Coulomb Excitations for a Short Linear Chain of Metallic Shells

Liubov Zhemchuzhna$^{1,3}$, Godfrey Gumbe$^{1,2}$, Andrii Iurov$^3$, Danhong Huang$^4$ and Bo Gao$^1$

$^1$Department of Physics and Astronomy, Hunter College of the City University of New York, 695 Park Avenue, New York, NY 10065, USA

$^2$Donostia International Physics Center (DIPC), P de Manuel Lardizabal, 4, 20018 San Sebastian, Basque Country, Spain

$^3$Center for High Technology Materials, University of New Mexico, NM 87106, USA

$^4$Air Force Research Laboratory, Space Vehicles Directorate, Kirtland Air Force Base, NM 87117, USA

A self-consistent-field theory is given for the electronic collective modes of a chain containing a finite number, $N$, of Coulomb-coupled spherical two-dimensional electron gases (S2DEGs) arranged with their centers along a straight line, simulating a narrow micro-ribbon of metallic shells. The separation between nearest-neighbor shells is arbitrary and because of the quantization of the electron energy levels due to their confinement to the spherical surface, all angular momenta $L$ of the Coulomb excitations and their projections $M$ on the quantization axis are coupled. However, for incoming light with a specific polarization, only one angular momentum quantum number is chosen. We show that when $N = 3$ the next-nearest-neighbor Coulomb coupling is larger than its value if they are located at opposite ends of a right-angle triangle forming the triad. Additionally, the frequencies of the plasma excitations depend on the orientation of the line joining them with respect to the axis of quantization since the magnetic field generated from the induced oscillating electric dipole moment on one sphere can couple to the induced magnetic dipole moment on another.

PACS numbers: 73.20.-r, 73.20.Mf, 78.20.Bh, 78.67.Bf

I. INTRODUCTION

Over the years, plasmon excitations have been investigated both experimentally and theoretically for topologically different nanostructures such as the two-dimensional electron gas (2DEG) and for systems with layers of 2DEG forming a layered electron gas (LEG) systems [1,2]. The LEG may be obtained in a multilayer semiconductor system by epitaxial growth such as GaAs/AlGaAs or in a type-II system such as GaSb A1Sb InAs quantum-well structures containing an electron and a hole gas layer in each unit cell [3]. Another class of nanostructures for which the Coulomb excitations have been studied is the spherical 2DEG (S2DEG) [4–6] which has been employed in modeling metallic dimers [7,8], clusters of carbon nanoparticles [9] and metallic chains of gold nanoparticles [10,11]. However, since the spherical geometry allows for possible anisotropic coupling (unlike the cylindrical geometry [12,13]) with an external light source by employing far-field polarization spectroscopy [11], the Coulomb excitations for the S2DEG allow for more variation in frequency than the 2DEG by employing shells of different radii, forming finite length chains with adjustable nearest-neighbor separations, or using bundles arranged in assorted configurations. Furthermore, we may model the S2DEG as an incompressible fluid [8] or as a point dipole [14] in which only nearest-neighbor dipole interactions through an EM field are assumed dominant [14]. But, in such a model, the dipoles have been assumed to point in a chosen direction (like in an antenna array) so that only one component of the angular momentum is employed, e.g., if $L = 1$ then only one of $M = 0, \pm 1$ plays a role. In this paper, we overcome this restriction in investigating longitudinal and transverse plasmon-polariton modes in a chain with a finite number $N$ of metallic shells. Although our formalism may be applied to arbitrary $N$, we present results when $N = 3$ since it affords us with the opportunity of comparing with the configuration when the shells are positioned with their centers at the vertices of a right-angle triangle. This example demonstrates the orientational dependence of the Coulomb matrix elements as well as the effects arising from the finite length of a linear chain.

Our model described below is drastically different from that in Ref. [14] because we include dynamically screened long-range Coulomb interactions and the orbital angular momenta and their projections onto the quantization axis are coupled. This means that the localized plasmons on each shell are coupled by the inter-sphere electron-electron Coulomb interaction. Also, an important difference between the present model and the point-dipole model is that the electromagnetic field generated by time-varying charge distributions or current is retarded, whereas in our model the inter-shell coupling is electrostatic. Since the polarization function for the S2DEG vanishes for $L = 0$, there are no plasmon excitations for $L = 0$ [4]. This is in contrast with the model in Ref. [11] which allows plasmon excitations when the dipoles have a fixed direction, i.e., which corresponds to a chosen projection for an unspecified angular momentum.

With the use of our formalism, we may directly simulate the modes of oscillation observable by employing circularly-polarized light or a helical light beam. That is, the plasmons are detected experimentally using an external polarizing...
field, which specifies a preferred direction, which is the $z$-axis in our case. Our primary goal is to consider a closely packed finite-length assembly of S2DEGs with all their centers on a straight line relative to the quantization axis. In such a system, the strength of the interaction between different nano shells varies with their separation as well as the relative orientation of the line joining their centers. With this in mind, it makes sense to distinguish the present investigation from both cases of a triad arranged at the vertices of a right-angle triangle [9] or an infinite linear array of periodically placed S2DEGs [10]. The assembly under consideration is shown schematically in Fig. 1. We refer to each shell as $j = 1, 2, 3, \cdots, N$, starting with the one on the far left. For $N = 3$, the middle shell is centered at the origin. We specify the distances between the S2DEGs as $a_{12} = a_1$ and $a_{23} = a_2$, so that $a_{13} = a_1 + a_2$. In all our numerical considerations, we investigate separately the cases corresponding to equal and unequal distances $a_1$ and $a_2$ in conjunction with equal and unequal radii of the shells. We consider either the case of three identical shells with $R_1 = R_2 = R_3$ or the situation when the middle shell is larger than the other two: $R_2 > R_1 = R_3$.

The spatial anisotropy of the plasmon excitations is just another example of the orientational dependence of the optical and transport properties of condensed matter systems. We now cite a few examples when such an anisotropy has been demonstrated. These include the electrical, thermal, mechanical and chemical properties of graphite along the $a$, $b$ and $c$ directions [15] and the elastic properties of carbon nanotube bundles [16]. Also, the dispersion relation of the high-frequency optical $\pi$-plasmons for graphite was calculated by Chiu, et al., [17] and it was shown that the plasmon excitations depend on whether the momentum transfer is parallel or perpendicular to the hexagonal plane lying in the Brillouin zone. The anisotropic conductivity of epitaxial graphene on SiC was reported in Ref. [18]. We note that there have been reports in which some of these anisotropic properties have been used in device applications. For example, in Ref. [19], the tuning of surface plasmon frequencies to more efficient optical sensors was investigated.

The rest of this paper is presented in the following way. In Sec. II the theoretical formulation for deriving the plasmon equation for three spherical shells whose centers are on a straight line. The Coulomb matrix elements are shown to depend on the relative orientation of this line-of-centers with respect to the axis of quantization for the angular momentum associated with the spherical geometry. The plasmon equation in general involves the coupling of all angular momenta and their projections on the quantization axis. But, in Sec. III we obtain the dielectric matrix assuming the impinging light source probing the Coulomb excitations has a specified polarization. Section IV is devoted to a presentation and discussion of our numerical results. We conclude with a summary of our results in Sec. V.

II. THEORETICAL FORMULATION OF THE PROBLEM

We turn our attention to a system of $N$ spherical shells with their centers on the $x$ axis. The center of one of the spheres is located at $x = 0$ with radius $R_0$ whereas the other spheres are centered at $x = -a_1$ and its radius is
\[ R_1, x = a_2 \text{ and radius } R_2, \text{ and so on. We assume no overlap of the shells so that we demand, for example, that the} \]
\[ \text{inequalities } a_1 > R_1 + R_0 \text{ and } a_2 > a_0 + a_2 \text{ are satisfied. In the absence of tunneling between the shells, the wave} \]
\[ \text{function for an electron on the } j \text{-th shell } (j = 1, 2, 3, \cdots, N) \text{ is given by} \]
\[ < r | j \nu > = \Psi_{jlm}(\vec{r} - (j - 1)a\hat{e}_x), \quad \Psi_{jlm}(\vec{r}) = f_j(r) \frac{1}{\sqrt{R_j^2}} Y_{lm}(\Omega), \] (1)
\[ \text{with } \nu = \{l, m\} \text{ and } f_j^2(r) = \delta(r - R_j). \text{ The energy spectrum has the form} \]
\[ \epsilon_{j,\nu} = \frac{\hbar^2 l(l + 1)}{2m^*R_j^2}. \] (2)
\[ \text{The equation of motion of the density matrix operator is} \]
\[ i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}], \] (3)
\[ \text{where } \hat{H} = \hat{H}_0 - e\Phi \text{ is the Hamiltonian of the electron on the surface of the sphere, } \hat{H}_0 \text{ is the free electron Hamiltonian} \]
\[ \text{and } \Phi \text{ is the induced potential. The potential } \Phi \text{ satisfies Poisson’s equation} \]
\[ \nabla^2 \Phi(\mathbf{r}, \omega) = \frac{4\pi e}{\varepsilon_s} \delta n(\mathbf{r}, \omega), \] (4)
\[ \text{where } \varepsilon_s = 4\pi \varepsilon_0 \varepsilon_b \text{ and } \varepsilon_b \text{ is the uniform background dielectric constant. Additionally, } \delta n(\mathbf{r}, \omega) \text{ is the induced electron density. We use linear response theory to calculate the induced particle density as} \]
\[ \delta n(\mathbf{r}, \omega) = \sum_{j,j',\nu,\nu'} \sum_{j,j';\nu,\nu'} < r | j \nu > < j' \nu' | \hat{\rho}_1(\mathbf{r}, \omega) | j' \nu' > < j' \nu' | \mathbf{r} >, \] (5)
\[ \text{where} \]
\[ < j \nu | \hat{\rho}_1(\mathbf{r}, \omega) | j' \nu' > = 2e \frac{f_0(\epsilon_{j\nu}) - f_0(\epsilon_{j'\nu'})}{\hbar \omega + \epsilon_{j'\nu'} - \epsilon_{j\nu}} < j \nu | \Phi(\mathbf{r}, \omega) | j' \nu' >, \] (6)
\[ \text{in terms of the Fermi-Dirac distribution function } f_0(\epsilon) \text{ and we express the induced potential as } \Phi(\mathbf{r}) = \frac{1}{V_0} \sum_{\mathbf{q}} \Phi(\mathbf{q}') e^{i\mathbf{q}' \cdot \mathbf{r}}, \]
\[ \text{where } V_0 \text{ is a normalization volume. Then Eq. (5) becomes} \]
\[ \delta n(\mathbf{r}, \omega) = \frac{2e}{V_0} \sum_{j,j',\nu,\nu'} \sum_{\mathbf{q}} \frac{f_0(\epsilon_{j\nu}) - f_0(\epsilon_{j'\nu'})}{\hbar \omega + \epsilon_{j'\nu'} - \epsilon_{j\nu}} < r | j \nu > < j' \nu' | \mathbf{r} > \]
\[ \times \sum_{\mathbf{q}'} \Phi(\mathbf{q}') < j \nu | e^{i\mathbf{q}' \cdot \mathbf{r}} | j' \nu' >, \] (7)
\[ \text{or by taking the Fourier transform with respect to } \mathbf{r} \]
\[ \delta n(\mathbf{q}, \omega) = \frac{2e}{V_0} \sum_{j,j',\nu,\nu'} \sum_{\mathbf{q}'} \frac{f_0(\epsilon_{j\nu}) - f_0(\epsilon_{j'\nu'})}{\hbar \omega + \epsilon_{j'\nu'} - \epsilon_{j\nu}} < j' \nu' | e^{-i\mathbf{q} \cdot \mathbf{r}} | j \nu > \]
\[ \times \sum_{\mathbf{q}'} \Phi(\mathbf{q}') < j \nu | e^{i\mathbf{q}' \cdot \mathbf{r}} | j' \nu' >. \] (8)
\[ \text{The matrix elements } < j \nu | e^{i\mathbf{q} \cdot \mathbf{r}} | j' \nu' > \text{ with wave functions } < r | j \nu > \text{ given by Eq. (1) may be calculated using} \]
\[ \text{the expansion of a plane wave in spherical waves} \]
\[ e^{i\mathbf{q} \cdot \mathbf{r}} = 4\pi \sum_{l,m} i^l j_l(qr) Y_{lm}^*(\hat{\mathbf{q}}) Y_{lm}(\hat{\mathbf{r}}) \] (9)

where \( j_l(x) \) is a spherical Bessel function. The result is

\[
<j_{\lambda\nu} | e^{i\mathbf{q} \cdot \mathbf{r}} | j'_{\lambda'\nu'}> = 4\pi \delta_{j,j'} \exp(i(j-1)qz) \\
\times \sum_{L,M} i^L j_L(qR_j) Y^*_{LM}(\hat{\mathbf{q}}) \int d\Omega \ Y_{lm}^*(\Omega) Y_{LM}(\Omega) Y_{l'm'}(\Omega),
\]

(10)

Substituting Eq. (10) into Eq. (8), we obtain after some algebra

\[
\delta n(\mathbf{q}, \omega) = (4\pi)^2 \frac{2e}{V_0} \sum_{l,m} \sum_{l',r} \sum_{j=1,2} f_0(\epsilon_{j,l}) - f_0(\epsilon_{j,l'}) \frac{1}{\hbar\omega + \epsilon_{j,l'} - \epsilon_{j,l}} (2l + 1)(2l' + 1) \left( \begin{array}{c} l \\ 0 \end{array} \right) \left( \begin{array}{c} l' \\ 0 \end{array} \right) \left( \begin{array}{c} L \\ 0 \end{array} \right)^2
\times e^{-i(j-1)qz} a \sum_{M} j_L(qR_j) Y_{LM}(\hat{\mathbf{q}})
\times \sum_{q_x'q_y'q_z'} e^{i(j-1)q_{z'}a} \Phi (q_{x}',q_{y}',q_{z}) j_L(q'R_j) Y^*_{LM}(\hat{\mathbf{q}}').
\]

(12)

in terms of Clebsch-Gordon coefficients. Taking the Fourier transform of Eq. (4) we have \( \Phi(\mathbf{q}) = -4\pi e\delta n(\mathbf{q})/\varepsilon s q^2 \). Using this relation in Eq. (11), we obtain

\[
\delta n(\mathbf{q}, \omega) = -\frac{8\pi e^2}{\varepsilon_s} (4\pi)^2 \frac{2e}{V_0} \sum_{j,L,M} \Pi_{j,L}(\omega) e^{-i(j-1)q_{z}a} j_L(qR_j) U_{j,L,M} Y_{LM}(\hat{\mathbf{q}}),
\]

(13)

where \( \Pi_{j,L}(\omega) \) is the density response function of the \( j \)-th nano shell with

\[
\Pi_{L}(\omega) = \sum_{l,l'} \frac{f_0(\epsilon_l') - f_0(\epsilon_{l'})}{\hbar\omega + \epsilon_{l'} - \epsilon_l} (2l + 1)(2l' + 1) \left( \begin{array}{c} l \\ 0 \end{array} \right) \left( \begin{array}{c} l' \\ 0 \end{array} \right) \left( \begin{array}{c} L \\ 0 \end{array} \right)^2
\]

(14)

and

\[
U_{j,L,M} = \frac{1}{L_x L_y L_z} \sum_{q_x q_y q_z} e^{i(j-1)q_{z}a} \frac{\delta n(q_x,q_y,q_z,\omega)}{q_x^2 + q_y^2 + q_z^2} j_L(qR_j) Y^*_{LM}(\hat{\mathbf{q}}).
\]

(15)

Here, \( L_x, L_y \) and \( L_z \) are normalization lengths, with \( V_0 = L_x L_y L_z \). Substituting the expression for \( \delta n(\mathbf{q}) \) given in Eq. (13) into Eq. (15), we obtain
We have explicitly by setting \( \rho \) to reduce to the result for isolated shells. Since \( \rho \rightarrow 0 \), plasmon modes with different values of \( L \) are zero. Consequently, plasmon modes with different values of \( L \) do not contribute to the plasmon excitation spectrum. However, it is given for comparison. The insets demonstrate the corresponding interaction potential matrix elements (same color) as a function of the ratio \( R_2/R_1 \) of the radii of the two shells for fixed separation \( a \) between their centers.

\[
\sum_{j'=1}^{N} \sum_{L'=0}^{L} \sum_{M'=0}^{L'} \left[ \delta_{j,j'} \delta_{L,L'} \delta_{M,M'} + \frac{2e^2}{\varepsilon s} \Pi_{j',L'}(\omega) V_{j' L' M', j LM}(R_j, R_j', a) \right] U_{j',L'M'} = 0 ,
\]

(16)

where

\[
V_{j' L' M', j LM}(R_j, R_j'; a) = 8 \int \frac{d^2 q}{q^2} j_L(qR_j) j_L(qR_j') Y_{LM}^*(\hat{q}) Y_{L'M'}(\hat{q}) e^{i(j-j')q.a} = \frac{2(2L+1)}{2R(2L+1)} \delta_{L,L'} \delta_{M,M'} \quad \text{when} \quad j = j' .
\]

(17)

We have explicitly by setting \( j = 1, 2 \) or \( j = 3 \) in turn for each of the three spheres

\[
\left[ 1 + \frac{2e^2}{\varepsilon s (2L + 1)} R_j \Pi_{j,LM}(\omega) \right] U_{j,LM} + \frac{2e^2}{\varepsilon s} \sum_{j' \neq j} \sum_{L',M'} \Pi_{j',L'}(\omega) V_{j' L' M', j LM}(R_j, R_j', a) U_{j',L'M'} = 0 ,
\]

(18)

If the spheres are identical, then we need only set \( j = 1 \), but still have to do the sum over \( j' = 1, 2, 3 \). The set of linear equations (18) have nontrivial solutions provided the determinant of the coefficient matrix of \( \{ U_{j,LM} \} \) is zero. Consequently, plasmon modes with different values of \( L \) on the two shells may now be coupled via the Coulomb interaction. Since \( V_{L,L'}(R_1, R_2; a) \rightarrow 0 \) in the limit \( a \rightarrow \infty \), this matrix is diagonal when \( a \gg R_1, R_2 \) and the plasmon mode equation reduces to the result for isolated shells

\[
\prod_{L} \varepsilon_{1, L}^{2L+1}(\omega) \varepsilon_{2, L}^{2L+1}(\omega) \varepsilon_{3, L}^{2L+1}(\omega) = 0 ,
\]

(19)
FIG. 3: (Color online) Particle-hole modes and plasmon excitations for a single S2DEG and for a linear assembly of three shells as a function of their radii. Panel (a) shows the particle-hole modes for a single S2DEG. Panel (b) presents the plasmon excitation frequency of a single S2DEG as a function of its radius. All the other plots in panels (c) through (f) demonstrate the dependence of the plasmon frequency as a function of radius \( R \) for three equivalent S2DEGs with \( R_1 = R_2 = R \) and with equal separations \( a_1 = a_2 = a = 2R + 0.1\, nm \). Panels (c) and (d) represent the plasmon branches of an \( x \)-aligned linear triad with various ranges of their radii, i.e., from 1.0 to 1.7 nm for (c) and 1.0 to 2.4 nm for (d). Plots in (e) and (f) show the corresponding plasmon dependence for the case of \( z \)-alignment. While plot (e) shows results for radii in the range from 1.1 to 1.5 nm, and plot (f) gives the dependence over a narrower range 1.2 to 1.3 nm.

where \( \varepsilon_{j,L}(\omega) \) is the dielectric function for the \( j \)-th shell. The significance of equations (18) for chosen \( L, M \) is that they give explicitly the effect of the Coulomb interaction on each shell through \( \varepsilon_{j,L}(\omega) \) as well as the coupling between the pair of shells through the Coulomb matrix elements \( V_{j,L;M,L,M}(R_j, R_j, a) \). Additionally, the nature of this coupling may be characterized in the following way when carrying out numerical calculations. For chosen \( L, M \) satisfying \( -L \leq M \leq L \), there are \( 2(2L + 1) \times 2(2L + 1) \times 2(2L + 1) \) elements in a block sub-matrix which includes \( 2(2L + 1) \) elements along the diagonal, equal to \( \varepsilon_{1,L}(\omega) \), \( 2(2L + 1) \) diagonal elements equal to \( \varepsilon_{2,L}(\omega) \) and \( 2(2L + 1) \) diagonal elements equal to \( \varepsilon_{3,L}(\omega) \). For example, if we consider the coupling between sub-matrices with angular momentum \( L = 1, 2, 3, \cdots, N \), then the dimension of the matrix is \( 3 \sum_{L=1}^{N}(2L + 1) = 3N^2 + 6N \). Specifically, if we use just the \( L = 1 \) sub-matrix, we have a 9 \( \times \) 9 matrix which we discuss below.
III. DIELECTRIC FUNCTION MATRIX CALCULATION

We now restrict our attention to the case when \( N = 3 \) and the angular momentum quantum number is chosen as \( L = 1 \). The zeros of the dielectric function for the three aligned S2DEGs, which determine the plasmon excitation energies of the system, may be obtained as the solution of a determinantal equation \( \text{Det} \, \mathcal{M}_e = 0 \), where \( \mathcal{M}_e \) is a complete \( 9 \times 9 \) matrix, including the dielectric function of each nanosphere, as well as the inter-sphere interaction potential elements. In our formalism above, we took the spherical shells as being centered on the \( x \)-axis. However, without loss of generality, the spheres may be placed along the axis of quantization, the \( z \)-axis. In either case, the dielectric matrix may be presented as a block matrix as follows:

\[
\mathcal{M}_e = \begin{pmatrix}
\mathcal{D}_1 & \mathcal{V}^A_{12} & \mathcal{V}^S_{13} \\
\mathcal{V}^A_{21} & \mathcal{D}_2 & \mathcal{V}^A_{23} \\
\mathcal{V}^S_{31} & \mathcal{V}^A_{32} & \mathcal{D}_3
\end{pmatrix},
\]

(20)

where, in our notation, the submatrix \( \mathcal{D}_i \) is diagonal. Each diagonal block consists of three identical elements, representing the dielectric function of an isolated S2DEG: We have

\[
\mathcal{D}_i = \begin{pmatrix}
\epsilon_{L=1}(R_i, \omega) & 0 & 0 \\
0 & \epsilon_{L=1}(R_i, \omega) & 0 \\
0 & 0 & \epsilon_{L=1}(R_i, \omega)
\end{pmatrix},
\]

(21)

for \( i = 1, 2 \) or 3. The coupling between different shells is given by the off-diagonal blocks \( \mathcal{V}^A_{jj'} \) and \( \mathcal{V}^S_{jj'} \), representing the interaction potentials between the adjacent \((1 - 2)\) and \((2 - 3)\) shells, and next-nearest-neighbors \((1 - 3)\). This geometrical arrangement leads to the main specific feature of our case of the aligned shells. In this regard, we consider an off-diagonal \( 3 \times 3 \) interaction matrix \( \mathcal{V}_{jj'} \), which may denote either \( \mathcal{V}^A_{jj'} \) or \( \mathcal{V}^S_{jj'} \) and include their common features as demonstrated in Fig. 1. We emphasize that the analytical formula of the matrix and the expression for each elements are identical for a next-nearest-neighbor or an adjacent pair of S2DEG’s, while the only difference comes from the distance between the shells, resulting in the value \( a_{12} + a_{23} \) for the next-nearest-neighbor pair. Specifically, for \( L = L' = 1 \), the matrix consists of nine elements determined by the \( M \) and \( M' \) as follows:

\[
\mathcal{V}_{jj'}^{M,M'}(R; a_{jj'}) = \Pi_{L=1}(R, \omega) \begin{pmatrix}
V_{M=-1,M'=-1} & V_{M=-1,M'=0} & V_{M=-1,M'=1} \\
V_{M=0,M'=-1} & V_{M=0,M'=0} & V_{M=0,M'=1} \\
V_{M=1,M'=-1} & V_{M=1,M'=0} & V_{M=1,M'=1}
\end{pmatrix}.
\]

(22)

Each matrix element depends on the orientation of the nanoshells and will be calculated below according to Eq. (17).

Each matrix element in Eq. (21) may be expressed as \( \epsilon_{L=1}(R, \omega) = 1 + 2e^2/(3\epsilon_s R) \Pi_{L=1}(\omega) \). Consequently, for the simplest case of three non-interacting shells of equal radius \( R \), the plasmon branches are obtained by solving for the zeros of the function

\[
\text{Det} \, \mathcal{M}_e = (\text{Det} \, \mathcal{D})^3 = (1 + 2e^2/(3\epsilon_s R) \Pi_{L=1}(\omega))^9
\]

(23)

i.e. we obtain a ninefold degenerate plasmon solution for a single isolated S2DEG. This solution corresponds to the result for interacting spheres as a function of their separation when both \( a_{12}/R_i \to \infty \) and \( a_{23}/R_i \to \infty \). In proceeding to take the inter-shell Coulomb coupling into account, we must distinguish between the \( z \)- and \( x \)-alignments, leading to different analytical forms for the interaction submatrix. Let us now consider the interaction matrix elements for both cases of alignment. We conclude that the result of the integration is non-zero only for certain elements, representing an interesting set of selection rules. The situations varies for each alignment. For \( x \)-alignment, the order of the remaining Bessel function is determined by the difference \(|M - M'|\) and the elements are classified correspondingly (see Eq. (31)). For example, all the elements with \(|M - M'| = 1\) are equal to zero due to the inherent symmetry of the polar integral. For \( z \)-alignment, the azimuthal angle \( \phi \) is determined by the phases of the spherical harmonics in Eq. (17), so that only elements with \( M = M' \) are non-zero, i.e. we obtain only two such elements.

We first consider the simplest case of three identical shells each of radius \( R \) and with the same number of filled energy levels or Fermi level \( L_F \). We set the separation \( a_{12} = a_{23} = a \), so that \( a_{13} = 2a \). In previous work, we obtained
FIG. 4: (Color online) Plasmon excitations for a linear assembly of three identical S2DEGs as a function of the separation $a$ ($a_1 = a_2 = a$). The radius of the spheres was chosen to be $R = R_1 = R_2 = 0.8\,\text{nm}$. The upper panels (a) and (b) correspond to the case of $x$-alignment, and the lower ones (c) and (d) to $z$-alignment. Each panel presents results for a specific range of the separation $a$: 1.7 to 5.0 $\text{nm}$ for (a) and (b), respectively. In panel (c), the range is 1.6 to 1.9 $\text{nm}$ and 1.6 to 6.0 $\text{nm}$ in panel (d). The solution for a system of non-interacting shells $\Omega_0 = 9.17\,\text{eV}/\hbar$ is indicated for comparison.

The pair-wise interaction potential matrix for two S2GEGS with radii $R_1$ and $R_2$, aligned along the z-axis with separation $\alpha$

\[
V_{jj'} = \Pi_{L=1}(R, \omega) \begin{pmatrix} v_1 & 0 & 0 \\ 0 & v_3 & 0 \\ 0 & 0 & v_1 \end{pmatrix},
\]  

where

\[
v_1 = V_{11,11} = \frac{6e^2}{\pi \epsilon_s} \int_0^\infty \frac{dq}{(aq)^3} \left\{ \sin(\alpha q) - \alpha q \cos(\alpha q) \right\} j_1(R_1,q)j_1(R_2,q)
\]

\[
v_3 = V_{10,10} = \frac{6e^2}{\pi \epsilon_s} \int_0^\infty \frac{dq}{(aq)^3} \left\{ 2\alpha q \cos(\alpha q) + ((\alpha q)^2 - 1) \sin(\alpha q) \right\} j_1(R_1,q)j_1(R_2,q)
\]

The $\alpha$-dependence accounts for the fact that two adjacent spheres (1–2 and 2–3) have equal separation $a$, whereas the far-removed pair 1 and 3 have their centers separated by distance $2a$.

For a $z$-aligned triad, each interaction matrix block matrix consists of only two different Coulomb potential matrix elements and, most crucially, is diagonal. This established fact results in the factorization of the determinant of the $M_\epsilon$ matrix. The resulting product matrix is

\[
\text{Det} \, \tilde{M}_\epsilon = \prod_{\lambda=1}^4 m_\lambda
\]
For \( z \)-aligned shells, the potential submatrix is not diagonal, so similar factorization is not possible and we have

\[
V_{jj'} = \Pi_{L=1}(R, \omega) \begin{pmatrix} v_1 & 0 & v_2 \\ 0 & v_3 & 0 \\ v_2 & 0 & v_1 \end{pmatrix}.
\]  

(31)

with the elements as follows:

\[
v_1 = V_{1-1,1-1} = V_{11,11} = \frac{3e^2}{\pi \epsilon_s} \int_0^\infty \frac{dq}{(aq)^3} \left\{ aq \cos(aq) + \left( (aq)^2 - 1 \right) \sin(aq) \right\} j_1(R_1q)j_1(R_2q)
\]

(32)

\[
v_2 = V_{1-1,11} = V_{11,1-1} = \frac{3e^2}{\pi \epsilon_s} \int_0^\infty \frac{dq}{(aq)^3} \left\{ 3aq \cos(aq) + (aq)^2 - 3 \right\} \sin(aq) \right\} j_1(R_1q)j_1(R_2q)
\]

(33)

As the final step of our discussion of the potential elements, we address the properties of the largest one, corresponding to \( L = L' = 0 \) and \( M = M' = 0 \). It does not contribute to the plasmons of our system because \( \Pi_{L=0}(\omega) = 0 \).
Clearly, it demonstrates complete spherical symmetry, i.e. this is the only element, having this same property for both \( x \) and \( z \) alignments. Also, due to its specific symmetry properties, this is the largest element. Some straightforward integration in Eq. (18) leads to the following expression:

\[
V_{00,00}(R_1, R_2, a) = \frac{3e^2}{\pi \epsilon_s} \int_0^\infty dq \, j_0(R_1q) j_0(R_2q) j_0(aq) \tag{34}
\]

In the following section, we employ these results to determine numerically the plasmon excitations when three shells are lined up along or perpendicular to the axis of quantization.

IV. NUMERICAL RESULTS

As the first step for our numerical results, we investigate the Coulomb interaction potential matrix elements \( V_{j', L', M'; j, L, M}(R_{j', R'_j}, a_{j,j'}) \), which are involved in determining the plasmon excitations of the assembly according to Eq. (17). The calculation of the potential matrix elements of each interacting pair of S2DEGs is similar to our previous considerations. All non-zero potential matrix elements are given in Fig. 2 for \( L = 1 \). We note the each inter-sphere matrix element has a strong dependence on the distance between the shells, so that the interaction is significant for a closely packed assembly with \( a_{jj'} \propto R_j + R'_j \). This behavior is similar to the single shell potential matrix element \( \approx 1/(2L+1)R_j \). The magnitude of each element at a given distance depends on the symmetry of the quantum state, i.e. the values of \( L, L' \) as well as \( M \) and \( M' \). The largest one corresponds to rotational symmetry when \( L = L' = 0 \) and \( M = M' = 0 \). However, it does not couple with irradiation with specific polarization and, therefore does not contribute to the plasmon excitation since the polarization function is identically zero for zero angular momentum. All other elements are of the same order of magnitude. Existence of non-zero potential matrix elements are given by specific selection rules, representing an interesting contribution of our work. Thus, due to symmetry of the interaction, the only non-zero elements for \( z \)-alignment are those with \( M = M' \), which is not the case for the alternative situation of \( x \)-alignment. Only the elements with \( L = L' = 1 \) contribute to the plasmon spectrum for both cases of shell alignment. As a result, we are left with three different non-zero interaction matrix elements in the case of \( x \)-alignment, while the shells aligned along the \( z \) axis exhibit only two of them, which is reflected in constructing the interaction matrices in Eq. (20). The insets in Fig. 2 show the behavior of each potential matrix element for the case of unequal radii of the interacting shells. We conclude that there is no pattern for such dependence, except that each element, either positive or negative, increases (the absolute value) as a function of \( \rho = R_2/R_1 \) for approximately equal radii \( R_1 \approx R_2 \).

We now turn to a discussion of our numerical results for the plasmons of a linear triad of S2DEGs for angular momentum \( L = 1 \). The plasmon excitation energies of three Coulomb-coupled S2DEGs are obtained by solving for the zeros of the determinant of the matrix in Eq. (18) when the S2DEGs are centered on the \( z \) axis and solving the general equation \( \Pi_{L,M}(\omega) = 0 \) with the interaction submatrix given in Eq. (24). In general, we must deal with a matrix of infinite order whose elements are given by the coefficients of Eq. (18) since all angular momenta corresponding to \( L = 1, 2 \cdots, \infty \) are coupled. However, for incoming light with a specific polarization, only one angular momentum quantum number might be needed in carrying out the calculation to determine the plasmon frequencies since in general the angular momentum of light may be carried by either orbital motion (helicity) or spin motion (circular polarization). If a finite angular momentum of light with \( L = 1 \) is used for incidence, the magnetic field generated from the induced oscillating electric dipole moment on one sphere can couple to the induced magnetic dipole moment on another displaced sphere. This results in a \( 9 \times 9 \) determinantal equation with elements corresponding to \( j = 1, 2 \) and 3 in Eq. (18) with \( L = 1 \) and \( M = 0 \pm 1 \). The resulting matrix consists of the \( 3 \times 3 \) diagonal blocks, related to the plasmons of each individual S2DEG and the remaining six off-diagonal \( 3 \times 3 \) submatrices with \( j \neq j' = 1, 2 \) and 3. The diagonal block could be either identical for the case of three equivalent shells, or different, depending on the radius and the number of electrons on each S2DEG. Each block is diagonal, which means that for non-interacting shells the total matrix is diagonal and its determinant may be easily factorized.

Both the intra- and inter-shell Coulomb interactions contribute to the plasmon excitation energies. First, we determine how the plasma frequencies depend on the radius of three identical S2DEGs. Our results are presented in Fig. 3. First, we present the single-particle excitation region (SPER) in the \( \omega-R \) plane as being identified by finite imaginary part of the non-interacting electron polarization function \( \Pi_{L,M}(\omega) \) with the \( R \)-dependence arising from the single-particle energies in Eq. (2). The SPER, which is also referred to as the particle-hole excitation region, shows the \( \omega-R \) regions where there is natural damping of the plasmon modes. We see by comparing our plots in Figs. 3(a) and 3(b) that the plasmons for a single S2DEG are undamped, well separated from the SPER and their energies.
decrease monotonically with increasing radius. We present our results in Figs. 3(c) through 3(f) for interacting shells. The two distinct cases of either $x-$ or $z-$alignment clearly lead to different solutions for the plasmon modes. Whereas for $x-$alignment, there are nine branches, there are only six solutions for the plasmons in a $z-$aligned assembly. The corresponding $a-$dependence (vs. the distance between the S2DEG centers) is displayed in Figs. 3(a) through 3(d). In general, the plasmon modes do not have uniform intensity. Specifically, the peaks are not strong for the lower frequency modes because of their proximity to the particle-hole mode region. We found that when the separation $a$ increases, the plasmon branches tend to the single degenerate solution denoted by $\Omega_0$, corresponding to non-interacting shells.

The mathematically simpler case when there is $z-$alignment, which allows one to factorize the determinantal equation for the matrix in Eq. (26), deserves some attention. Our calculations yield each plasmon mode as a numerical solution of the determinantal equation, and present our results in Fig. 5. Once again, we confirm that there are six distinct branches, corresponding to the four factored matrices, two of them are quadratic resulting in two solutions each. Two of the solutions are doubly-degenerate. The branches are not symmetric in intensity with respect to the horizontal line $\Omega_0$.

So far, in this paper, we presented numerical results when the radii of the spherical shells are equal and also when the separations between nearest-neighbors are equal. Figures 6(a) through 6(d) examine the behavior of the plasmon modes of a linear assembly with unequal nearest-neighbor separations as well as when the S2DEGs have different radii and chemical potentials, which corresponds to more realistic situation of fullerene aggregates. First, in this regard, we have investigated the mathematically simpler case of $z-$aligned shells with equal radius $R = 0.8$ nm but unequal distances between their centers. In this regard, there is no symmetry of the interaction submatrices and we may no longer use the matrix factorization in Eq. (26). Instead, we obtain a lower- order factorization, which consists of two multipliers, each of cubic order. Therefore, we still have six solutions, but there is no degeneracy of the frequencies. Once the ratio $\frac{a_3}{a_1}$ is increased, the electrostatic interaction between the nearest-neighbor shells which we refer to as (2) and (3), and naturally between next-nearest-neighbor shells (1) and (3) is decreased, with the plasmon frequency of the assembly tending to the single-shell plasmon mode frequency $\Omega_0 = 9.17, eV/\hbar$.

The remaining plasmon branches are similar to those of the interaction between (1) and (2). These branches are symmetric with respect to the asymptotic line $\Omega_0$, as we obtained for the case of two interacting $z$-aligned shells [7]. When the distances between nearest-neighbor S2DEGs are comparable, the plasmon modes do not behave as $\pm \psi_i$, which is a new feature compared to all the previously considered cases [7, 9].

Finally we address the case when the radius of the middle shell (2) is larger than the radius of the other two: $R_2 > R_1 = R_3$ with $\rho = R_2/R_1 > 1$. Now we have two asymptotic lines $\Omega_0^{(1)}$ and $\Omega_0^{(2)}$. The larger solution $\Omega_0^{(1)}$ corresponds to the two spheres with lower radius $R_1 = R_3$, i.e. is double degenerate, which results in a stronger peak (see Fig. 6(c) and (d)). The plasmon modes are strongly asymmetric. We also conclude that only two branches have their asymptotes along the line $\Omega_0^{(2)}$, corresponding to the middle shell (2).

V. CONCLUDING REMARKS

In this paper, we carried out a model calculation of the plasmon relation for a narrow ribbon of fullerene atoms or metallic shells which were simulated by a linear array of S2DEGs. In neglecting the width of the ribbon, we only investigated effects arising from the edges along the length and not the width of the narrow ribbon. The coupling between plasmon excitations for the 2D electron gases on the surfaces of an finite number of shells is introduced using the random-phase approximation. We demonstrated that the quantization of the energy levels for each 3DEG on the surface of a spherical shell leads to Coulomb matrix elements depending on the angular momentum $L$ and its component $M$. These Coulomb matrix elements represent the inter-shell coupling of the plasmon excitations and are clearly anisotropic, depending on the angle the line-of-centers makes with the quantization axis leading to anisotropy in the plasmon coupling with respect to the direction of the probe field. Furthermore, we proved that the strength of the inter-shell Coulomb interaction does not only depend on the distance between shells but also on the direction of the line joining these centers. We presented detailed results for the plasmon excitation frequencies as functions of the separation between shells and their radii. The effects of unequal separation between nearest-neighbor shells and when the shells have unequal radii were also investigated.

From an experimental point of view, when light with a specified finite orbital or spin angular momentum is incident on the ribbon, the magnetic field generated from an induced oscillating electric dipole on any sphere may couple to an induced magnetic dipole on one of the spheres in the array where the coupling strength is determined by their orientational direction either parallel or perpendicular to the probe $\mathbf{E}$ field. This leads to dimerization of pairs of S2DEGs confined on two separate shells. Therefore, the spectra of the plasma excitations are different in the cases when the quantization axis is parallel or perpendicular to the array axis.
FIG. 6: (Color online). Plasmons for an asymmetric linear assembly of S2DEG’s. The upper panel demonstrates the plasmon solutions for three equivalent fullerenes with different distances between their centers: $a_2 = 1.2 a_1$ for plot (a) and $a_2 = 1.2 a_1 -$ for (b). Distances are specified according to the schematics in Fig.1. The range of the smaller distance $a_1 = a_{12}$ is 1.6 – 2.6 nm for both plots (a) and (b). The solution for a system of non-interacting shells $\Omega_0 = 9.17 \text{eV}/\hbar$, being the asymptotic solution, is provided for comparison. The lower panels (c) and (d) demonstrate the plasmons for three different spheres with $R_2 \neq R_1 = R_3$, $R_2/R_1 = 1.05$ and 1.02, correspondingly. The distances between the spheres are equal: $a_1 = a_2 = a$. Each plot has two asymptotic solutions - $\Omega_0^{(1)} = 9.17 \text{eV}/\hbar$, corresponding to $R_1 = 0.8 \text{nm}$, $\Omega_0^{(2)} = 8.48 \text{eV}/\hbar$ for $R_2 = 0.84 \text{nm}$ (panel (c)) and $\Omega_0^{(1)} = 8.87 \text{eV}/\hbar$ for $R_2 = 0.82 \text{nm}$ (panel (d)). The distance $a$ between the centers of the spheres is displayed in the range of 1.75 – 2.25 nm for both plots (a) and (b). We chose the case of z-alignment for all the plots.

This work covers fundamental aspects such as anisotropy, many-particle quantum effects and electron-plasmon interactions for a novel plasmonic material. Applications such as biosensors for health care, devices for telecommunications, and near-field instrumentation may be explored. We note that our model calculations may not only be applicable to metallic particulates but also have broader implications to fullerenes. The numerical results we derived demonstrate significant new information in the area of plasmonics and are experimentally observable. In this connection, there have already been some experimental measurements showing similar effects in nanoparticles [20]. Also, our work has a bearing on that of hybridization for surface plasmons in metallic dimers [7, 8] in which the plasmon frequencies depend on whether the quantization axis is parallel or perpendicular to the inter-particle axis.

Acknowledgments

This research was supported by contract # FA 9453-13-1-0291 of AFRL.
