

Conduction-band plasmons in cluster-type compounds: Application to fullerides and quantum-dot arrays

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We analyze collective excitations of carriers in three- and two-dimensional crystals made up of cluster-type units (fullerenes, quantum dots, etc.). This class of compounds is unique in that the electrons are essentially confined to the individual clusters, while the latter are both large in size and close packed. We derive a general expression for the dispersion law of conduction-band plasmons, and apply it to alkali-metal-doped fullerides and quantum-dot arrays. We find that the dispersion relation is modified from the case of a homogeneous electron gas: it becomes measurably steeper and acquires a downward slope. This change is due to the appearance of a term which is determined by the density distribution of electrons within a unit cluster. Related electron-energy-loss spectroscopic data on the doped fullerides are discussed.

I. INTRODUCTION

Recent progress in carbon-cluster and quantum-dot preparation techniques^{1,2} has led to the appearance of a new class of building blocks for materials. Two- and three-dimensional arrays of quantum dots and carbon fullerenes, respectively, make up periodic structures representing crystals with unusual and flexible characteristics. For example, by doping fullerene crystals one can obtain new types of conductors, superconductors, and insulators (see, e.g., the reviews in Refs. 1 and 3).

By tuning the confinement potentials it is likewise possible to couple neighboring quantum dots by weak electrical channels, creating a conducting two-dimensional (2D) array.² Doped fullerene monolayers could serve as another class of conducting 2D cluster lattices.

Such compounds are unique in that even when they possess a conduction band, the electrons are primarily confined to the individual cluster or dot. This means that the characteristics of the individual structural unit will be reflected in the properties of the conductor. The electronic states of an isolated unit are quantized into discrete levels, giving rise to a well-defined series of energy bands in the crystal. At the same time, in structures built up of fullerenes or quantum dots the constituents are both quite large and close-packed, i.e., they fill up most of the primitive lattice cell. This important feature distinguishes them from conventional conductors.

In other words, compounds of this type exhibit two degrees of electron delocalization. First, within each unit cell the electrons are distributed throughout, and strongly bound to, the entire cluster, dot, etc. Second, if the electrons are able to tunnel weakly between cells, the crystal becomes a conductor. As a result, the spectra of such conductors can display a variety of unorthodox features.

We will refer to this developing class of materials as "cluster-type" compounds. In addition to fullerenes and quantum dots, building blocks for such conducting crystals may include, e.g., large aromatic molecules⁴ or ligand-stabilized metal clusters.⁵

This paper is devoted to an analysis of collective electronic excitations (plasmons) in cluster-type conducting crystals. In ordinary metals, bulk plasma oscillations of the electron gas have a weak positive dispersion: plasmon energy increases slowly with the wave vector.^{6,7} In the present case, however, because of the high degree of electron confinement to the interior of large unit cells, the character of conduction-band plasmons can be altered significantly.

For example, in the doped C₆₀ materials the dispersion can acquire a *negative* slope and become rather steep. This conclusion is related to recent experimental observations,⁸ as will be discussed below. We will show that this behavior is governed by the distribution of electrons on the fullerene cage.⁹ Similarly, we show that the dispersion of collective excitations in a 2D conducting array of quantum dots can be made noticeably different from that of the usual 2D electron gas.

The plan of the paper is as follows. Section II contains an analysis of the linear response of conduction electrons in three-dimensional cluster-type crystals. In Sec. III we derive the plasmon dispersion relation for the doped fullerides. In Sec. IV a similar analysis is outlined for a two-dimensional array of semiconductor quantum dots. Section V contains the summary.

II. CONDUCTION-BAND PLASMONS IN CLUSTER-TYPE CRYSTALS

A. Equation for the self-consistent field

Our analysis of conduction-band plasmons is based on the linear response equation in the random-phase approx-

imation (RPA). As is well known, the RPA has proven successful in describing collective electron oscillations in bulk metals and semiconductors (see, e.g., Refs. 6, 7, and 11), and in two-dimensional and layered systems (e.g., Ref. 12), as well as in isolated carbon and metal clusters (e.g., Refs. 13 and 14). Here we will use it to treat cluster-based bulk materials.

The self-consistent-field equation which describes the total electric potential within the sample, $V(\mathbf{r}, \omega) \exp(i\omega t)$, in the absence of external fields reads

$$\varepsilon V(\mathbf{r}, \omega) = \int \int \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \Pi(\mathbf{r}_1, \mathbf{r}_2, \omega) V(\mathbf{r}_2, \omega) d^3 r_1 d^3 r_2, \quad (1)$$

where ε is the background dielectric constant, and $\Pi(\mathbf{r}_1, \mathbf{r}_2, \omega)$ is the RPA polarization operator:

$$\begin{aligned} \Pi(\mathbf{r}_1, \mathbf{r}_2, \omega) = & \sum_{\lambda\lambda'} \frac{f_\lambda - f_{\lambda'}}{E_\lambda - E_{\lambda'} + \omega + i\delta} \chi_\lambda(\mathbf{r}_1) \chi_{\lambda'}^*(\mathbf{r}_1) \\ & \times \chi_\lambda^*(\mathbf{r}_2) \chi_{\lambda'}(\mathbf{r}_2). \end{aligned} \quad (2)$$

Here E_λ and χ_λ are single-electron level energies and wave functions, respectively, and f_λ 's are the occupation numbers; atomic units are used throughout.

Equation (1) has nontrivial solutions for certain values of frequency ω . These eigenvalues correspond to self-sustaining plasma oscillations of the electron system.

Since we are considering cases when electrons are primarily confined to individual cells, the tight-binding approximation is a natural starting point for the description of electronic states in such crystals. Consequently, we write the Bloch functions as superpositions of electronic orbitals ϕ_α of an isolated cluster:

$$\chi_\lambda(\mathbf{r}) = \chi_{\lambda, \alpha}(\mathbf{r}) = N^{-1/2} \sum_{\mathbf{T}_i} e^{i\mathbf{k} \cdot \mathbf{T}_i} \phi_\alpha(\mathbf{r} - \mathbf{T}_i). \quad (3)$$

The summation is over all the lattice translation vectors \mathbf{T}_i , and the total number of cells N serves as the normalization constant. We use the term "cluster" for brevity when referring to the crystal building blocks.

The Coulomb potential can be expanded in a three-dimensional Fourier series: $|\mathbf{r} - \mathbf{r}_1|^{-1} = 4\pi \mathcal{V}_c^{-1} \sum_{\mathbf{p}} (1/p^2) \exp[i\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}_1)]$, where \mathcal{V}_c is the crystal volume. Since plasmons represent a wave running through the periodic lattice, we seek the self-consistent potential $V(\mathbf{r}, \omega)$ in the following Bloch-like form:

$$V(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \sum_{\mathbf{G}} v_{\mathbf{G}}(\mathbf{q}) e^{i\mathbf{G} \cdot \mathbf{r}}. \quad (4)$$

Here \mathbf{q} is the crystal momentum of the plasmon, and \mathbf{G} 's are the reciprocal-lattice vectors. The dependence of V and v on ω is implied, but no longer explicitly indicated.

These expansions are now substituted into Eq. (1) together with the wave functions (3). If we neglect overlap integrals involving pairs of wave functions centered on different lattice sites, i.e., $\phi_\alpha(\mathbf{r} - \mathbf{T}_i)$ and $\phi_{\alpha'}(\mathbf{r} - \mathbf{T}_j)$, $i \neq j$, the result is

$$\begin{aligned} v_{\mathbf{G}}(\mathbf{q}) = & \frac{4\pi}{\mathcal{V}_c \varepsilon |\mathbf{q} + \mathbf{G}|^2} \\ & \times \sum_{\mathbf{G}_1} v_{\mathbf{G}_1}(\mathbf{q}) \sum_{\lambda\lambda'} F_{\lambda\lambda'}(\omega) A_{\alpha'\alpha}(-\mathbf{q} - \mathbf{G}) \\ & \times A_{\alpha\alpha'}(\mathbf{q} + \mathbf{G}_1) \delta_{\mathbf{k}, \mathbf{k} + \mathbf{q}}. \end{aligned} \quad (5)$$

Here $F_{\lambda\lambda'}$ is the energy factor of the RPA polarization operator:

$$F_{\lambda\lambda'}(\omega) \equiv \frac{f_{\alpha, \mathbf{k}} - f_{\alpha', \mathbf{k}'}}{E_{\alpha, \mathbf{k}} - E_{\alpha', \mathbf{k}'} + \omega + i\delta} \quad (6)$$

and

$$A_{\alpha\alpha'}(\mathbf{q}) \equiv \int d^3 r \phi_\alpha^*(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} \phi_{\alpha'}(\mathbf{r}). \quad (7)$$

We have made use of the identity $N^{-1} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{T}) = \delta_{\mathbf{k}, 0}$.

A comment is in order regarding the neglect of matrix elements involving electronic wave functions centered on neighboring clusters. In the tight-binding picture, the effect of overlap of such wave functions is twofold. First, it broadens the energy levels of individual clusters and gives rise to a real, albeit narrow, conduction band. When we are considering electronic transitions within the conduction band, this broadening makes the key contribution [$\sim (\Delta\mathcal{E})^{-1}$, where $\Delta\mathcal{E}$ is the conduction bandwidth] to the polarization operator (6) and thereby to Eqs. (1) and (5). Second, the overlap contributes additional terms to the electronic matrix elements. In our treatment we fully take into account the dispersion of the conduction band which represents the leading-order effect. The remaining second factor, i.e., additional matrix elements, would contribute small further corrections (cf. Ref. 15).

Equation (5) is a general one and can be employed, for example, to analyze collective modes involving all electrons present in the unit cell; in the limit of large intermolecular separation these would correspond to the resonances of an isolated cluster. Our aim here is to consider the behavior of conduction-band plasmons, that is, collective motion of the tunneling carriers. As opposed to the aforementioned case, these modes are present only when clusters are joined in a crystal, because they arise due to the existence of the conduction band.

B. Resonance frequencies of conduction electrons

Let the cluster orbital giving rise to the conduction band be denoted by α_0 . In a cluster-type conductor, the width of the conduction band is much smaller than the interband separation. Let us consider the case when the frequency of the conduction band plasmon, ω_0 , is also much smaller than the energy of the lowest-frequency interband transition. As will be discussed below, such is the case, for example, in the doped fullerenes. Consequently, when solving equation (5) for ω_0 we can neglect all interband transitions and retain only the terms with $\alpha = \alpha' = \alpha_0$.

The summation over $\lambda \equiv \{\alpha, \mathbf{k}\}$ and $\lambda' \equiv \{\alpha', \mathbf{k}'\}$ in the self-consistent-field Eq. (5) then reduces to one over the

crystal momentum \mathbf{k} of the conduction electrons only. The dependence on \mathbf{k} remains only in energy factor (6), and we can write (\mathbf{k} can be treated as a continuous variable)

$$\frac{1}{\mathcal{V}_c} \sum_{\mathbf{k}\mathbf{k}'} F_{\mathbf{k}\mathbf{k}'} \delta_{\mathbf{k}', \mathbf{k}-\mathbf{q}} = 2 \int \frac{d^3k}{(2\pi)^3} \frac{f_{\mathbf{k}}^0 - f_{\mathbf{k}+\mathbf{q}}^0}{\mathcal{E}_{\mathbf{k}} - \mathcal{E}_{\mathbf{k}+\mathbf{q}} + \omega_0 + i\delta}. \quad (8)$$

Here $\mathcal{E}_{\mathbf{k}} \equiv E_{\alpha_0, \mathbf{k}}$ are the band energies of the conduction electrons, the functions $f_{\mathbf{k}}^0$ are the electron gas occupation factors ($f_{\mathbf{k}}^0$ is 0 if $k < k_F$, and 1 if $k > k_F$, k_F is the Fermi wave vector), and the factor of 2 accounts for the spin multiplicity. This integral is precisely the retarded polarization propagator $\Pi_0^R(\mathbf{q}, \omega_0)$ encountered in the theory of the electron gas.⁷ It is equal to

$$\Pi_0^R(\mathbf{q}, \omega_0) = n_e \frac{q^2}{m^* \omega_0^2} \left[1 + \frac{3}{5} \left[\frac{k_F q}{m^* \omega_0^2} \right]^2 + \dots \right], \quad (9)$$

where n_e is the volume density of the conduction electrons, and m^* is their effective mass.

Thus in the case of low conduction-band plasmon frequencies Eq. (5) becomes

$$v_{\mathbf{G}}(\mathbf{q}) = \frac{4\pi}{\varepsilon |\mathbf{q} + \mathbf{G}|^2} A_{\alpha_0 \alpha_0}(-\mathbf{q} - \mathbf{G}) \Pi_0^R(\mathbf{q}, \omega_0) \times \sum_{\mathbf{G}_1} v_{\mathbf{G}_1}(\mathbf{q}) A_{\alpha_0 \alpha_0}(\mathbf{q} + \mathbf{G}_1). \quad (10)$$

Notice that the function v can be sought in the form $v_{\mathbf{G}}(\mathbf{q}) = A_{\alpha_0 \alpha_0}(-\mathbf{q} - \mathbf{G}) |\mathbf{q} + \mathbf{G}|^{-2} F(\mathbf{q})$. Substituting this into Eq. (10), we finally obtain an eigenvalue equation for the resonance frequency ω_0 .

$$\frac{4\pi}{\varepsilon} \Pi_0^R(\mathbf{q}, \omega_0) \sum_{\mathbf{G}} \frac{1}{|\mathbf{q} + \mathbf{G}|^2} |A_{\alpha_0 \alpha_0}(\mathbf{q} + \mathbf{G})|^2 = 1. \quad (11)$$

It can be seen from this equation that the frequency of the plasma oscillation is periodic in the reciprocal lattice: $\omega_0(\mathbf{q} + \mathbf{G}) = \omega_0(\mathbf{q})$. The problem of calculating the dispersion of the resonance frequency reduces to that of evaluating the matrix element A and performing the summation over the reciprocal-lattice vectors \mathbf{G} . From definition (7), we see that

$$A_{\alpha_0 \alpha_0}(\mathbf{q} + \mathbf{G}) = \int d^3r |\phi_{\alpha_0}(\mathbf{r})|^2 e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} = \int d^3r \mathcal{N}_{\alpha_0}(\mathbf{r}) e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}}. \quad (12)$$

\mathcal{N}_{α_0} is the density distribution of the conduction electrons on an individual cluster; integration is performed over a single cluster. Equations (11) and (12) constitute the main result of this section.

We see that the dispersion of the carrier plasmon in cluster-type materials is determined by the distribution of the conduction electrons in the unit cell. The fact that this distribution occupies a large volume of the unit cell, while at the same time the tight-binding description remains valid, is responsible for the peculiar character of

the collective modes. In Sec. III we apply the formalism to doped fulleride crystals.

III. NEGATIVE DISPERSION OF CARRIER PLASMONS IN FULLERIDES

A C_{60} molecule contains 180 carbon σ electrons and 60 π electrons. In C_{60} -based solids, these electrons remain tightly bound to their parent clusters, and occupy very narrow completely filled energy bands. A pure fullerene solid is an insulator. In doped fullerenes of composition $A_n C_{60}$, where A is an alkali metal, the alkali atoms donate their valence electrons to the clusters. There, the extra n electrons populate the lowest unoccupied t_{1u} molecular orbital (LUMO). When $n=3$, this orbital is exactly half-filled. It is found¹ that $A_3 C_{60}$ are conductors, i.e., that the t_{1u} electronic orbital gives rise to a narrow conduction band of ≈ 0.6 -eV width.¹⁶⁻¹⁸

Fullerene-based materials display a number of collective electronic states. These include high-frequency π ($\omega \approx 6$ eV) and $\pi + \sigma$ ($\omega \approx 27$ eV) plasmons involving all the π and σ cluster electrons,^{8,17} as well as a low-frequency plasmon which appears at $\omega_0 \approx 0.5$ eV and is due solely to the conduction band. The latter collective state has been seen in both electron-energy-loss (EELS) (Refs. 8 and 17) and optical¹⁸ measurements. The energy of the lowest-frequency interband transition in $K_3 C_{60}$ and $Rb_3 C_{60}$ fullerenes is ≈ 1.5 eV,^{8,17,18} which is considerably higher than ω_0 . Thus the formalism developed in Sec. II is directly applicable here, and we can use Eqs. (11) and (12) to derive the dispersion law of the valence electron plasmon.

What valence electron density \mathcal{N}_{α_0} is appropriate to employ in Eq. (12) in the case of a fulleride solid? A physically reasonable picture is that of the donated electrons distributed approximately uniformly over the surface of the fullerene cage. Although the t_{1u} LUMO states of an isolated cluster are not fully spherically symmetric but have angular momentum $L=5$ character,^{19,20} when three electrons are donated to this orbital they can be expected to distribute themselves in a symmetric manner. Further effective averaging will occur in the fulleride solid due both to crystal-field effects and to the orientational disorder²¹ of the constituent clusters.²² Thus it is justified to take $\mathcal{N}_{\alpha_0}(\mathbf{r}) \approx (4\pi R^2)^{-1} \delta(r-R)$, where R is the fullerene radius. [In fact, the π -electron cloud of the carbon fullerenes has a finite thickness of ≈ 1.5 Å.¹⁹ This can be included in our calculation by using a spherical shell of finite thickness for $\mathcal{N}_{\alpha_0}(\mathbf{r})$ in Eq. (12); the effect is to replace the cage radius \bar{R} by an effective radius $\bar{R} \approx 1.03R$.] With this expression for the valence electron density, the matrix element (12) becomes

$$A_{\alpha_0 \alpha_0}(\mathbf{q} + \mathbf{G}) = \frac{\sin |\mathbf{q} + \mathbf{G}| \bar{R}}{|\mathbf{q} + \mathbf{G}| \bar{R}}. \quad (13)$$

This expression can now be substituted into the eigenvalue equation (11). We are interested in the dispersion behavior of long-wavelength plasmons (those with $q \ll G$, where \mathbf{q} is in the first Brillouin zone), and therefore need to keep only the leading-order term in \mathbf{q} ($\sim q^2$). Conse-

quently, when evaluating the sum over reciprocal-lattice vectors in equation (11), we can neglect \mathbf{q} in all terms with $\mathbf{G} \neq 0$. The sum over these terms becomes proportional to $S \equiv \sum_{\mathbf{G} \neq 0} \sin^2(\mathbf{G}\bar{R})/(\mathbf{G}\bar{R})^4$, and can be calculated based on the known fulleride crystal structure.

The compound K_3C_{60} has fcc structure with the lattice constant $a = 14.25 \text{ \AA}$ (for Rb_3C_{60} , $a = 14.44 \text{ \AA}$), and the radius of the C_{60} cluster is $R = 3.55 \text{ \AA}$.¹ The lengths of reciprocal-lattice vectors up to $G = 12\sqrt{3}\pi/a$ are available in tabulated form,²³ and their contributions can be summed explicitly. The remainder can be estimated by replacing summation over G by integration. Since the factor $\sin^2 x/x^4$ decays very rapidly, the sum S converges quickly. For the K_3C_{60} crystal it is found to be equal to $S = 0.13$.

Combining this with the contribution of the $G = 0$ term equal to $\sin^2(q\bar{R})/(q\bar{R})^4$, we find that to leading order in q the eigenvalue equation (11) now becomes

$$\frac{4\pi}{\varepsilon} \Pi_0^R(\mathbf{q}, \omega_0) \frac{1}{q^2} [1 - 0.20(q\bar{R})^2 + \dots] = 1. \quad (14)$$

Using expression (9) for the polarization operator, we can solve for the collective resonance frequency ω_0 . We find the following dispersion relation:

$$\omega_0 = \omega_p [1 - 0.10(q\bar{R})^2 + \frac{9}{10}(q\lambda_{\text{TF}})^2 + \dots]. \quad (15)$$

Here the screened plasma frequency is $\omega_p = (4\pi n_e / \varepsilon m^*)^{1/2}$, and the Thomas-Fermi screening length parameter is $\lambda_{\text{TF}} = (6\pi n_e / \varepsilon_F)^{-1/2}$ (ε_F is the Fermi energy of the conduction electrons).

If the size of the cluster were small, the second term in brackets would be negligible, and we would recover the familiar plasmon dispersion relation of the electron gas.⁷ However, as we emphasized earlier, the present case is unique in that the electrons are arranged on the surface of a *large* molecule. As a result, the second term dominates, and the dispersion relation changes sign and becomes much steeper. In other words, the plasmon group velocity becomes negative.

Indeed, for the alkali-metal-doped fullerides with three conduction electrons per unit cell and $\varepsilon_F \approx 0.2 - 0.3 \text{ eV}$,¹⁶⁻¹⁸ we have $\lambda_{\text{TF}} \approx 0.4 \text{ \AA}$, while $R \approx 3.5 \text{ \AA}$. This means that the new negative-dispersion term dominates the plasmon dispersion relation by an order of magnitude, and we can write

$$\omega_0 = \omega_p [1 - \gamma(qR)^2 + \dots], \quad (16)$$

where $\gamma \approx 0.1$. Within the Brillouin zone then, the plasma frequency can decrease by as much as $\sim 10 - 20 \%$.²⁴ This dispersion law can be probed by electron-energy-loss spectroscopy.

As mentioned above, a Drude-Lorentz analysis of optical reflectivity spectra of K_3C_{60} (Ref. 18) has yielded a conduction electron resonance frequency $\omega_p \approx 0.5 \text{ eV}$. This agrees with EELS data^{8,17} for low momentum transfer which show a well-defined loss peak at this energy.

The aforementioned EELS measurements⁸ for a film sample of nominal composition $\text{K}_{2.5}\text{C}_{60}$ (with 15% C_{70} ; energy resolution 0.14 eV) suggest a small decrease in the

position of the loss peak as the electron momentum loss Δq increases from $\Delta q = 0.2$ to 0.6 \AA^{-1} . The analysis we have described here provides a basis for such unusual behavior. For a quantitative comparison with the theory, there is a need for high-resolution EELS data on crystalline samples of optimal stoichiometry (e.g., K_3C_{60}) and controlled crystal orientation. In this way, the predicted negative dispersion of conduction-band plasmons can be mapped out. Furthermore, as described above [Eq. (12)], the magnitude of the dispersion coefficient can be related directly to the distribution of valence electrons on the surface of the fullerene units.

IV. CARRIER PLASMONS IN 2D ARRAYS

In this section we consider the conduction-band plasmon spectrum of a 2D cluster-type array, e.g., one made up of semiconductor quantum dots with weak electron tunneling between them.²⁵

Quantum dots have disklike shapes, with radii of a few hundred nanometers and small thicknesses (several tens of \AA).² They can contain from a few to dozens of mobile electrons, which are strongly squeezed in the z direction (disk axis), but delocalized over the area of the dot (in the x - y plane). The electrons are thus confined to the lowest quantum state in the z direction, and occupy a series of discrete levels in the plane of the dot. Let us assume that the wave functions of the higher-lying electronic levels in neighboring dots overlap slightly, so that there appears a narrow 2D conduction band. Following the approach developed in preceding sections, we can derive a dispersion relation for the collective plasma resonances of this conduction band.

We again need to find the eigenfrequencies of the linear-response equation (1), but in the present case periodicity is present only in the x and y directions. The tight-binding electronic wave functions thus have the following form:

$$\chi_\lambda(\mathbf{r}) = N^{-1/2} \sum_{\vec{T}_i} e^{i\vec{k} \cdot \vec{T}_i} \phi_\alpha(\vec{\rho} - \vec{T}_i) \xi(z). \quad (17)$$

The vector $\vec{\rho}$ is a 2D coordinate in the x - y plane, \vec{T}_i 's are the 2D lattice translation vectors, and $\xi(z)$ is the wave function of the lowest quantum state in the z direction. By writing the 3D Fourier expansion for the Coulomb interaction (see Sec. II) and integrating over the z component of the wave vector, we obtain the following series:

$$|\mathbf{r} - \mathbf{r}_1|^{-1} = 2\pi \mathcal{A}_c^{-1} \sum_{\vec{k}} (1/k) \exp[i\vec{k} \cdot (\vec{\rho} - \vec{\rho}_1) - k|z - z_1|],$$

where \vec{k} is a 2D wave vector, and \mathcal{A}_c is the area of the array.

We substitute these factors into the linear-response equation, and notice that it can be simplified by multiplying both sides by $|\xi(z)|^2$ and integrating over z . As a result, we arrive at the same equation we dealt with in Secs. II and III, with the following differences: (1) instead of $V(\mathbf{r})$ the equation involves the modified function $\tilde{V}(\vec{\rho}) \equiv \int V(\vec{\rho}, z) |\xi(z)|^2$; and (2) instead of the 3D

Coulomb fourier factor $4\pi/p^2$ we have the factor $2\pi I(\lambda)/\lambda$, where²⁶

$$I(\lambda) = \int \int |\xi(z)|^2 |\xi(z_1)|^2 e^{-\lambda|z-z_1|} dz dz_1. \quad (18)$$

Further analysis then proceeds identically to that in the preceding sections. We expand $\tilde{V}(\vec{p})$ in a 2D series analogous to Eq. (4), once again neglect the small contribution of the overlap integral to the matrix elements of $\tilde{V}(\vec{p})$, and concentrate on the case when the plasma resonance frequency of the conduction electrons is much lower than interband spacing. (As we shall see below, the plasmon dispersion relation has the form $\omega_0 \propto q^{1/2}$, so that the last assumption is a very good one for small momenta q .) The analogs of Eqs. (11) and (12) in the present quasi-2D case are

$$\frac{2\pi}{\varepsilon} \Pi_0^{2D}(\vec{q}, \omega_0) \sum_{\vec{g}} \frac{I(|\vec{q}+\vec{g}|)}{|\vec{q}+\vec{g}|} |A_{\alpha_0\alpha_0}(\vec{q}+\vec{g})|^2 = 1 \quad (19)$$

and

$$A_{\alpha_0\alpha_0}(\vec{q}+\vec{g}) = \int d^2\rho \mathcal{N}_{\alpha_0}(\rho) e^{i(\vec{q}+\vec{g})\cdot\vec{\rho}}. \quad (20)$$

The RPA polarization propagator in 2D is given by^{28,29}

$$\Pi_0^{2D}(\vec{q}, \omega_0) = \frac{m^*}{\pi} [(1-\alpha^{-2})^{-1/2} - 1], \quad (21)$$

where $\alpha = \omega_0/(qv_F)$, and v_F is the Fermi velocity.

The plasmon dispersion relation is seen to be determined by the radial distribution $\mathcal{N}_{\alpha_0}(\vec{p})$ of the conduction electrons within an individual quantum dot, a situation parallel to the earlier 3D case.

If we assume that this distribution is approximately uniform, $\mathcal{N}_{\alpha_0} \approx 1/(\pi R^2)$, where R is the dot radius, then from Eq. (20)

$$A_{\alpha_0\alpha_0}(\vec{q}+\vec{g}) = \frac{2J_1(|\vec{q}+\vec{g}|R)}{|\vec{q}+\vec{g}|R}. \quad (22)$$

The function $I(\lambda)$, Eq. (18), has been evaluated in Ref. 26 for the case of a thin disk; it is given by

$$I(\lambda) = \frac{2}{\lambda Z_0} \left[1 + \frac{(\lambda z_0)^2}{2[4\pi^2 + (\lambda z_0)^2]} - \frac{(2\pi)^4(1-e^{-\lambda z_0})}{\lambda z_0[4\pi^2 + (\lambda z_0)^2]^2} \right], \quad (23)$$

where z_0 is the confinement thickness of the quantum dot.

For small values of q , $A_{\alpha_0\alpha_0}(\vec{q}) \approx 1 - (qR)^2/8$. Due to the large coefficient of the q^2 term, it will typically dominate other contributions to Eq. (19). We then find the following dispersion relation for carrier plasmons in a conducting 2D quantum-dot array: $\omega_0 = a q^{1/2} [2J_1(qR)/(qR)]$, or

$$\omega_0 = a q^{1/2} [1 - \gamma_0(qR)^2 + \dots], \quad (24)$$

where $\gamma_0 \approx \frac{1}{8}$, $a = (2\pi n_e)/(m^* \varepsilon)$, and n_e is the number of tunneling electrons per unit area. Once again, we see that

if the radius of the dot were small ($R \rightarrow 0$), we would recover the plasmon dispersion law for a 2D electron gas.^{12,28} The fact that we are dealing with an array based on large clusters brings about an additional term which contributes a noticeable downward slope.

Equation (24) is valid when the $(qR)^2$ term dominates over other corrections present in Eq. (19). These include linear terms $\sim z_0 q$ and $\sim (a_0 \varepsilon/m^*) q$ contributed by the function $I(q)$ and by the polarization propagator $\Pi_0^{2D}(\vec{q}, \omega_0)$, respectively (a_0 is the Bohr radius). In realistic cases both z_0 and $a_0(\varepsilon/m^*)$ are smaller than R by well over an order of magnitude, which means that the $-\gamma_0(qR)^2$ term in Eq. (24) will become dominant for $qR \gtrsim 0.1$. Another correction linear in q comes from the sum over $\vec{g} \neq 0$ in Eq. (19). The precise value of this sum depends on the geometry of the 2D lattice, but the sum converges very quickly and for not too small values of (qR) will not lead to substantial deviations from the dispersion relation (24).

From the foregoing discussion it follows that the dispersion law (24) should be detectable in conduction-band plasmon spectra of 2D arrays, for example by EELS methods. It is also evident that the ability to vary the geometry and composition of quantum-dot crystals allows for great flexibility in tuning the spectral behavior of plasmons.

V. SUMMARY

Collective excitations of conduction electrons in 3D and 2D lattices based on cluster-type units (fullerenes, quantum dots, etc.) display unusual dispersion characteristics. This is due to the unique features of this class of compounds: the electrons are essentially confined to, and delocalized within, the individual clusters, while at the same time the cluster units are large in size and packed closely together.

Employing the linear response equation and the tight-binding approach, we have obtained a general expression for the conduction-band plasmon dispersion. The main conclusions can be summarized as follows.

(1) The dispersion law of the carrier plasmon in cluster-type materials is uniquely determined by the electron-density distribution within a unit cluster. Conversely, a measurement of the plasmon dispersion relation can be used to characterize the distribution of carriers within the unit cell. These effects represent a contribution which is different in principle from those found in conventional conductors.

(2) The plasmon dispersion relation acquires terms typically proportional to $(qR)^2$, where q is the plasmon momentum, and R is the dimension of the cluster. Since R is large, these terms dominate the dispersion characteristics.

(3) In realistic cases, the coefficient of the aforementioned terms is negative. This means that instead of the weak positive dispersion characteristic of the 3D homogeneous electron gas, the conduction plasmons in cluster-type compounds can display a strong negative dispersion. In other words, the plasmon group velocity increases in magnitude and changes sign.

Similarly, in 2D compounds the negative-dispersion term adds a measurable downward trend to the momentum dependence of the collective resonance frequency.

(4) The formalism was applied to 3D alkali-metal-doped C_{60} fulleride crystals and to 2D arrays of semiconductor quantum dots. In the former case, it was pointed out that the low-energy peak of the EELS loss function should display a decrease in energy with increasing momentum transfer.

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- ¹D. W. Murphy, M. J. Rosseinsky, R. M. Fleming, R. Tycko, A. P. Ramirez, R. C. Haddon, T. Siegrist, G. Dabbag, J. C. Tully, and R. E. Walstedt, *J. Phys. Chem. Solids* **53**, 1321 (1992).
- ²D. Heitmann and J. P. Kotthaus, *Phys. Today* **46** (6), 56 (1993), and references therein.
- ³W. E. Pickett, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, New York, in press), and references therein.
- ⁴*Proceedings of the International Conference on Low Dimensional Conductors*, edited by A. J. Epstein and E. M. Conwell [*Mol. Cryst. Liq. Cryst.* **86** (1982)].
- ⁵M. P. J. van Staveren, H. B. Brom, and L. J. de Jongh, *Phys. Rep.* **208**, 1 (1991).
- ⁶P. M. Platzman and P. A. Wolff, *Waves and Interactions in Solid State Plasmas* (Academic, New York, 1973).
- ⁷A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
- ⁸E. Sohmen, J. Fink, and W. Krätschmer, *Europhys. Lett.* **17**, 51 (1992).
- ⁹Negative dispersion is encountered in the case of plasmons on a metallic surface and is caused by the spillout of surface charge (see, e.g., Ref. 10). Effects discussed in the present work have a different origin.
- ¹⁰P. J. Feibelman, *Prog. Surf. Sci.* **12**, 287 (1982); E. Lipparini and F. Pederiva, *Z. Phys. D* **22**, 553 (1992).
- ¹¹*The Dielectric Function of Condensed Systems*, edited by L. V. Keldysh, D. A. Kirzhnits, and A. A. Maradudin (North-Holland, Amsterdam, 1989).
- ¹²T. Ando, A. B. Fowler, and F. Stern, *Rev. Mod. Phys.* **54**, 437 (1982).
- ¹³G. F. Bertsch, A. Bulgac, D. Tománek, and Y. Wang, *Phys. Rev. Lett.* **67**, 2690 (1991).
- ¹⁴V. V. Kresin, *Phys. Rep.* **220**, 1 (1992).
- ¹⁵W. Que and G. Kirczenow, *Phys. Rev. B* **36**, 6596 (1987).
- ¹⁶S. C. Erwin and W. E. Pickett, *Phys. Rev. B* **46**, 14257 (1992).
- ¹⁷E. Sohmen and J. Fink, *Phys. Rev. B* **47**, 14532 (1993).
- ¹⁸Y. Iwasa, K. Tanaka, T. Yasuda, T. Koda, and S. Koda, *Phys. Rev. Lett.* **69**, 2284 (1992).
- ¹⁹G. A. Gallup, *Chem. Phys. Lett.* **187**, 187 (1991).
- ²⁰V. de Coulon, J. L. Martins, and F. Reuse, *Phys. Rev. B* **45**, 13671 (1992).
- ²¹P. A. Heiney, *J. Phys. Chem. Solids* **53**, 1333 (1992).
- ²²Density-functional calculations of electronic densities in K-doped fullerenes have been described, e.g., by S. Saito and A. Oshiyama, *Phys. Rev. B* **44**, 11536 (1991); J. L. Martins and N. Troullier, *ibid.* **46**, 1766 (1992); M. Schlüter, M. Lannoo, M. Needels, G. A. Baraff, and D. Tománek, *J. Phys. Chem. Solids* **53**, 1473 (1992).
- ²³*International Tables for X-ray Crystallography*, 2nd ed. (Kynoch, Birmingham, 1965), Chap. 7.1.
- ²⁴Plasmons in electron gas can decay by Landau damping (excitation of electron-hole pairs) when the following inequality is satisfied (Ref. 7): $\omega > (qk_F + q^2/2)/m^*$. With ω described by the dispersion relation derived here, and $m^* \sim 2.5m_e - 4m_e$ (Refs. 17 and 18), we find that the Landau damping channel opens for plasmon momenta $q \gtrsim 0.3 \text{ \AA}^{-1}$.
- ²⁵Collective excitations in an array of quantum dots in the absence of tunneling were analyzed, e.g., in Ref. 26; some steps in our analysis follow this work. Tunneling plasmons in a 2D array with 1D tunneling were considered in Ref. 27.
- ²⁶W. Que, G. Kirczenow, and E. Castaño, *Phys. Rev. B* **43**, 14079 (1991).
- ²⁷W. Que, *Phys. Rev. B* **47**, 1636 (1993).
- ²⁸F. Stern, *Phys. Rev. Lett.* **18**, 546 (1967).
- ²⁹V. Z. Kresin and H. Morawitz, *J. Supercond.* **1**, 89 (1988).