

CALCULATION OF THE POLARITON EFFECT IN THE FULLERENE MONOLAYER

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The theoretical investigation of the electronic structure of the fullerene cluster solid predicts that in the high frequency region the optical response of the chain and layered cluster structures has the polariton phenomena like in the insulator solid. The dispersion of the dipole collective modes in 1D and 2D systems is presented. The analogy between these fullerene excitations and the low-dimensional exciton-polariton is traced.

I. INTRODUCTION

The discovery of new artificial "atoms" - the fullerenes inspires a flow of publications on the electronic structure, optical and electrical properties of this new material. Most stable cluster C_{60} having the nearly spherical symmetry will be considered below mainly. We will discuss the particular problem of the collective excitation (plasmon) in the fullerene polymerized structures. However this narrow problem lights the question how is the fullerene solid excitation built. We modeled the collective excitation in the chain and in the plane of the fullerene clusters supposing that the individual cluster possesses the dipole collective excitation. Then the excitation in the solid is the linear combination of the single cluster dipole modes. The algorithm is the same like for the formation of the Frenkel exciton in organic insulators.

In the spherical approximation the collective intra-cluster modes are multipolar electrical modes and in the Born limit only the dipolar one is excited by the light. It is important to know the dielectric function of the clustered solid which determines all electro-dynamical properties of the fullerene structure. In the high frequency region the excitation of the single cluster is the surface plasmon^{1,2}. It is well-known as from semi-empirical models as from the more accurate computing (see³⁻⁸ for details and references). For the solid the Coulomb interaction between clusters should be taken into account. The problem of the interaction between the modes is very complicated even though one uses the spherical symmetry approximation. The amount of multipole-multipole matrix elements of the interaction is huge. However, we showed^{9,10} that high-pole interaction can be neglected.

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In the paper we consider only dipole-dipole interaction between the collective modes on the different clusters and calculated their RPA frequencies for the chain and for the monolayer of the fullerene molecules. It is well known that in these cases the dielectric function has the transverse excitation branch due to the inhomogeneity in the one direction. We calculated for the one-dimensional chain^{9,11} the dispersion laws for the bands of the transverse collective inter-cluster modes. We address such a linear structure result to the orthorhombic polymerized phase of the fullerene.

Recently obtained by the photopolymerization and by the vacuum deposition techniques monolayers of the fullerene will be interesting object for this discussion. We investigated the coupling between the optically active modes of the 2D-plane and the photons in the soft X-ray region^{12,13}.

The paper is constructed as follows. First, it deals with the bases of the model, in the Sec. II the hydrodynamic derivation of the fullerene cluster surface plasmon will be done. In the Section III the Coulomb interaction between the clusters will be considered in the simplest case of the interaction in the dimer. The next section is devoted to the calculation of the Frenkel Coulomb excitons in the fullerene low-dimensional structures without regard for the retardation effect. First, in the 1D case we will obtain the transverse optically active excitations in the fullerene chain in the soft X-ray region. Then the calculation will be presented for the 2D fullerene plane. The retarded interaction via the transverse photons will be included into the calculation in the last section.

II. THE SINGLE CLUSTER: SURFACE PLASMON

It is very natural to consider the C_{60} molecule as a spherically scrolled graphite sheet. The 2D graphite is a semi-metal that means that the π electrons of the monolayer are delocalized in the plane like a 2D electron gas. The situation is very similar to the plain semiconductor quantum well which confines the electrons in direction normal to the well.

Let us remember how the spherical plasmon was considered in frame of the spherical shell model of the fullerene molecule^{1,2}. Following Ref.² we use the spherical oscillation of the electron density σ_{LM} . For the central symmetry of fullerene sphere we use the expansion of all quantities in the complete spherical harmonics¹⁴ $P_L(r)Y_{L,M}(\Omega)$ those form a complete set on a sphere. The electric potential is the solution of Laplace equation for empty space inside, $\varphi^{\text{in}}(r < R)$, and outside, $\varphi^{\text{out}}(r > R)$, the spherical shell of molecule. We wrote it in multipole power expansion:

$$\begin{aligned}\varphi^{\text{in}}(r, \Omega) &= \sum_{L,M} \frac{\varphi_{LM}}{R^L} |\mathbf{r}|^L Y_{L,M}(\Omega), \\ \varphi^{\text{out}}(r, \Omega) &= \sum_{L,M} \varphi_{LM} R^{L+1} \frac{1}{|\mathbf{r}|^{L+1}} Y_{L,M}(\Omega).\end{aligned}\tag{1}$$

At the spherical geometry a radial jump in electric field is given by:

$$\frac{2L + 1}{R} \varphi_{LM} = 4\pi\sigma_{LM} \tag{2}$$

and we get the response of the sphere in the block-diagonal form¹ in the subspace of angular momentum $L = \text{const}$. The next equation can be considered as the definition of χ , the response function:

$$\sigma_{LM} = -\chi_L \varphi_{LM}^{\text{act}}, \tag{3}$$

where $\varphi_{LM}^{\text{act}} = \{\varphi^{\text{xt}} + \varphi^{\text{ind}}\}_{LM} = \varphi_{LM}^{\text{xt}} + 4\pi R\sigma_{LM}/(2L + 1)$ is the acting potential, L, M are the multipole power indexes (or the angular momentum and its projection onto z-axis). The selfconsistency of the calculation is provided by the including of the depolarization of the molecule through φ^{ind} in the full acting potential.

The eigenvalue equation for the single sphere excitation frequency arises from Eqs.(2) and (3) under the zero external potential. The expressions written above are based on the classical electrodynamics. The explicit form of the response function $\chi_L(\omega)$ could be obtained by nonstationary perturbation theory or some any way^{1,2}. However it is not false to find it classically from the simplest electron liquid model^{5,15}. The result corresponds to the plasmon on the surface of metal spherical shell of radius R and electron density $n = 240/4\pi R^2$. We put the classic charge liquid equations as follows:

$$\begin{cases} m\dot{v} = -\nabla\varphi \\ \dot{\sigma} + n\nabla v = 0 \end{cases} \tag{4}$$

The first is a Newton law and the second is a linearized continuity equation, where n, v are the electron liquid density and its velocity. Assuming potential φ to be a harmonic function we get the response in multipolar expansion:

$$\sigma_{L,M} = \frac{nL(L + 1)}{m^*R^2\omega^2} \varphi_{L,M}^{\text{act}}. \tag{5}$$

It is shown¹⁶ that the response function and hence the polarizability of the spherical molecule with closed shell electron structure has no dependence on M -quantum number.

The momentum substitution (as it has been discussed in¹) instead of the ratio of the angular momentum to the radius leads in the limit $L \gg 1$ to the well known formula of the square root dependence of the surface plasmon energy on its momentum :

$$\omega_L = \sqrt{\frac{2\pi ne^2 L}{m^* R}} \propto \sqrt{k_{\parallel}} \tag{6}$$

Thus the Spherical Shell Quantum Well model transforms in the normal Quantum Well at the large sphere radius: $R \rightarrow \infty$, with the momentum and electron density fixed: $k_{\parallel} = \frac{L}{R} = \text{const}, n = \text{const}$.

So far we got the bare cluster polarizability which is incomplete because of the high electron density providing strong coulomb correlation. We intend to account it in the

simplest form - Random Phase Approximation (RPA)^{4,8}. The selfconsistent solution for the dynamic polarizability $\alpha_{LM}(\omega)$ is:

$$\alpha_L = -\frac{\sigma_{L,M}}{e\varphi_{L,M}^{xt}} = \frac{\chi_L}{1 + \frac{4\pi R}{2L+1}\chi_L} . \quad (7)$$

It includes a big depolarization factor that reveals the surface electron density screening effect upon the response. The poles of the polarizability determine the excitations spectrum.

III. COULOMB INTERACTION IN THE DIMER

In the Section II we evaluated the response of C_{60} which has the pole at the frequency of the single cluster surface plasma excitation. We did it within hydrodynamic model only for the sake of simplicity. In the solid the single cluster modes do interact and split. The simplest case of the two interacting clusters was considered in¹⁰. Here we will reproduce some important points which will be useful for us below.

The fullerene dimer was discovered, first, as the new bispherical C_{119} macromolecule¹⁷ and, now, it is widely discussed in respect with the polymerization of the solid fullerene. Each cluster in the fullerene dimer possesses the triply degenerated dipole plasmon before the switching the Coulomb interaction on. After the switching on one expects that the z-polarized plasmon has to split from x-,y-polarized excitations, where the z-axis is along the dimer axis (see Fig.III).

The potential of the second sphere has to be included into Eq.(3) along with the external potential for the first sphere of the dimer (see^{10,13}). The equation system for eigenmodes of the dimer reads as:

$$\begin{cases} \sigma_{LM}^{(1)} = \chi_L^{(1)}(\varphi_{LM}^{ext} + \frac{4\pi R}{2L+1}\sigma_{LM}^{(1)} + (\hat{\gamma}\sigma^{(2)})_{LM}) \\ \sigma_{LM}^{(2)} = \chi_L^{(2)}(\varphi_{LM}^{ext} + \frac{4\pi R}{2L+1}\sigma_{LM}^{(2)} + (\hat{\gamma}\sigma^{(1)})_{LM}) \end{cases} \quad (8)$$

When parameters of two electron systems are equal, χ is the same for both globes. Moreover, we solve the equation for the only collective excitation frequency, therefore the following equation is substituted for the χ_L :

$$\frac{4\pi R}{2L+1}\chi_L(\omega) \simeq -\omega_L^2/\omega^2 . \quad (9)$$

where: $\omega_p = \sqrt{\frac{4\pi ne^2}{m^*R}}$,

$$\omega_L = \omega_p \sqrt{\frac{L(L+1)}{2L+1}} = \sqrt{\frac{4\pi ne^2}{m^*R}} \sqrt{\frac{L(L+1)}{2L+1}} \quad (10)$$

is the characteristic frequency of the L^{th} component of the high frequency response is the single cluster surface plasmon frequency.

Iterative diagonalization of this system (8) in the space $L \otimes L'$ will bring frequencies of all new modes with any accuracy. This is provided by exponential diminishing of $\hat{\gamma}$ with $L + L'$ rising¹⁰. Evidently, the coupling as the electrical induction is weaker for higher multipole degree of potential. It can be compared with the coupling between planes¹⁸, when the electric field of plasmon has typical decrement k in z direction, which can be mapped onto L/R . For simplicity of analysis we will preserve only dipole-dipole interaction (the same we will resolve Eq.(8) within the first order perturbation theory on the small parameter $(R/H)^{L+L'}$ when this equation is diagonal in $L = L'$ indexes). Then the coupling constant reads as $\gamma_{LM}\delta_{LL'}$.

Nontrivial solution of Eqs.(8) exists in the absence of the external potential if the determinant of the system is equal to zero:

$$\det \begin{vmatrix} \left(1 - \frac{\omega_1^2}{\omega^2}\right) & \frac{\omega_1^2}{\omega^2} \gamma_{1M} \\ \frac{\omega_1^2}{\omega^2} \gamma_{1M} & \left(1 - \frac{\omega_1^2}{\omega^2}\right) \end{vmatrix} \delta_{1L'} = 0 \quad (11)$$

Here $\delta_{1L'}$ stands for the symbol of the reduction of the submatrices in the double angular momentum representation space $L \otimes L'$ when we omit all terms excepting dipole-dipole one. The coupling constant γ_{1M} will be given explicitly later. Then the simple variable transformation $\sigma_{g(u)} = \sigma^{(1)} \pm \sigma^{(2)}$ divides Eq.(11) in two parts – secular equations for even and odd plasmon modes:

$$\omega_{g(u)}^2 = \omega_1^2 (1 \pm \gamma_{1M}). \quad (12)$$

From Eq.(12) we obtain the frequencies of the odd and even dipole modes in the diagonal approximation:

$$\omega_{g(u)} = \omega_1 \sqrt{1 \pm \gamma_{1M}} = \omega_1 \sqrt{1 \pm \frac{1+3(-1)^M}{2} \left(\frac{R}{H}\right)^3}, \quad (13)$$

where $\hbar\omega_1 \simeq 28$ eV – frequency of bare dipole plasmon in C_{60} . Eq. (13) corresponds to dipole-dipole interaction between globes which does not mix different angular momentum subspaces. The dipole-quadrupole coupling is prohibited and the next order corresponds to $L = 1 \rightarrow L + 2$, the weak dipole-octuplet coupling. This correction contains an additional factor $(R/H)^2$ and is neglected.

These two, odd and even, excitations have different symmetry. Even mode can be described as the dipole of doubled charge. While the potential induced by surface charge density of the second, odd, mode has only the next quadrupole order in the multipole expansion. Each mode frequency is splitted into excitations of two polarizations – across and along the molecule axis, see Fig. III. Even mode with longitudinal polarization with $M = 0$ (z -type) is slightly, about 7.1%, shifted up from C_{60} plasmon position (29.8 eV), but x - and y -type modes ($M = \pm 1$) are shifted down less

in factor of $\sqrt{2}$ (about 27.2 eV). The reason for the splitting is that the dipole-dipole interaction energy depends on the dipole orientations as: $W_{zz} = -2W_{xx} = -2W_{yy}$, therefore the z -mode lies above the x - and y -modes.

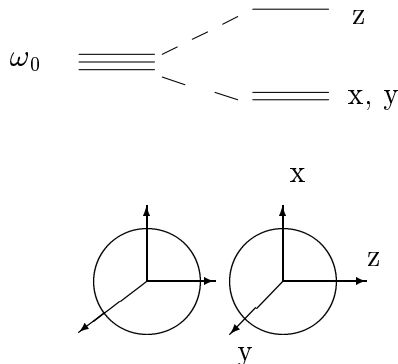


FIG. 1. The dumb-bell model system of two coupled thin spherical shell quantum wells describes the plasmon excitation in the dimer. Each single molecule possesses a triply degenerated spherical dipole excitation, - x -, y - and z -polarization plasmons. The splitting between the frequencies of two states of the dimer, x -, y - and z -plasmon is about some percents of plasmon frequency (see the text). Two additional odd modes exist. They are not optically active, due to quadrupole character of these modes, and are not shown in Figure.

Actually, for C_{119} $R/H \simeq 0.42$ and this parameter is not really small factor. We have made direct numerical diagonalization of matrix (11) up to 45×45 size to compare exact frequencies of coupled modes. For dipole mode the result converges at 3×3 matrix. The diagonal coupling correction for dipole mode is less than 3%. We deduce that this mode is mainly (97%) dipolar, hence coupling with higher multipole modes is small enough. We will discuss it in¹⁶ at length. For the polymerized fullerene, the dimer intercenter distance H is between the bare fullerene nearest neighbor distance, $\simeq 10 \text{ \AA}$ and the cluster diameter $2R$. The details of the crystal structure still unclear.

IV. THE CHAIN: PLASMON MODE DISPERSION

The Coulomb interaction between the dimer clusters which has been evaluated in the Section III results in the new modes with slightly shifted and splitted frequency. These plasma modes have different symmetry. What will happen in the case of the chain and the 2D lattice of the interacting clusters? According to the simplest group consideration, the plasmons in these systems have the quasi-momentum because of the Hamiltonian is invariant relatively to the translation. The allowed plasmon frequencies, depending on its quasi-momentum, form the band with the width determined by the characteristic interaction energy which is much less than the plasma frequency.

So we will obtain the slightly dispersing 1D or 2D crystal excitation with the different polarization depending on the mode.

In the simplest case of the linearly polymerized fullerene the composed plasmon can be constructed from the plasma excitation of the single molecule in the tight-binding continuum approximation. We replace the variables in a standard way:

$$\sigma_M(k) = \sum_{n=0}^N e^{-iknH} \sigma_M(x - nH) \quad (14)$$

where $n = 0, \dots, N$ is the number of molecule in the chain, M is the polarization index, k is the wave vector of the chain plasmon which obeys to the cyclic boundary condition.

We will obtain the energy band for this plasmon (the 1D analogy of Eq.(12)) in the first order of the coupling (diagonal approximation of $\hat{\gamma} \propto \gamma_{LM}\delta_{LL'}$). The 1D lattice sum reads as:

$$\sum_n \frac{\cos(kHn)}{n^3}. \quad (15)$$

It is the special Lerch phi-function of 3 order. For the small values of k one can replace sum by the proper integral and perform the integration preserving the terms of the order of k^2 . It gives the asymptotical behavior of the exact result. We will be interested in the coupling of the chain plasmon with the light, hence the corresponding wave vector will be small. The plasmon spectrum in this region is well described by the following expression obtained in continuum approximation:

$$\omega(k) \simeq \omega_1 \sqrt{1 + \frac{1 + 3(-1)^M}{2} \left(\frac{R}{H}\right)^3 \left(2\zeta(3) - (kH)^2 \left[-\ln kH + \frac{3}{2}\right]\right)} \quad (16)$$

here $\zeta(3)$ is the zeta-function which gives the result in the full neglecting of the spatial dispersion of the dipoles ($\zeta(3) \simeq 1.202$). Two modes with the transverse and longitudinal polarizations are splitted at zero wave vector. The reason for it is the same as discussed in the end of Section III. Higher one is the longitudinal mode, *i.e.* the dipole momentum (and also the electric field) is directed along the chain. It has $M = 0$. The second is of the transverse type and twice degenerated (x - and y -polarizations), $M = \pm 1$. Now we note that the resulted excitation is exactly the same as a Frenkel exciton in 1D crystals. The Frenkel exciton (the same small radius exciton) exists in the insulator solid where the charge carriers are quite localized and corresponds to the collective mode of the interacting indistinguishable dipoles. We point out that for the 1D chain the interaction can be summed as the special function (see¹⁶ for details).

It is interesting that the expression Eq.(16) results from the hydrodynamic model for the very thin metal wire similarly the C_{60} surface plasmon corresponds to the metal sphere.

The analytical form for the ends of the plasmon band comes from the nearest neighbor approximation. It is valid for the large wave vector of the excitation when the interaction decays very rapidly with the distance. The motion equation for the plasmon reads as:

$$\sigma_M(z) = -\chi_{-1} \left[\varphi_M^{\text{xt}} + \gamma_{1M} \varphi_M(z+1) + \gamma_{1M} \varphi_M(z-1) \right] \quad (17)$$

where M is the polarization index, γ_{1M} is the corresponding to the polarization dipole-dipole interaction strength or the coupling: $\gamma_{10} = -2(R/H)^3$ and $\gamma_{1\pm 1} = (R/H)^3$; $\varphi_M(z \pm 1)$ is the induced potential. It respects to $\sigma_M(z \pm 1)$, the M -th component of the density fluctuation on $(z \pm 1)$ -th cluster. Similarly to 1D phonon branch one produces the Fourier transformation of the Hamiltonian (or the motion equation Eq.(17)), that gives for dipole plasmon two branches as before:

$$\omega(k) \simeq \omega_1 \sqrt{1 - [1 - (kH)^2/2] \frac{1 + 3(-1)^M}{2} \left(\frac{R}{H}\right)^3} \quad (18)$$

V. PLASMON EXCITON IN THE PLANE

In the very similar manner as for the 1D Frenkel exciton we write the expression for the coupled modes as:

$$\begin{cases} \sigma_z(x, y) = -\chi_L \left(\varphi_z(x, y) + \varphi_z^{\text{latt}}(x, y) \right) \\ \sigma_x(x, y) = -\chi_L \left(\varphi_x(x, y) + \varphi_x^{\text{latt}}(x, y) \right) \\ \sigma_y(x, y) = -\chi_L \left(\varphi_y(x, y) + \varphi_y^{\text{latt}}(x, y) \right) \end{cases} \quad (19)$$

where φ_M^{latt} are the components of the lattice sum of the single dipole potentials. It is very natural to choose the normal variables as σ_z with the polarization along the z -axis, σ_{\parallel} with the polarization along \mathbf{k} , the wave-vector of the collective excitation and σ_{\perp} with the polarization vector in the plane transverse to \mathbf{k} . One needs to take the lattice sum of the fields from all the interacting dipoles. The calculation can be carried out in the continuum approximation. The problem is the same as for the Frenkel exciton when the dipole-dipole lattice sum arises. The motion equation system reads as follows:

$$\begin{cases} \left(\frac{\omega^2}{\omega_1^2} - 1 \right) \varphi_z(\mathbf{p}) + \frac{3R}{4\pi} \sum_q \left(\frac{R}{r_{\mathbf{pq}}} \right)^3 \varphi_z(\mathbf{q}) = 0 \\ \left(\frac{\omega^2}{\omega_1^2} - 1 \right) \varphi_{\parallel}(\mathbf{p}) - \frac{3R}{4\pi} \sum_q \left(\frac{R}{r_{\mathbf{pq}}} \right)^3 \left\{ \frac{3x_{\parallel}^2}{r_{\mathbf{pq}}^2} \varphi_{\parallel}(\mathbf{q}) - \varphi_{\parallel}(\mathbf{q}) + \frac{3x_{\perp}^2}{r_{\mathbf{pq}}^2} \varphi_{\perp}(\mathbf{q}) \right\} = 0 \\ \left(\frac{\omega^2}{\omega_1^2} - 1 \right) \varphi_{\perp}(\mathbf{p}) - \frac{3R}{4\pi} \sum_q \left(\frac{R}{r_{\mathbf{pq}}} \right)^3 \left\{ \frac{3x_{\perp}^2}{r_{\mathbf{pq}}^2} \varphi_{\perp}(\mathbf{q}) - \varphi_{\perp}(\mathbf{q}) + \frac{3x_{\parallel}^2}{r_{\mathbf{pq}}^2} \varphi_{\parallel}(\mathbf{q}) \right\} = 0 \end{cases} \quad (20)$$

After some cumbersome integration one gets the dispersion of the Frenkel excitons in the following form:

$$\left\{ \begin{aligned} \omega_{\parallel} &= \omega_1 \sqrt{1 - \frac{3}{2} \left(\frac{R}{H}\right)^3 (2 - 3kH - (kH)^2 + o((kH)^4))} \\ \omega_z &= \omega_1 \sqrt{1 - \frac{3}{2} \left(\frac{R}{H}\right)^3 \left(1 - kH + \frac{(kH)^2}{4} + o((kH)^4)\right)} \\ \omega_{\perp} &= \omega_1 \sqrt{1 + \frac{3}{2} \left(\frac{R}{H}\right)^3 \left(1 - 2kH - \frac{5(kH)^2}{4} + o((kH)^4)\right)}. \end{aligned} \right. \quad (21)$$

where the integrals are the general hypergeometric series which are linear on their parameter kH at small quasi-momentum k . The value of the characteristic wavenumber $k_0 = \omega_1/c = \alpha\sqrt{Na_B}/(R\sqrt{R})$ is determined by the intersection point of the light line \mathbf{ck} and the X-ray Frenkel exciton frequency $\omega_1 \simeq 28$ eV where $\alpha = 1/137$ is the fine structure constant, $N = 240$ is the number of the valence electrons, and a_B is the effective Bohr radius of the electron. The characteristic value of k_0 corresponds the wavelength $\simeq 450$ Å. Thus the dispersion of the exciton is linear on its momentum in the interesting region.

In the very similar manner as for the 1D case we write the expression for the coupled modes as:

$$\left\{ \begin{aligned} \sigma_z(x, y) &= -\chi_L (\varphi_z(x, y) + \gamma_1\varphi_z(x, y + 1) + \gamma_1\varphi_z(x + 1, y) \\ &\quad + \gamma_1\varphi_z(x, y - 1) + \gamma_1\varphi_z(x - 1, y)) \\ \sigma_x(x, y) &= -\chi_L (\varphi_x(x, y) + \gamma_1\varphi_x(x, y + 1) + \gamma_0\varphi_x(x + 1, y) \\ &\quad + \gamma_1\varphi_x(x, y - 1) + \gamma_0\varphi_x(x - 1, y)) \\ \sigma_y(x, y) &= -\chi_L (\varphi_y(x, y) + \gamma_0\varphi_y(x, y + 1) + \gamma_1\varphi_y(x + 1, y) \\ &\quad + \gamma_0\varphi_y(x, y - 1) + \gamma_1\varphi_y(x - 1, y)) \end{aligned} \right. \quad (22)$$

where $\gamma_1 = (R/H)^3$ and $\gamma_0 = -2(R/H)^3$ are Coulomb dipole-dipole interaction parameters for two polarizations as before. To avoid the longer formula we take the 2D square lattice and suppose the lattice constant to be equal to the nearest neighbour distance, H . That seems to be close to the actual case of the polymerized fullerene. In the nearest neighbor approximation, which is valid for large values of \mathbf{k} close to the Brilluene zone end, the spectrum of three plasma branches reads as follows:

$$\left\{ \begin{aligned} \omega_z &= \omega_1 \sqrt{1 + 2\left(\frac{R}{H}\right)^3 (\cos(k_x H) + \cos(k_y H))} \sim \omega_1 \sqrt{1 + \frac{R}{H})^3 (kH)^2} \\ \omega_{\parallel} &= \omega_1 \sqrt{1 - \left(\frac{R}{H}\right)^3 2 \cos(kH)} \sim \omega_1 \sqrt{1 + 2\frac{R}{H})^3 (3 - (kH)^2)} \\ \omega_{\perp} &= \omega_1 \sqrt{1 + \left(\frac{R}{H}\right)^3 \cos(kH)} \sim \omega_1 \sqrt{1 - \frac{R}{H})^3 (6 - (kH)^2)} \end{aligned} \right. \quad (23)$$

VI. POLARITON

We derived the Coulomb spectrum of the transverse and longitudinal collective modes of the planar fullerene structure in the last section. It is well known that the standard Frenkel exciton couples with the light. The resulting excitation, the exciton polariton, is derived as pole of the "dressed" Green function.

The derivation of the X-ray Frenkel exciton polariton will be presented here following the Ref.¹⁹. First, we define the polarizability of the elementary cell of the polymerized fullerene layer via the dipole momentum of the single excitation. The dynamic polarizability relates the induced dipole to the external field.

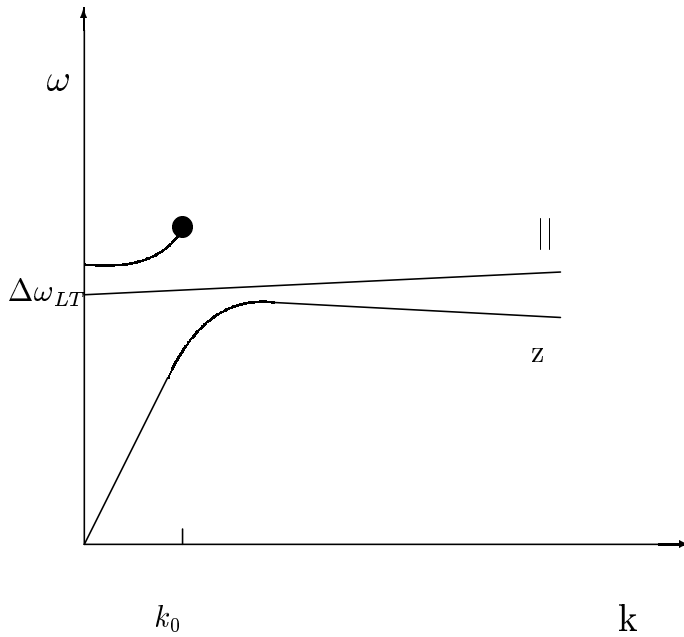


FIG. 2. The long wave length part of the plasmon-Frenkel-exciton polariton dispersion for the fullerene plane. Three branches on the figure correspond to the longitudinal mode (in the middle), and two z -polarized branches, because of the transverse retarded polariton exciton has the spectrum with two branches. The higher branch decays at large k and ends in the point where the decay becomes larger than the real part of the frequency. The frequency of the lower transverse branch coincides with the photon line for the small k and coincides with the unperturbed Coulomb exciton dispersion for the large k . The longitudinal branch frequency does not change due to retarded interaction.

Because of the longitudinal excitation does not interact with the transverse field and the scalar and longitudinal Coulomb interaction are included in expression Eq.(21) excepting the retarding interaction, first branch will not change. It will be given by the upper line of the Eq.(21). Let consider then the situation for the transverse mode.

In general, the mixing between the photon and the dipole excitation results in two branches. The upper branch is decaying for the low-dimensional excitation. The transverse modes have to decay because of the photon radiation when the energy and momentum conservation fulfilled when the energy of the excitation is equal or larger than the energy of the photon having the same wavenumber as the exciton. It corresponds to the frequency of this new mixed mode which is higher than the photon line $\hbar ck$. The lower branch can not excite the photon in vacuum, therefore its frequency has zero imaginary part. However, this excitation has the exponentially decaying field along the fullerene plane like the longitudinal exciton. The method of calculation of the 1D and 2D retarded excitation frequencies is given in Ref.¹⁹ and will not be discussed here in details. As a result, in the region of small $k \ll k_0$ the upper branch has the following complex frequency:

$$\omega_j(k) \simeq \omega_j(0) \left(1 - \gamma_j k H \left[1 - 2\pi \left(\frac{R}{H} \right)^3 \sqrt{\frac{R}{N a_B}} \right] \right) + i 4 \left(\frac{R}{H} \right)^3 \sqrt{\frac{R}{N a_B}} c H k^2 \quad (24)$$

where the parameter γ_j is $\left(\frac{R}{H}\right)^3$ for the z -mode and twice more, $2\left(\frac{R}{H}\right)^3$ for the \perp -mode. The frequency $\omega_j(0)$ is the frequency of the Coulomb exciton at zero wavenumber, taken without the retardation effect. Surely we hold in this expression only linear on k terms in the real part and the lowerest term in the imaginary part is proportional to the k^2 . So far the region of the defined excitation is $k < \sqrt{R/4H\gamma_j\alpha}k_0$, for the larger k the imaginary part of the energy is larger than the real and this polariton does not exist.

VII. SUMMARY AND DISCUSSION

In summary, we predict in the first time that in the fullerene solid the Frenkel-type transverse excitations exist¹². We obtained in the paper the dispersion of the collective electron excitations in the 1D and 2D crystals of the fullerene clusters including the radiative decay. The typical frequency of such excitation depends mainly on the electron density in the single cluster, the frequency of the single cluster surface plasmon is about 25-28 eV. The calculated band width is about some electron-Volts.

We distinguish the surface plasmon on the single cluster and the Frenkel excitation in the lattice of the fullerene clusters (1D, 2D or 3D crystal). The excitation of the single cluster has the definite dipole momentum and is localized in the volume of the cluster. It looks like the simple dipole excitation of the fullerene super-atom. Similarly to the dipolar insulator, the single cluster plasmon mixes with all the neighbors. The resulting wave of the dipole momentum in the cluster medium is the new delocalized excitation which has the X-ray frequency due to the large number of electrons within a single cluster participate in the charge oscillation. This excitation is the X-ray plasmon-Frenkel exciton.

We addressed ourselves above only to the dipole excitations because we will be interested in the optical response of the system. We used the simple hydrodynamical

model for the estimation of the energy of single cluster mode and then for the calculation of the cluster polarizability. The linear chain possesses two transverse modes and a longitudinal one with the different frequency. The similar situation for the fullerene monolayer differs mainly in the value of the mode splitting.

The dispersion of the frequency of the X-ray Frenkel exciton is due to the Coulomb interaction between the dipoles on the different sites of the lattice. The total energy of the interaction between two clusters can be expanded in a series on the multipole components of the induced and external fields. We demonstrated¹⁰ that the dipole plasma frequency is changed virtually due to the dipole-dipole interaction. The splitting energy is weak by the magnitude. For the L^{th} multipole cluster-cluster interaction the small parameter of the problem is the ratio of the cluster radius to the nearest-neighbor distance $(R/H)^{2L}$. Hence the splitting decreases very rapidly with the multipole index L , moreover the mixing between the different multipoles decreases even faster (see¹¹ for more details).

So far we mentioned all main assumptions of our model: (*i*) the fullerene cluster is treated as the spherical, that is right until one interests in the collective excitation with the multipole index less than 3; (*ii*) the plasma high frequency limit (or the classical hydrodynamic approach) we hope to be valid, though the question about the influence of the single electron spectrum on the plasma modes stills open; (*iii*) the neglecting of the mixing between the different multipoles seems to be very natural, for the dipole mode it is exactly; (*iv*) the non-uniformity of the actual polymerized structure is beyond our scope, it will be considered in respect with the future experiments on X-ray optics.

In summary, we present the semi-classical simple model predicting the X-ray polariton phenomenon in the polymerized fullerene chain and plane. The frequency dispersion laws for the transverse and longitudinal polarization excitations were derived in the continuum approximation for the non-retarding part of the Coulomb interaction. The polariton spectrum was evaluated along with the decay rate for the small wavenumber region to be compared with future X-ray optics experiment.

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