Landau damping of quantum plasmons in metal nanostructures

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\textit{New Journal of Physics} 15 (2013) 023011 (15pp)
Received 22 October 2012
Published 6 February 2013
Online at http://www.njp.org/
doi:10.1088/1367-2630/15/2/023011

\textbf{Abstract.} Using the random phase approximation with both real space and discrete electron–hole (e–h) pair basis sets, we study the broadening of surface plasmons in metal structures of reduced dimensionality, where Landau damping is the dominant dissipation channel and presents an intrinsic limitation to plasmonics technology. We show that for every prototypical class of systems considered, including zero-dimensional nanoshells, one-dimensional coaxial nanotubes and two-dimensional ultrathin films, Landau damping can be drastically tuned due to energy quantization of the individual electron levels and e–h pairs. Both the generic trend and oscillatory nature of the tunability are in stark contrast with the expectations of the semiclassical surface scattering picture. Our approach also allows to vividly depict the evolution of the plasmons from the quantum to the classical regime, and to elucidate the underlying physical origin of hybridization broadening of nearly degenerate plasmon modes. These findings may serve as a guide in the future design of plasmonic nanostructures of desirable functionalities.

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\textit{New Journal of Physics} 15 (2013) 023011
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1. Introduction

Surface plasmon describes the collective excitation of the conduction electrons at a metal surface [1]. In recent years, a rapidly expanding field [2, 3] has been to exploit novel aspects of surface plasmons defined at the surfaces or interfaces of elegantly fabricated metal nanostructures to trap light with wavelengths much larger than the nanoscale for a wide range of applications. This development stems from the fact that the properties of surface plasmons sensitively depend on the size, shape and dielectric environment of the metal nanostructures, rendering to plasmonics immense application potential in surface-enhanced spectroscopies [4, 5], biological and chemical sensing [6, 7], nanolithography [8, 9], solar cells [10], etc. Traditionally, surface plasmon is described within the classical picture, where the optical response of a system is obtained by solving electromagnetic Maxwell equations with bulk dielectric properties of the constituent materials. However, as the characteristic lengths of the plasmonic materials become smaller and smaller, intriguing phenomena may emerge beyond the expectations of the classical picture [11–14], demanding more accurate, quantum mechanical treatments [15–17].

To date, studies of surface plasmons have been predominately focused on their frequency tunability [18, 19]. In contrast, much less effort has been devoted to plasmon lifetime [20], an equally important aspect of surface plasmon. For practically every plasmonics application, it is highly desirable to have as long a lifetime as possible once the surface plasmons are excited. Competing lifetime broadening mechanisms considered previously include inhomogeneous broadening [22, 23], boundary scattering, radiation damping and Landau damping. For example, for spherical particles of radius $L$, boundary scattering has been found within a semiclassical picture to result in a $\propto 1/L$ correction to the linewidth of surface plasmons [24]. As the fabrication techniques continue to improve and the system sizes continue to shrink into the quantum regime, both inhomogeneous broadening and radiation damping can be greatly suppressed, making Landau damping the dominant lifetime broadening mechanism. In this regime, the boundaries of the systems are actually part of the physical conditions defining the confined electron energy levels that contribute to Landau damping, via plasmon–electron interactions [25]. This dominant intrinsic damping channel is expected to exhibit significant tunability, because the quantized electronic states depend sensitively on the size and shape of the metal nanostructures.

$^6$ In the field of ultra-fast plasmonics, the usually very short lifetime of plasmon is utilized to design switches [21]. However, a well-controlled lifetime of plasmon is still favorable.
In this paper, we present a comprehensive study of plasmon lifetime in a series of highly confined geometries, including zero-dimensional (0D) nanoshells, one-dimensional (1D) coaxial nanotubes and two-dimensional (2D) ultrathin films, using the random phase approximation (RPA) combined with the widely used real space and the discrete electron–hole (e–h) pair basis sets. These prototypical structures can exhibit a wide frequency tunability \([19, 26]\), a salient feature highly desirable for developing plasmonics technology. Furthermore, the present study shows that the linewidth of the plasmons can also be sensitively tuned, as represented by their strong oscillations as a function of the system size in the quantum regime. Such an oscillatory behavior deviates qualitatively from the expectations of the classical surface scattering picture, and can be rationalized by the size dependence of the quantized e–h pairs contributing to the Landau damping. Our approach also allows us to reveal the underlying physical origin of the hybridization broadening mechanism of nearly degenerate plasmon modes. These findings amount to an improved understanding of the underlying physical mechanisms for intrinsic lifetime broadening of surface plasmons, and may prove to be instrumental in the future design of plasmonic devices.

2. Methods

In this study, we first use the real-space RPA approach to evaluate electron density–density responses \([26–40]\). Furthermore, we also use the e–h pair basis set \([41–49]\) to evaluate the state–state responses in order to reveal the underlying composition of the plasmon resonance. Here, we briefly introduce the methodology, and some detailed equations are presented in the appendix.

The calculation of electronic structure of the ground state is carried out by using the jellium approximation. In this mode, the positive charge density of the ion background is

\[
n_b(r) = n_0[\Theta(r - r_1) - \Theta(r - r_2)],
\]

where \(\Theta(r)\) is the Heaviside step function, \(n_0\) is the average electron density depending on the Wigner–Seitz radius \(r_s\) of different materials as \(n_0 = 3/(4\pi r_s^3)\) and \(r_{1,2}\) indicates the positions of two boundaries in the \(r\)-direction, which is the coordinate perpendicular to the surface of the corresponding prototypical geometry.

Within jellium approximation, we have the translational and/or rotational symmetries in all three prototypical systems. The wavefunction can be obtained by simply solving a reduced 1D Kohn–Sham (KS) Hamiltonian

\[
H_{KS}u(r) = \left(-\frac{1}{2}\frac{d^2}{dr^2} + V_{\text{eff}}[n(r)]\right)u(r) = Eu(r),
\]

where \(u(r)\) is the modified radial wavefunction, which has a different form for each prototypical structure. Due to the reduction of dimensions, an additional centrifugal potential \(V_{\text{geo}}(r)\) is introduced into effective potential

\[
V_{\text{eff}}[n(r)] = V_{\text{geo}}(r) + V_H[n(r)] + V_{\text{xc}}[n(r)],
\]

where \(V_H\) is the Hartree potential and \(V_{\text{xc}}\) is the exchange-correlation potential. More details of \(u(r)\) and \(V_{\text{eff}}[n(r)]\) are presented in the appendix.

The properties of excited states can be examined by studying the response of a system to a certain external perturbation. Plasmon resonance corresponds to a strong absorption due
to the collective electronic oscillation in response to an external electric field. One common way to study this resonance starts from the evaluation of the density–density response function \( \chi(\mathbf{r}, \mathbf{r}', \omega) \), which is defined in the linear regime by the following equation:

\[
n_{\text{ind}}(r, q, \omega) = \int d\mathbf{r}' \chi(r, r', \omega, q) V_{\text{ext}}(r', q, \omega), \tag{4}
\]

where \( n_{\text{ind}} \) is the induced charge density due to the external perturbation \( V_{\text{ext}} \) and \( \chi(r, r', \omega, q) \) is the reduced density–density response function with quantum number(s) \( q \) introduced by symmetries. For a many-body system, it is not so straightforward to evaluate \( \chi \) based on ground-state information, since the system also responds to the potential from the induced charge \( n_{\text{ind}} \).

To finally sort out \( \chi \), we can first write the induced charge density in a different expression as

\[
n_{\text{ind}} = \chi^0 V_{\text{tot}} = \chi^0 (K n_{\text{ind}} + V_{\text{ext}}), \tag{5}
\]

where we have ignored the variables of the functions for convenience; \( V_{\text{tot}} \) is the total field including both the external field \( V_{\text{ext}} \) and the additional potential \( K n_{\text{ind}} \) contributed by the induced charge; \( \chi^0 \) is the so-called non-interacting density–density response function, since the interaction between quasiparticles is now viewed as part of external perturbation to the ground state; the explicit forms of \( V_{\text{ext}} \) and \( K \) are discussed in the appendix. Now combining equations (4) and (5), we obtain the Dyson-type equation for \( \chi \) as

\[
\chi = \frac{\chi^0}{1 - \chi^0 K}. \tag{6}
\]

Within the real-space RPA approach, \( \chi^0 \) can be evaluated by using the ground-state wavefunction \( \psi \) as

\[
\chi^0(r, r', \omega) = \sum_{a, b} \frac{f_a - f_b}{\omega + i\eta + E_a - E_b} \chi_0^a(r) \chi_0^b(r') \chi_0^a(r') \chi_0^b(r), \tag{7}
\]

where \( a, b \) labels the initial and final electronic states, respectively; \( E_a \) and \( f_a \) are the energy and occupation number of a given state; \( \omega \) is the energy of the external perturbation; \( i\eta \) is an infinitesimal imaginary energy, whose physical meaning will be detailed below.

Finally, the plasmon resonance can be observed from the absorption \( S \) of the system, which is evaluated by using the imaginary part of \( \chi \) as

\[
S(\omega) = \int d\mathbf{r} d\mathbf{r}' V_{\text{ext}}^*(\mathbf{r}, \omega) \text{Im} \chi(\mathbf{r}, \mathbf{r}', \omega) V_{\text{ext}}(\mathbf{r}', \omega). \tag{8}
\]

As we emphasized at the beginning of this section, an alternative way to calculate the absorption is to study the state–state response function by expanding the response function under the e–h pair basis set. Under this basis set, the non-interacting response function has a simple diagonal form,

\[
\chi^0(ab, a' b') = \frac{f_a - f_b}{\omega + (E_a - E_b)} \delta_{aa'} \delta_{bb'}. \tag{9}
\]

We can then find the singularities of \( \chi \) in equation (6) by solving the linear equation

\[
\Phi(p) - \sum_{p'} \frac{f_p}{\omega - E_p} K(p, p') \Phi(p') = 0, \tag{10}
\]

where \( p = \{a, b\} \) corresponds to the pair configuration, \( E_p = E_b - E_a \) is the pair energy, and \( f_p = f_a - f_b \) is the change in the e–h pair number. We define \( \Phi(he) = x \) for \( f_p = 1 \) and...
\( \Phi(eh) = y \) for \( f_p = -1 \), which essentially corresponds to creating and annihilating an e–h pair in the system, respectively. We can further expand equation (10) into

\[
(\omega - E_x) x - \sum_{x'} K(x, x') x' - \sum_{y'} K(x, y') y' = 0,
\]

\[
(\omega - E_y) y + \sum_{x'} K(y, x') x' + \sum_{y'} K(y, y') y' = 0.
\]

The above equation can be written in a more compact form by defining the Hamiltonian \( H_{\text{RPA}} \) as

\[
H_{\text{RPA}} (X Y) = \begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix}
\]

with

\[
A = K_{XX} + E_{XX} = K_{YY} - E_{YY},
\]

\[
B = K_{XY} = K_{YX},
\]

where \( K_{XX} \) is the interaction matrix between \( he \) configurations, \( E_{XX} \) is the diagonal matrix \( E_x \delta(x, x') \) and similar definitions stand for the other matrices. The normalization condition of the eigenstates is defined as

\[
X^2 - Y^2 = 1,
\]

which consistently corresponds to one e–h pair excitation. To calculate the absorption of eigenstates, we simply add up contributions from all different pairs by

\[
S = \sum_x | \langle x | V_{\text{ext}} | 0 \rangle x |^2 + \sum_y | \langle y | V_{\text{ext}} | 0 \rangle y |^2.
\]

The underlying physics here is presented as follows: \( \chi^0 \) is the Green’s function of the non-interacting e–h pair Hamiltonian \( H_0 = (f_b - f_a)(E_a - E_b) \delta_{ab,a'b'} \). The interaction \( K \) (bare Coulomb interaction in RPA) between different e–h pairs is then treated as a perturbation to the non-interacting e–h pair system. By solving the effective Hamiltonian \( H_{\text{RPA}} \), combined with \( H_0 \) and \( K \), we can obtain a new set of ‘quasi’ e–h pair states, and each of such quasi e–h pair states is a superposition of the non-interacting e–h pairs. In particular, among these eigenstates of \( H_{\text{RPA}} \) are one or more special states, namely the plasmon modes, that encompass maximal numbers of the non-interacting e–h pairs in a constructive way. These are also the modes interacting most strongly with the external field.

These two approaches, which essentially expand the response equation \( \chi^0 \) under different basis sets, should give the same absorption results. However, in numerical approaches, the absorption result of real-space calculation is obtained by scanning the energy axis with a certain resolution. For higher resolution, both the scanning interval and artificially introduced infinitesimal \( i\eta \) should be very small, which requires more computing time. In this case the e–h pair basis set becomes superior. It can be seen from equations (12) and (16) that the absorption spectrum is directly obtained by solving the eigen-energy and states of \( H_{\text{RPA}} \). The important difference will be shown in the next section.

\( \text{New Journal of Physics 15 (2013) 023011 (http://www.njp.org/)} \)
For electronic levels in the ground state, we use a jellium model with the Wigner–Seitz radius \( r_s = 3.0 \) and work function \( W = 4.6 \) eV, representing silver (Ag). The interlayer spacing \( d_m = 0.236 \) nm along the Ag (111) direction is used as the unit of length. In this study, we consider only the dipole response of systems, namely the angular momentum \( l \) of plasmon equals 1 as presented in the appendix.

The collective excitations of Ag have been studied in bulk and semi-infinite systems, where the important contributions of the localized electrons in the \( d \) orbitals \([50, 51]\) and surface states \([52, 53]\) have been well established. On the other hand, because of their localized nature, the contributions of those electronic states are destined to be weakly size dependent. Therefore, in the present study of the metallic nanostructures, we use a jellium model to focus on the delocalized sp electrons, which are dominantly responsible for the unique size-dependent properties in the strongly confined regime. In this sense, the present study provides an important complementary understanding of plasmonics in metal systems, and when combined with the knowledge gained from the earlier studies on the localized \( d \) electrons and surface states, conveys a more complete physical picture of the collective electronic responses of various metal systems ranging from bulk- to nano-materials.

3. Results and discussion

Figure 1 displays the thickness dependence of the plasmon energy and linewidth in three different confined geometries, each case with two structure examples. For each geometry, when the thickness is large, each surface supports a plasmon mode independently. As the thickness decreases, an antisymmetric \( \omega^+ \) and a symmetric \( \omega^- \) modes will be formed due to the coupling between the two surface modes. The frequency dispersions of these two plasmon modes can be first estimated using the hydrodynamic model \([54, 55]\), as shown by the solid lines in figure 1. The obtained real-space RPA results (dots) for the \( \omega^- \) mode are very close to the hydrodynamic results, suggesting that for the plasmon energy dispersions, one can ignore the detailed electronic structures. However, they are crucial for the linewidth broadening. Here, we also note that we have focused on the \( \omega^- \) mode in this RPA study, because the \( \omega^+ \) mode is usually strongly damped due to its much higher energy, playing a much less significant role in plasmonics.

Some intriguing features can be observed in the Landau damping of the \( \omega^- \) modes\(^8\). Firstly, the pronounced oscillations exist in all confined structures. Here we note that similar oscillations have been reported for other geometries \([39, 56–58]\), but the underlying physical origin remains elusive and will be fully revealed later using the e–h pair basis set. Secondly, the trends in the linewidth deviate drastically from the \( 1/L \) dependence expected from the semiclassical surface scattering picture. These observations imply that one cannot describe those systems using simple phenomenological dielectric functions.

Now we start from the detailed electronic structure to elucidate the origin of the oscillations in the plasmon linewidth, using thin films as representative systems. Because of the strong confinement, the energy levels of thin films consist of a series of subbands and each electronic

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8 In the real-space RPA approach, a numerical broadening procedure must be applied to extract the linewidth of the plasmon mode. This amounts to introducing a finite \( \eta \) in the unperturbed response function \( \chi_0 \). In the linewidth plots of figure 1, we have subtracted this initial broadening used in our calculations, 0.1 eV for 0D and 0.04 eV for 1D and 2D, to highlight the intrinsic linewidths due to Landau damping.
Figure 1. Thickness dependence of the plasmon energy and linewidth in different confined geometries. The top panels ((a)–(c)) are the energy spectra, including both the hydrodynamic (lines) and RPA (circles) results. The bottom panels ((d)–(f)) are the linewidths from the RPA calculations, where the dotted lines connecting the circles are just a guide to show the oscillations. For all the geometries, the external field is modeled within the dipole scattering regime. For 0D and 1D, we have the fixed inner radius \(2d_m\) (red solid lines and solid circles) and \(4d_m\) (green dashed lines and open circles), respectively. For 1D and 2D, the momentum transferred to an e–h pair is given by \(k = 0.025\) au (red solid lines and open circles) and \(k = 0.05\) au (green dashed lines and solid circles).

state is labeled by the subband index \(n\) and the momentum parallel to the film plane. Consequently, an e–h pair can be labeled by the band index difference \(|\Delta n|\) and momentum difference \(k\) between the electron and hole states. In addition, because of the mirror symmetry in thin films, we can divide the e–h pairs into two decoupled groups, \(|\Delta n|\) odd or even, which contribute to the \(\omega^+\) and \(\omega^-\) plasmon modes, respectively.

Using the e–h pair basis, we have calculated the detailed absorption modes of thin films with different thicknesses. Figure 2 contrasts the absorption spectra calculated without or with the e–h pair interactions, focusing on the \(\omega^-\) mode with even \(|\Delta n|\), where the e–h pairs with transitions from the confined states to the vacuum continuum have very minimal effects on the plasmon energy and linewidth, and can therefore be ignored. In the non-interaction case (figures 2(a) and (d)), we can clearly see that the absorption spectra are made of disconnected bands due to the discretization of the individual electron levels, where the width of each band comes from the variation in kinetic energy \((\frac{1}{2}k_a^2 - \frac{1}{2}k_b^2)\) for a fixed \(k = k_a - k_b\). As \(k\) increases, the disconnected bands will expand in width and will eventually fill the gaps between them (see figure 3(a) and later discussions for more details). In contrast, for a semi-infinite metal, the corresponding absorption spectrum for the non-interacting case would produce only one continuum. When the interactions between the e–h pairs are switched on, we obtain figures 2(b) and (e), which exhibit absorptions due to both the disconnected bands and the isolated plasmon modes.
modes. Because of the presence of a sum rule in the spectral weights, the plasmon modes gain their absorption strength from the non-interacting absorption bands, and therefore can be classified by their main contributors. For example, the one with the strongest absorption around 3 eV in figure 2(b) and 4 eV in figure 2(e), corresponding to the $\omega^-$ modes, inherits their high absorption strength from the intra-subband e–h pairs ($|\Delta n| = 0$). For $|\Delta n| = 2$ at small $k$, each absorption band contributes a plasmon mode, with the first two modes confined in the gap region, and the third one far away from the originated band. As $k$ increases, all the low-lying plasmon modes will disappear by merging the absorption bands, leaving the one with the highest energy the only surviving plasmon mode of the resultant single e–h pair continuum; this surviving mode eventually evolves into the bulk plasmon mode [30]. The above discussions vividly depict the evolution of the plasmons from the quantum to the classical regime.

An advantage of using the e–h pair basis set is that the collective modes are obtained naturally as eigenstates of the Hamiltonian matrix $H_{\text{RPA}}$, which allows us to easily identify multiple plasmon modes originating from the intra- and inter-band transitions. This is in sharp contrast with the widely used real-space RPA approach, where initial numerical broadening must be introduced to resolve the isolated collective mode(s). To further demonstrate the power of this approach, we compare the absorption spectra obtained using the e–h pair basis set (figure 2(b)) with its counterpart obtained via numerical broadening in figure 2(c). We can clearly see that in the latter case the inter-band plasmon modes (arrows) with weak absorption strengths are ‘washed out’ by such a numerical broadening and become indistinguishable, leaving only the $\omega^-$ mode as the clearly observable mode.

We now return to the oscillatory nature of the linewidths shown in figure 1. Instead of showing the thickness dependence, we study the momentum dependence of the linewidth, where the e–h pair spectra show continuous variations. The underlying reason can be elucidated by
Figure 3. (a) Dispersion relations of the $\omega^-$ plasmon (solid line) and the non-interacting e–h pairs (color) for a thin film of thickness $4d_m$. (b) Linewidth of the plasmon (solid line) and density of the e–h pairs (dashed line) along the plasmon dispersion curve shown in (a). The black solid and red hollow arrows indicate the corresponding vertical axes for the black solid and red dashed lines, respectively. The vertical dashed blue line passing through the figure indicates the momentum transfer analyzed in figure 2.

comparing the dispersions of the plasmon and the non-interacting e–h pairs in figure 3(a). When the plasmon energy (solid line) passes through the gap regions of the e–h pair spectra, Landau damping should be strongly suppressed due to the lack of decay channels. In figure 3(b), following the plasmon dispersion curve (solid line), we plot the corresponding e–h pair density and linewidth. Indeed, for the momentum $k \geq 0.03$ au, the magnitude of the plasmon linewidth correlates well with the e–h pair density. However, deviations from this trend are clearly visible for smaller momenta. First, no peaked values in the linewidth are observed at the locations where the interband e–h pairs are highly peaked. This can be understood from the fact that the $\omega^-$ mode is dominantly contributed by the intra-band transitions, and the coupling between the intraband and interband e–h pairs is very weak. More intriguing in figure 3(b) is the peak in the linewidth at momenta where the e–h pair density shows minima. To resolve this counter-intuitive observation, we go back to figure 2, where we have compared the absorption spectra with and without numerical broadening for $k = 0.014$ au (indicated by the vertical dashed line passing through figure 3). By comparing figures 2(b) and 3(b), we can clearly see that the unexpected linewidth peak is due to the numerical broadening of two nearly degenerate plasmon modes, which otherwise would have been overshadowed if using the conventional real-space approach. This broadening mechanism due to plasmon hybridization is different.
from the well-recognized Landau damping mechanism, where a plasmon mode loses its coherence to the e–h continuum. In comparison with the case that the plasmon peak passes through the interband e–h pair spectrum, this broadening indicates a larger interaction between the plasmons than plasmon/e–h pair coupling. Furthermore, such a hybridization broadening of nearly degenerate plasmon modes can also take place inside an e–h pair continuum, as indicated by the plasmon linewidth peak around $k = 0.03$ in figure 3(b).

4. Conclusions

In summary, we have performed a comprehensive study of the energy and linewidth of plasmons in various quantized metal structures. We found that Landau damping, as the main dissipation channel in this regime, can be drastically tuned owing to energy quantization of the individual electron levels and e–h pairs. The generic oscillatory nature of the tunability is in stark contrast with the expectations of a semiclassical surface scattering picture. The use of an e–h pair basis also allows us to illustrate the evolution of the plasmons from the quantum to the classical regime, and to reveal the underlying physical origin of strong hybridization broadening of nearly degenerate plasmon modes. These findings are expected to guide the future design of plasmonic nanostructures of wide applicability.

Acknowledgments

We have benefited from fruitful discussions with Dr Adolfo Eguiluz, Dr Shiwu Gao, Dr Feng Hao and Dr Ke Zhao. This work was partially supported by the US NSF (grant number DMR-0906025), the US DOE (grant numbers DEFG0205ER46209 and BES-CMCSN) and the NNSF of China (grant number 11034006). DX was supported by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, the US DOE.

Appendix. Equations for different prototypical structures

Due to the existing rotational and translational symmetries in our prototypical systems, the excitation of plasmon modes should satisfy the energy conservation and also the (angular) momentum conservation. We then expand all related quantities in our systems based on the corresponding conserved quantum numbers. For the wave function, we have

$$\psi_{0D}(r, \Omega) = \phi_{n,l}(r) Y_{l,m}(\Omega) = \frac{u(r)}{\sqrt{4\pi r^2}} Y_{l,m}(\Omega),$$

$$\psi_{1D}(r, \theta, z) = \phi_{n,l}(r) e^{i\theta} e^{ikz} = \frac{u(r)}{\sqrt{2\pi r L}} e^{i\theta} e^{ikz},$$

$$\psi_{2D}(r, r_\parallel) = \phi_{n}(r) \frac{e^{ik_\parallel r_\parallel}}{L} = \frac{u(r)}{L} \phi_{n}(r) e^{ik_\parallel r_\parallel},$$

where $Y_{l,m}(\Omega)$ is the spherical harmonics function, satisfying the normalization condition $\int d\Omega |Y_{l,m}(\Omega)|^2 = 4\pi$, $L$ is the size-dependent normalization factor, $n$ is the quantum number in the $r$ direction, $l$ is the angular momentum, $m$ is the magnetic quantum number, $k$ is the momentum in the direction with translational symmetry, $\phi(r)$ is the wavefunction in the
direction and \( u(r) \) is its modified form satisfying the normalization relation \( \int dr |u(r)|^2 = 1 \). Inserting the wavefunction equation (A.1) into the KS equation, we can obtain the centrifugal potential \( V_{geo}(r) \) in the reduced 1D KS equation as

\[
V_{geo,0D}(r) = \frac{l(l+1)}{2r^2}, \quad V_{geo,1D}(r) = \frac{(l+\frac{1}{2})(l-\frac{1}{2})}{2r^2}, \quad V_{geo,2D}(r) = 0. \tag{A.2}
\]

On the other hand, the Hartree potential \( V_H \) is

\[
V_{H,0D}[n(r)] = 4\pi \int dr' \left[ r'^2 \rho(r') \right] \frac{1}{r_s}, \quad V_{H,1D}[n(r)] = -4\pi \int dr' \left[ r'^2 \rho(r') \right] \ln r_s, \quad V_{H,2D}[n(r)] = -4\pi \int dr' \left[ \rho(r') \right] r_s, \tag{A.3}
\]

where \( r_s = \max(r, r') \) and \( \rho(r) = n(r) - n_b(r) \) is the charge density, including the contributions from both ions and electrons. For the exchange-correlation potential \( V_{xc} \) we use the Perdew–Zunger local density approximation functional.

Due to the rotational and translational symmetries, all quantities in our systems can be factorized with certain quantum numbers and evaluated correspondingly. For the response function \( \chi^0 \), we have

\[
\chi_{0D}^0(r, r') = \sum_{l,m} \chi_{0D}^0(r, r'; l) Y_{lm}(\Omega) Y_{lm}^*(\Omega'), \\
\chi_{1D}^0(r, r') = \sum_{l,q} \chi_{1D}^0(r, r'; l, q) e^{i(l-\theta)} e^{iq(z-z')}, \tag{A.4}
\]

\[
\chi_{2D}^0(r, r') = \sum_q \chi_{2D}^0(r, r'; q) e^{iq(r_l-r_l')},
\]

where \( l \) and \( q \) correspond to the angular momentum and momentum of e–h pairs, respectively. The Coulomb interaction can also be expanded in different geometries as

\[
V_{H,0D}(r, r') = \sum_{l,m} \frac{f_l}{r_s^{l+1}} \frac{4\pi}{2l+1} Y_{lm}(\Omega) Y_{lm}^*(\Omega'), \\
V_{H,1D}(r, r') = \sum_{l,q} 4\pi I_l(qr_s) K_1(qr_s) e^{i(l-\theta)} e^{iq(z-z')}, \tag{A.5}
\]

\[
V_{H,2D}(r, r') = \sum_q \frac{2\pi}{q} e^{iq(r_{r<s})} e^{iq(r_l-r_l')},
\]

where \( r_s = \min(r, r') \) and \( I(K)_l \) is the modified Bessel function. The additional interaction \( Kn_{ind} \) mentioned in the main text is the so-called electron–electron interacting kernel, where \( K \) including the Coulomb interaction and exchange-correlation part \( V_{xc}' = dV_{xc}[n(r)]/dn \) has the
to utilize the relation between Green’s function $G(r, r')$ in big parentheses is the Wigner 3 symbol $(\Phi_1)$ and momentum of electronic states, respectively, the system size increases, the Hamiltonian matrix will become very large, making the inverse as follows:

$$K_{0\text{D}}(r, r') = \frac{r_<^l}{r_>^{l+1}} \cdot \frac{2\pi}{2l+1} \cdot \frac{\delta(r, r')}{r^2} V_{xc}.$$  

$$K_{1\text{D}}(r, r') = 4\pi I(r) K(r) + \frac{\delta(r, r')}{r} V_{xc}',$$  

$$K_{2\text{D}}(r, r') = \frac{2\pi}{q} e^{q(r_e-r_o)} + \delta(r, r') V_{xc}' . \tag{A.6}$$

One way to evaluate $\chi^0$ from equation (7) is by using its modified form

$$\chi^0(r, r') = \sum_{a,b} f_a \left[ \frac{\Psi_{a,b}}{\omega + i\eta - (\epsilon_b - \epsilon_a)} + \frac{\Psi^{*}_{a,b}}{-\omega - i\eta - (\epsilon_b - \epsilon_a)} \right] \tag{A.7}$$

with $\Psi_{a,b} = \phi_a(r) \phi_b(r) \phi_a^{*}(r') \phi_b^{*}(r')$. The explicit reduced forms of different systems are listed as follows:

$$\chi^0_{0\text{D}}(r, r'; l) = \sum_{a,b} f_a \Phi_{a,b} \frac{(2l_a + 1)(2l_b + 1)}{4\pi} \left( \begin{array}{ccc} l & l_a & l_b \\ 0 & 0 & 0 \end{array} \right) \left[ \frac{1}{\omega + i\eta - (\epsilon_b - \epsilon_a)} + \frac{1}{-\omega - i\eta - (\epsilon_b - \epsilon_a)} \right] , \tag{A.8}$$

$$\chi^0_{1\text{D}}(r, r'; l, q) = \sum_{a,b} f_a \Phi_{a,b} \delta_{l_a+l_b} \left[ \frac{1}{\omega + i\eta - (\epsilon_b - \epsilon_a) - \frac{1}{2} q^2 - k_a q} \right] + \frac{1}{-\omega - i\eta - (\epsilon_b - \epsilon_a) - \frac{1}{2} q^2 + k_a q} \right] , \tag{A.9}$$

$$\chi^0_{2\text{D}}(r, r'; q) = \sum_{a,b} f_a \Phi_{a,b} \left[ \frac{1}{\omega + i\eta - (\epsilon_b - \epsilon_a) - \frac{1}{2} q^2 - k_a \cdot q} \right] + \frac{1}{-\omega - i\eta - (\epsilon_b - \epsilon_a) - \frac{1}{2} q^2 + k_a \cdot q} \right] , \tag{A.10}$$

where $\epsilon$ is the state energy in the confined dimensions; $l_{a,b}$ and $k_{a,b}$ are the angular momentum and momentum of electronic states, respectively, $\Phi_{a,b} = \phi_a(r) \phi_b(r) \phi_a(r') \phi_b(r')$; the expression in big parentheses is the Wigner 3 symbol.

To perform the summation of the infinite number of states $b$, a commonly used method is to utilize the relation between Green’s function $G$ and Hamiltonian $H$ [27, 30, 34]

$$G(r, r', E) = \sum_b \frac{\phi_b(r) \phi_b(r')}{E - H} , \tag{A.11}$$

where the Green’s function can be solved from

$$(E - H)G = \delta(r - r') . \tag{A.12}$$

Then we just need to perform the finite-term summation $\sum_a f_a$ for initial states. However, as the system size increases, the Hamiltonian matrix will become very large, making the inverse
process become slow. More importantly, for the 1D and 2D systems, the summation \( \sum_a f_a \) is actually an integration for the momentum \( k_a \), and the inaccuracy will then be introduced by doing this integration numerically. So, for the 1D and 2D systems, we can use the second method to first integrate the momentum \( k \) in the formulae, which gives

\[
\chi_{1D}(r', l, q) = \sum_{a,b} f_a \Phi_{a,b} \ln \left[ \frac{(k_+ q - \frac{1}{2} q^2) - \epsilon_{a,b} + \omega + i\eta}{(k_- q - \frac{1}{2} q^2) - \epsilon_{a,b} + \omega + i\eta} \right]
\]

(A.13)

for the 1D system, where \( k_{\pm} = \pm q \sqrt{2(E_F - \epsilon_a)} \), and

\[
\chi_{2D}(r', q) = -\frac{i}{2\pi q^2} \sum_{a,b} f_a \Phi_{a,b} \left[ \sqrt{2(E_F - \epsilon_a) q^2 - \left( -\frac{1}{2} q^2 - \epsilon_{a,b} + \omega + i\eta \right)^2} \right. \\
- \frac{1}{q} \sqrt{2(E_F - \epsilon_a) q^2 - \left( -\frac{1}{2} q^2 - \epsilon_{a,b} + \omega + i\eta \right)^2} \\
- \left( \sqrt{- \left( -\frac{1}{2} q^2 - \epsilon_{a,b} + \omega + i\eta \right)^2} - \sqrt{- \left( -\frac{1}{2} q^2 - \epsilon_{a,b} + \omega + i\eta \right)^2} \right) \right] 
\]

(A.14)

for the 2D system \([26, 29, 40]\) with \( \epsilon_{a,b} = \epsilon_b - \epsilon_a \).

In the end, the external field for the absorption calculation can also be factorized as

\[
V_{ext,0D}(r) = r' Y_{l,m}(\Omega), \\
V_{ext,1D}(r) = I_l(k,r) e^{i\theta} e^{iqz}, \\
V_{ext,2D}(r) = e^{iqr} e^{iq r_z}.
\]

(A.15)

References

[1] Kreibig U and Volmer M 1995 Optical Properties of Metal Clusters (Berlin: Springer)
[2] Barnes W L, Dereux A and Ebbesen T W 2003 Surface plasmon subwavelength optics Nature 424 824–30
[3] Ozbay E 2006 Plasmonics: merging photonics and electronics at nanoscale dimensions Science 311 189–93
[4] Kneipp K, Wang Y, Kneipp H, Perelman L T, Itzkan I, Dasari R R and Feld M S 1997 Single molecule detection using surface-enhanced Raman scattering (SERS) Phys. Rev. Lett. 78 1667–70
[5] Xu H X, Bjerneld E J, Käll M and Börjesson L 1999 Spectroscopy of single hemoglobin molecules by surface enhanced raman scattering Phys. Rev. Lett. 83 4357–60
[6] Matsubara K, Kawata S and Minami S 1988 Optical chemical sensor based on surface plasmon measurement Appl. Opt. 27 1160–3
[7] Anker J N, Hall W P, Lyandres O, Shah N C, Zhao J and Van Duyne R P 2008 Biosensing with plasmonic nanosensors Nature Mater. 7 442–53
[8] Srituravanich W, Fang N, Sun C, Luo Q and Zhang X 2004 Plasmonic nanolithography Nano Lett. 4 1085–8
[9] Luo X G and Ishihara T 2004 Surface plasmon resonant interference nanolithography technique Appl. Phys. Lett. 84 4780–2
[10] Atwater H A and Polman A 2010 Plasmonics for improved photovoltaic devices Nature Mater. 9 205–13
[11] Zuloaga J, Prodan E and Nordlander P 2009 Quantum description of the plasmon resonances of a nanoparticle dimer Nano Lett. 9 887–91
[12] Zhao K, Troparevsky M C, Xiao D, Eguiluz A G and Zhang Z Y 2009 Electronic coupling and optimal gap size between two metal nanoparticles Phys. Rev. Lett. 102 186804
[13] Scholl J A, Koh A L and Dionne J A 2012 Quantum plasmon resonances of individual metallic nanoparticles Nature 483 421–7
[14] Savage K J, Hawkeye M M, Esteban R, Borisov A G, Aizpurua J and Baumberg J J 2012 Revealing the quantum regime in tunnelling plasmonics Nature 491 574–7
[15] Chang J-J and Langreth D C 1972 Deep-hole excitations in solids: I. Fast-electron–plasmon effects Phys. Rev. B 5 3512–22
[16] Chang J-J and Langreth D C 1973 Deep-hole excitations in solids: II. Plasmons and surface effects in x-ray photoemission Phys. Rev. B 8 4638–54
[17] Esteban R, Borisov A G, Nordlander P and Aizpurua J 2012 Bridging quantum and classical plasmonics with a quantum-corrected model Nature Commun. 3 825
[18] Jensen T R, Malinsky M D, Haynes C L and Van Duyne R P 2000 Nanosphere lithography: tunable localized surface plasmon resonance spectra of silver nanoparticles J. Phys. Chem. B 104 10549–56
[19] Prodan E and Nordlander P 2003 Structural tunability of the plasmon resonances in metallic nanoshells Nano Lett. 3 543–7
[20] Zaremba E and Persson B N J 1987 Dynamic polarizability of small metal particles Phys. Rev. B 35 596–606
[21] MacDonald K F, Sámon Z L, Stockman M I and Zheludev N I 2009 Ultrafast active plasmonics Nature Photon. 3 55–8
[22] Klar T, Perner M, Grosse S, von Plessen G, Spirk W and Feldmann J 1998 Surface-plasmon resonances in single metallic nanoparticles Phys. Rev. Lett. 80 4249–52
[23] Stietz F, Bosbach J, Wenzel T, Vartanyan T, Goldmann A and Träger F 2000 Decay times of surface plasmon excitation in metal nanoparticles by persistent spectral hole burning Phys. Rev. Lett. 84 5644–7
[24] Kreibig U and Fragstein C V 1969 The limitation of electron mean free path in small silver particles Z. Phys. 224 307–23
[25] Kawabata A and Kubo R 1966 Electronic properties of fine metallic particles: II. Plasma resonance absorption J. Phys. Soc. Japan 21 1765–72
[26] Yuan Z and Gao S W 2006 Linear-response study of plasmon excitation in metallic thin films: layer-dependent hybridization and dispersion Phys. Rev. B 73 155411
[27] Zangwill A and Soven P 1980 Density-functional approach to local-field effects in finite systems: photoabsorption in the rare gases Phys. Rev. A 21 1561–72
[28] Ku W and Eguiluz A G 1999 Plasmon lifetime in $k$: a case study of correlated electrons in solids amenable to ab initio theory Phys. Rev. Lett. 82 2350–3
[29] Prodan E, Lee A and Nordlander P 2002 The effect of a dielectric core and embedding medium on the polarizability of metallic nanoshells Chem. Phys. Lett. 360 325–32
[30] Prodan E and Nordlander P 2002 Electronic structure and polarizability of metallic nanoshells Chem. Phys. Lett. 352 140–6
[31] Prodan E, Nordlander P and Halas N J 2003 Effects of dielectric screening on the optical properties of metallic nanoshells Chem. Phys. Lett. 368 94–101

New Journal of Physics 15 (2013) 023011 (http://www.njp.org/)
[36] Silkin V M, Chulkov E V and Echenique P M 2004 Band structure versus dynamical exchange-correlation effects in surface plasmon energy and damping: a first-principles calculation Phys. Rev. Lett. 93 176801
[37] Pitarke J M, Silkin V M, Chulkov E V and Echenique P M 2007 Theory of surface plasmons and surface-plasmon polaritons Rep. Prog. Phys. 70 1–87
[38] Silkin V M, Kazansky A K, Chulkov E V and Echenique P M 2010 Time-dependent screening of a point charge at a metal surface J. Phys.: Condens. Matter 22 304013
[39] Yuan Z and Gao S W 2008 Landau damping and lifetime oscillation of surface plasmons in metallic thin films studied in a jellium slab model Surf. Sci. 602 460–4
[40] Eguiluz A G 1983 Dynamical density response function of a metal film in the random-phase approximation Phys. Rev. Lett. 51 1907–10
[41] Rowe D J 1968 Methods for calculating ground-state correlations of vibrational nuclei Phys. Rev. 175 1283–92
[42] Bertsch G F and Broglia R A 1994 Oscillation in Finite Quantum Systems (Cambridge: Cambridge University Press) p 69
[43] Rowe D J 1985 Microscopic theory of the nuclear collective model Rep. Prog. Phys. 48 1419
[44] Wambach J 1988 Damping of small-amplitude nuclear collective motion Rep. Prog. Phys. 51 989
[45] Drozdz S, Nishizaki S, Speth J and Wambach J 1990 The nuclear response within extended RPA theories Phys. Rep. 197 1–65
[46] Bernath M, Spina M E and Pacheco J M 1994 Microscopic description of the plasmon resonance in small deformed metal clusters Phys. Rev. B 49 10764–7
[47] Catara F, Piccitto G, Sambataro M and Van Giai N 1996 Towards a self-consistent random-phase approximation for Fermi systems Phys. Rev. B 54 17536–46
[48] Gambacurta D, Grasso M, Catara F and Sambataro M 2006 Extension of the second random-phase approximation Phys. Rev. C 73 024319
[49] Gambacurta D and Catara F 2008 Particle–hole excitations within a self-consistent random-phase approximation Phys. Rev. B 77 205434
[50] Liebsch A 1993 Surface-plasmon dispersion and size dependence of me resonance: silver versus simple metals Phys. Rev. B 48 11317–28
[51] Liebsch A 1993 Surface plasmon dispersion of Ag Phys. Rev. Lett. 71 145–8
[52] Pitarke J M, Nazarov V U, Silkin V M, Chulkov E V, Zaremba E and Echenique P M 2004 Theory of acoustic surface plasmons Phys. Rev. B 70 205403
[53] Silkin V M, Pitarke J M, Chulkov E V and Echenique P M 2005 Acoustic surface plasmons in the noble metals Cu, Ag and Au Phys. Rev. B 72 115435
[54] Prodan E and Nordlander P 2004 Plasmon hybridization in spherical nanoparticles J. Chem. Phys. 120 5444–54
[55] Prodan E, Radloff C, Halas N J and Nordlander P 2003 A hybridization model for the plasmon response of complex nanostructures Science 302 419–22
[56] Bréchignac C, Cahuzac P, Leygnier J and Sarfati A 1993 Optical response of large lithium clusters: evolution toward the bulk Phys. Rev. Lett. 70 2036–9
[57] Molina R A, Weinmann D and Jalabert R A 2002 Oscillatory size dependence of the surface plasmon linewidth in metallic nanoparticles Phys. Rev. B 65 155427
[58] Weick G, Molina R A, Weinmann D and Jalabert R A 2005 Lifetime of the first and second collective excitations in metallic nanoparticles Phys. Rev. B 72 115410