,37–39] confirmed the presence of the collective plasmon mode in the confined one-dimensional electronic systems of a few atoms. Recent theoretical studies of plasmon excitations have been mostly done via calculating the dipole response [8–11] and other characteristic responses [37–39] 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 a 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.

In this letter, we attempt to present an eigen equation of plasma collective oscillation in confined systems, and use the eigen equation to find all plasmon excitations of the systems by solving the equation, and then compare the eigen-plasmon excitations with the ones obtained by the way mentioned above to check whether any new collective excitation exists in the systems. 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].

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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. It has been shown in refs. [8,9] and in the present work 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 calculations made for atomic chains by ab initio time-dependent density functional theory. We predict that a new mode of collective excitations exists in the atomic chain systems in refs. [8–11,37–39]. We expect that this result will prompt theoretical and experimental investigations for finding new modes of plasmons in confined low-dimensional systems.

According to the time-dependent density functional theory (TDDFT), the induced-charge density [40] can be written as

\[
\rho(r, \omega) = \int d^3r \Pi(r, r', \omega)V(r', \omega),
\]

where the Kohn-Sham response function, i.e., the density-density response function of noninteracting electrons with unperturbed density \( \rho_0 \), is defined by

\[
\Pi(r, r', \omega) = \frac{\delta \rho[V](r, \omega)}{\delta V(r', \omega)} |_{V[\rho_0]},
\]

(2)

Here we have transformed the time domain into the frequency domain. In eq. (1), the perturbation potential is

\[
V(r, \omega) = V^{xc}(r, \omega) + V^{in}(r, \omega),
\]

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

\[
V^{in}(r, \omega) = \frac{1}{4\pi\varepsilon_0} \int d^3r' \rho(r', \omega) \frac{|r-r'|}{|r-r'|} + \int d^3r' K_{xc}(r, r', \omega)\rho(r', \omega)
\]

(4)

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

\[
\Pi(r, r', \omega) = 2e^2 \sum_{mn} \frac{f(E_m) - f(E_n)}{E_m - E_n - \omega - i\gamma} \times \psi_m^*(r)\psi_n(r)\psi_n^*(r')\psi_m(r'),
\]

(5)

where \( f(E_m) \) is the Fermi function, \( \psi_n(r) \) is the energy eigen function of electrons in the unperturbed system, and \( E_n \) is the eigen energy. The unperturbed eigen states can be obtained using local density functional theory. Substituting eq. (5) in eq. (1), we have

\[
\rho(r, \omega) = 2e^2 \sum_{mn} \frac{f(E_m) - f(E_n)}{E_m - E_n - \omega - i\gamma} \times \psi_m^*(r)\psi_n(r)\left[V^{xc}_{nm}(\omega) + V^{in}_{nm}(\omega)\right],
\]

(6)

where \( V^{xc}_{nm}(\omega) = \int d^3r V^{xc}(r, \omega, \psi_n^*(r)\psi_m(r) \). Combining eq. (6) with eqs. (4), we can obtain the self-consistent equation for \( V^{in}(r, \omega) \)

\[
V^{in}(r, \omega) = 2e^2 \sum_{mn} \frac{f(E_m) - f(E_n)}{E_m - E_n - \omega - i\gamma} \times \int d^3r K(r, r', \omega)\psi_n^*(r')\psi_n(r')\left[V^{xc}_{nm}(\omega) + V^{in}_{nm}(\omega)\right],
\]

(7)

where \( K(r, r', \omega) = 1/4\pi\varepsilon_0 |r-r'| + K_{xc}(r, r', \omega) \). Multiplying eq. (7) by \( \psi_m^*(r)\psi_n(r) \) and integrating over the space yields

\[
\sum_{mn} \left[\delta_{m'n',nm} - M_{m'n',nm}(\omega)\right] V^{in}_{nm}(\omega) = \sum_{mn} M_{m'n',nm}(\omega)V^{xc}_{nm}(\omega),
\]

(8)

with

\[
M_{m'n',nm}(\omega) = 2e^2 \sum_{mn} \frac{f(E_m) - f(E_n)}{E_m - E_n - \omega - i\gamma} \times \int d^3r \int d^3r' \psi_m^*(r)\psi_n(r)K(r, r', \omega)\psi_n^*(r')\psi_m(r').
\]

Now one can calculate the collective charge oscillation (eq. (6)) by solving eq. (8). Setting \( V^{xc}_{nm}(\omega) = 0 \), eq. (8) becomes

\[
\sum_{mn} \left[\delta_{m'n',nm} - M_{m'n',nm}(\omega)\right] V^{in}_{nm}(\omega) = 0.
\]

(9)

This is the plasmon eigen equation we want. With the equation all the plasmons of a system may be found and are not dependent on the applied external fields. It is worth pointing out that using the symmetry of \( V^{in}_{nm}(\omega) \) and \( M_{m'n',nm}(\omega) \), 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 the eigen equation (9), the plasmon excitation energy \( \hbar\omega \) can be determined by \( A(\omega) = \text{det} \left[\delta_{m'n',nm} - M_{m'n',nm}(\omega)\right] = 0 \). However, there would be not real solutions due to the finite small imaginary part \( i\gamma \). In the practical calculation a small imaginary part \( i\gamma \) is necessary, and the eigen-plasmon excitation energy \( \hbar\omega \) is obtained by \( \text{Re} [A(\omega)] = 0 \), with \( \text{Im} [A(\omega)] \sim 0 \). This implies that the spectrum function \( \text{Im} [1/A(\omega)] \) will show a peak at the plasmon energy \( \hbar\omega \). Here we want to point out that the eigen resolution should be exactly real when \( i\gamma = 0 \), and \( A(\omega) \) will give an infinite peak at the plasmon frequency. This eigen-equation
Applying the external potential \( V_{\text{ext}}(x,t) = -E_0 x e^{-i\omega t} \), a resonance peak of the dipole response function (c) appears at the eigen excitation. Here the number of electrons \( N_e = 12 \), and the number of electrons \( N_e = 12 \). The energy (frequency) is normalized by \( \pi^2 \hbar^2 / 2m_e a^2 \), and \( m_e \) is the mass of the electrons.

method not only lets us find out all the plasmon modes of a system, but it also greatly reduces the amount of computation in comparison with the original TDDFT.

First we study the plasmon excitation in a quasi-one-dimensional electron gas (Q1DEG) confined within a quantum well with length equal to \( (N + 1)a \) and width equal to \( 2a \), where \( a \) is a virtual lattice constant and taken as 3.5 nm in our calculation. For this model, the unperturbed wave function is 
\[
\psi_0(r) = \frac{1}{\sqrt{N}} \sin\left(\frac{n\pi r}{a}\right),
\]
With this model an atomic chain of \( N \) atoms may be mimicked. A similar model was employed by Gao and Yuan [7] to study the plasmon excitations in atomic chains. Their calculations indicate that, in comparison with the pure RPA, the exchange term \( K_{\text{ex}}(r,r',\omega) \) gives rise to only a very slight shift in plasmon frequency. In the present work, we are only interested in the qualitative investigation of the plasmon excitation, in particular finding out all of the collective excitations in the confined systems. Therefore, we will ignore the exchange term \( K_{\text{ex}}(r,r',\omega) \) to simplify our calculation.

Our calculation shows that some plasmon eigen modes correspond to the peaks of the dipole absorption spectra induced by a local uniform field such as \( V_{\text{ext}}(x,t) = -E_0 x e^{-i\omega t} \) [7], but for other eigen modes there is not the appearance of the absorption peak. In fig. 1(a) we show an eigen mode by a peak of the spectrum function \( \text{Im}[1/A(\omega)] \) at frequency \( \omega \approx 0.3058 \), and in fig. 1(b) one can find that this frequency is the zero point of \( \text{Re}[A(\omega)] \), where the number of atoms \( N = 12 \), and the number of electrons \( N_e = 12 \). The energy (frequency) is normalized by \( \pi^2 \hbar^2 / 2m_e a^2 \), and \( m_e \) is the mass of the electrons. In addition, taking \( V_{\text{ext}}(x,t) = -E_0 x e^{-i\omega t} \) as in ref. [7], we calculate the dipole response function (absorption spectrum) \( P(\omega) = \omega \int x \text{Im}[\rho(r,\omega)] dx dy \) by using eqs. (6) and (8), and the result is shown in fig. 1(c). One can find that a dipole response peak appears at the same frequency as in fig. 1(a). In fig. 2(a) and (b) we show another eigenplasmon excitation around the frequency \( \omega \approx 0.5392 \). However, in fig. 2(c) one can find that there is no peak in the dipole response function. This indicates that the eigen mode of the plasmon shown in fig. 2 cannot be excited by this applied external field, or this eigen mode is not a dipolar plasmon. In addition, we also calculate the induced electric-field energy [37] and the charges \( \int |\rho(r,\omega)| dx dy \) as a function of the external-field frequency, but we do not find any resonance to appear at the eigen frequency equal to 0.5393. So, we believe that this excitation mode cannot be excited with such a uniform external field.

In order to understand the nature of these eigen plasmons and find out why some of their modes cannot be excited by a uniform external field, we now study the charge distribution in the eigen states of collective oscillations. By setting \( V_{\text{ext}}(x,t) = 1 \) we calculate the charge density \( \rho(r,\omega) \) in the eigen oscillations at frequency \( \omega = 0.3058 \) and 0.5392, and show the results in fig. 3(a) and fig. 3(b) respectively. One can find that the charge distributions of the two plasmon modes are very different. In fig. 3(a), as shown in ref. [7], both the real and imaginary profiles

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Fig. 1: An eigen plasmon of the dipole mode in the Q1DEG is shown by a peak of the spectrum function \( \text{Im}[1/A(\omega)] \) (a), and corresponds to a zero-point of the function \( \text{Re}[A(\omega)] \) (b). Applying the external potential \( V_{\text{ext}}(x,t) = -E_0 x e^{-i\omega t} \), a resonance peak of the dipole response function (c) appears at the eigen excitation. Here the number of electrons \( N_e = 12 \), and the number of electrons \( N_e = 12 \). The energy (frequency) is normalized by \( \pi^2 \hbar^2 / 2m_e a^2 \), and \( m_e \) is the mass of the electrons.

Fig. 2: An eigen plasmon of the new mode is shown by a peak of the spectrum function \( \text{Im}[1/A(\omega)] \) (a), and by a zero point of the function \( \text{Re}[A(\omega)] \) (b). In the plot of the dipole response function (c), there is no resonance peak for this mode of the plasmon. The parameters are the same as in fig. 1.
of the charge density distribution are antisymmetric and likely exhibit Friedel oscillations across the systems. However, in fig. 3(b) the charge density distribution is symmetric, so in this mode of collective excitation the motion of the electrons is similar to the vibration of atoms in the breathing mode of phonons. It is the symmetric charge density distribution to cause this mode unable to be excited by a uniform external field, because in this case the electric dipole moment vanishes. The symmetric distribution of the charge density would give rise to a quadrupole moment, corresponding to the quadrupole plasmon mode. The quadrupole plasmon resonance modes in nanostructures have been widely reported [41–45]. To the best of our knowledge, however, this type of plasmon excitation has not been reported for the one-dimensional atomic cluster systems. Here, we want to point out that both the asymmetry and symmetry of the charge densities originate from the intrinsic property of the eigen states, unlike the argument in ref. [7] where the antisymmetric charge density was ascribed to the antisymmetric external field. In fact, below we will show that the plasmons of the antisymmetric charge density can be excited by both external fields \( V^{\text{ext}}(x,t) = -xe^{-i\omega t} \) and \( V^{\text{ext}}(x,t) = -x^2e^{-i\omega t} \), while the plasmons of the symmetric charge density cannot be excited by \( V^{\text{ext}}(x,t) = -xe^{-i\omega t} \), but can be excited by \( V^{\text{ext}}(x,t) = -x^2e^{-i\omega t} \).

For the plasmons of the symmetric charge density, the dipolar moment vanishes, and the interaction energy of the system in a uniform applied field vanishes, so such mode of the plasmons cannot be excited by the uniform field. However, the symmetric distribution of charge density gives the quadrupole moment \( D \), and the interaction energy of the quadrupole is \( D \cdot \nabla E \), therefore we predict that the quadrupole mode of the plasmon should be excited by the nonuniform external field. In fig. 4(a) and (b) we plot the dipole and quadrupole strengths as functions of the external-field frequency, where the external potentials are \( V^{\text{ext}}(x,t) = -E_0xe^{-i\omega t} \) and \( V^{\text{ext}}(x,t) = -F_0x^2e^{-i\omega t} \) in fig. 4(a) and (b), respectively. Here, the quadrupole strength is defined as \( Q_e(\omega) = \omega \int (x - \frac{a}{2})^2 \Im[\rho(x,\omega)]dx \). In the dipole response function, one can find similar results to those in refs. [7] and [8], which are that the energy redshift and response intensity increase with the system length. As was pointed out in refs. [7] and [8], the increase in intensity results from the accumulation of collectivity in the dipole oscillation. The redshift of the resonance frequency at increased system length can be understood by the reduction of the energy gaps involved in the dipole excitation. Similar behaviors are also found in the quadrupole functions, and compared with the dipole response function, the main plasmon resonance peaks show general blueshifts for all system lengths.

**Fig. 3:** (Color online) The distribution of the induced-charge density for the eigen plasmon of dipole mode (a) and quadrupole mode (b).

**Fig. 4:** (Color online) (a) The dipole response of the Q1DEG as a function of the external-field frequency \( \omega \), obtained by applying the external potential \( V^{\text{ext}}(x,t) = -E_0xe^{-i\omega t} \) for different system lengths \( L = (N + 1)a \). Here \( N \) is the number of atoms with interatomic distance \( a = 0.35 \text{ nm} \), and \( N_e \) the number of electrons. (b) The quadrupole response function obtained by applying the external potential \( V^{\text{ext}}(x,t) = -F_0x^2e^{-i\omega t} \). Compared with the dipole response function, the main plasmon resonance peaks show general blueshifts for all system lengths.
In conclusion, we have presented an eigen-equation method for studying plasmons, which is based on TDDFT. Using this method, we have studied the plasmons in the confined Q1DEG systems, and predicted a new type of plasmons, i.e., the quadrupole plasmons, which has not been reported in the one-dimensional systems. Differently from the dipole plasmons that correspond to the antisymmetric distribution of induced charge, the new type of plasmons correspond to the symmetric charge distribution, indicating that the motion of charges in this mode of plasmon oscillation is similar to the atomic vibration in the breathing mode of phonons. Since the dipole moment vanishes in the quadrupole mode of plasmons, their excitation can be achieved only by applying a nonuniform external field, and the quadrupole plasmons may display as the resonance peaks of quadrupole response function. We expect that this result will prompt theoretical and experimental investigations for finding new modes of plasmons in confined systems, and affect nanoplasmonic device engineering and nanoscale photochemistry.

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REFERENCES

[1] Savage K. J., Hawkeye M. M., Esteban R., Borisov A. G., Aizpurua J. and Baumberg J. J., Nature (London), 491 (2012) 574.
[2] Aizpurua J., Hoffmann G., Apell S. P. and Berndt R., Phys. Rev. Lett., 89 (2002) 156803.
[3] Johansson P., Phys. Rev. B, 58 (1998) 10823.
[4] Bergman D. J. and Stockman M. I., Phys. Rev. Lett., 90 (2003) 027402.
[5] Prodan E., Radloff C., Halas N. J. and Nordlander P., Science, 302 (2003) 419.
[6] Aizpurua J., Hanarp P., Sutherland D. S., Kall M., Bryant G. W. and Garcia de Abajo F. J., Phys. Rev. Lett., 90 (2003) 057401.
[7] Gao S. and Yuan Z., Phys. Rev. B, 72 (2005) 121406(R).
[8] Yan J. and Gao S., Phys. Rev. B, 78 (2008) 235413.
[9] Yan J., Yuan Z. and Gao S., Phys. Rev. Lett., 98 (2007) 216602.
[10] Nayan N., Turkowski V. and Rahman T. S., Phys. Rev. Lett., 109 (2012) 157404.
[11] DePrince A. E., Pelton M., Guest J. R. and Gray S. K., Phys. Rev. Lett., 107 (2011) 196806.
[12] Oulton R. F., Sorger V. J., Zentgraf T., Ma R.-M., Gladden C., Dai L., Bartal G. and Ziang X., Nature, 461 (2009) 629.
[13] Nakamura K., Tanabe K. and Atwater H., Appl. Phys. Lett., 93 (2008) 121904.
[14] Okamoto K., Niki I., Shivakumar A., Narukawa Y., Mukai T. and Scherer A., Nat. Mater., 3 (2004) 601.
[15] Fang N., Lee H., Sun C. and Zhang X., Science, 308 (2005) 534.
[16] Nie S. and Emory S. R., Science, 275 (1997) 1102.
[17] Xu H. X., Bierneld E. J., Käll M. and Börjesson L., Phys. Rev. Lett., 85 (1999) 4357.
[18] Bell A. T., Science, 299 (2003) 1688.
[19] Ozbay E., Science, 311 (2006) 189.
[20] Lin J., Mueller J. P. B., Wang Q., Yuan G., Antoniou N., Yuan X. C. and Capasso F., Science, 340 (2013) 331.
[21] Hirsch L. R., Stafford R. J., Bankson J. A., Sershon S. R., Rivera B., Price R. E., Hazle J. D., Halas N. J. and West J. L., Proc. Natl. Acad. Sci. U.S.A., 100 (2003) 13549.
[22] de Heer W. A., Selby K., Kresin V. et al., Phys. Rev. Lett., 59 (1987) 1805.
[23] Brechignac C., Cahuacil Ph., Carlier F. and Leygnier J., Chem. Phys. Lett., 164 (1989) 433.
[24] Fallgren H. and Martin T. P., Chem. Phys. Lett., 168 (1990) 233.
[25] Selby K., Vollmer M., Masui J., Kresin V., Heer W. A. and Knight W. D., Z. Phys. D - At. Mol. Clust., 12 (1989) 477.
[26] Wang C. R. C., Pollack S., Cameron D. and Kappes M. M., J. Chem. Phys., 93 (1990) 3787.
[27] Tigglesbaumer J., Koller L., Meiwes-Broer K.-H. and Liebsch A., Phys. Rev. A, 48 (1993) 1749.
[28] Ekardt W., Phys. Rev. B, 31 (1985) 6560.
[29] Yannouleas C., Broglia R. A., Brack M. and Bortignon P. F., Phys. Rev. Lett., 63 (1989) 255.
[30] Serra Ll., Garcia F., Barranco M. et al., Phys. Rev. B, 39 (1989) 8247.
[31] Bernath M., Yannouleas C. and Broglia R. A., Phys. Lett. A, 156 (1991) 307; Bernath M., Spina M. E. and Pacheco J. M., Phys. Rev. B, 49 (1994) 10764.
[32] Kresin V. V., Phys. Rev. B, 45 (1992) 14321.
[33] Yannouleas C., Vigezzi E. and Broglia R. A., Phys. Rev. B, 47 (1993) 9849.
[34] Rubio A., Balbas L. C. and Alonso J. A., Z. Phys. D - A. Mol. Clust., 26 (1993) 284.
[35] Kummel S., Andrae K. and Reinhard P. G., Appl. Phys. B, 73 (2001) 293.
[36] Nilus N., Wallis T. M. and Ho H., Science, 297 (2002) 18533.
[37] Muniz R. A., Haas S., Levi A. F. J. and Grigorenko I., Phys. Rev. B, 80 (2009) 045413.
[38] Cassidy A., Grigorenko I. and Haas S., Phys. Rev. B, 77 (2008) 245404.
[39] Grigorenko I., Haas S. and Levi A. F. J., Phys. Rev. Lett., 97 (2006) 086806.
[40] Petersilka M., Gossmann U. J. and Gross E. K. U., Phys. Rev. Lett., 76 (1996) 1212.
[41] Chen F., Alemu N. and Johnston R. L., AIP Adv., 1 (2011) 032134.
[42] Zhang Y., Jia T. Q., Feng D. H. and Xu Z. Z., Appl. Phys. Lett., 98 (2011) 163110.
[43] Wu S., Liu J., Zhou L., Wang Q., Zhang YL., Wang G. and Zhu Y., Appl. Phys. Lett., 99 (2011) 141104.
[44] Hao E. C., Schatz G. C., Johnson R. C. and Hupp J. T., J. Chem. Phys., 117 (2002) 5963.
[45] Andrae K., Reinhard P.-G. and Suraud E., Phys. Rev. Lett., 92 (2004) 173402; Tribelsky M. I. and Lukyanchuk B. S., Phys. Rev. Lett., 97 (2006) 263902.