The composed plasmons in the chain of joined spheres

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Model of coupled spherical quantum wells is applied to C_{119} molecule [1], which consists of two globes having dumb-bell shape. Within the model a dipole collective excitation series obtained. Two types of coupled oscillation exist with energy shifted up and down from C_{60} molecule plasmon energy depending on dipole polarization.

Recently observed photopolymerization and chemical polymerization of fullerene molecules gives an example of chain of connected globes. In tight-binding approximation the energy band for composed collective oscillations of chain of fullerene molecules is obtained.

Optically active, transverse collective excitation with energy about 28 eV slightly disperged is obtained.

I. INTRODUCTION

In this paper a peculiar kind of composed plasma excitation is discussed, which could exists in one dimensional (1D) array of nanoobjects, for example, in polymerized fullerene molecules in solid. Last years we investigated Spherical Shell Quantum Well (SSQW) model for fullerene molecule [1,2]. Within it we obtained in a very simple way collective excitations on single C_{60} molecule. Recently developed other fullerene molecule C_{119} is proposed to consist of two usual fullerene globes connected [4]. In a such case one can imagine electrons on C_{119} behaving as two 2-dimensional electron gases (2DEG) with a join. So when treating C_{60} as SSQW, it is very natural use a model of joined quantum wells [3] for C_{119}.

In case of C_{119} molecule there is electromagnetic mixing of plasmons on different globes. We considered only the displacement current, minding a reason for tunneling current to be negligible. This approach gives us description of suggested collective excitation of C_{119} electron system. In a lower dipole approximation one gets two types of coupled oscillation. First, a polarized along the molecule axis oscillation. Second, having higher energy, a polarized across the axis oscillation. Evidently, as usual transverse wave it is doubly degenerate.

For chain of C_{60} molecules we will obtain in a standard way a band of 1D composed plasmons. As for C_{119} molecule there are longitudinal and two transverse waves relatively to chain axis. Energy dependence on wave vector of excitation will be discussed.

II. PLASMON IN TWO COUPLED SSQW

Let us first reproduce here some results concerning coupling between plasmons obtained within spherical shell model of fullerene molecule [1,2,5]. We will write the Coulomb coupling between two spheres and in next section we will treat this interaction between neighboring molecules in a usual tight-binding approach. The electron surface charge density under external potential φ undergoes deviations from equilibrium value n determined by χ, response function of 2DEG on the sphere surface. In accordance with [5] we define spherical oscillation of electron density to be induced by a potential as:

$$\sigma^i_{LM} = \chi^i_L \quad \varphi^{act}_L \tag{1}$$

where χ is a response function of single sphere, L, M are multipole power indexes (or angular momentum and its projection onto z-axis), index $i = 1, 2$ denotes the first and second sphere of C_{119} molecule, and $\varphi^{act} = \varphi^{ext} + \varphi^{ind} = \varphi^{ext}_{LM} + \frac{4\pi R}{2L+1}\chi_L \sigma_{LM}$ is acting potential, included for selfconsistence of calculation.

Considering central symmetry of each of joined sphere, we use expansion of all quantities into spherical harmonics and get response of one globe in block-diagonal form [2] in subspace of angular momentum $L =$ const. In spherical geometry a radial jump in electric field is given by:

$$\frac{2L+1}{R}\,\varphi^i_{LM} = 4\pi\sigma^i_{LM} \tag{2}$$

where we divided induced potential in two parts from two globes of radius R. We get eigenvalue equation arising from Eq.(1) and (2) under zero external potential. For single C_{60} molecule, using spherical approximation, eigenvalue secular equation is diagonal in the angular momentum representation and is readily solved. Frequency of eigen mode has a simple analytical form in a high frequency limit of response function, when a main gain into response of electron system is brought by collective excitation. Then according to [5], we wrote $\omega_L^{(i)}$, frequency of plasmon on $i^{\rm th}$ single sphere. This solution correspond to surface plasma oscillation in a SSQW, which is very close to spherical wave of electron liquid on a metal sphere surface [2]. It turns to have same frequency for modes with $-L < M < L$. It possesses a definite angular momentum, L, (like a 2D plasmon wave vector) and its frequency $\omega_L^{(i)}$ depends on square root of L.

As for plasmon with a coupling, let concern first a similar problem of coupled plasmon modes in two parallel metal planes displaced at distance d. Charge density waves in two planes are coupling through $e\sigma^{(1)}\, g\,\varphi^{(2)}$, attenuated Coulomb interaction from second plane where $g = e^{-kd}$ is a degree of decay and play role of coupling constant. It results in energy of odd and even modes:

$$\omega^2_{g\,(u)} = \omega^2_k\,(1 \pm e^{-k\,d}) \tag{3}$$

In a limit of weak coupling $g = 0$ it returns free plasmon energies. Under strong coupling and $k\,d \ll 1$, odd frequency becomes acoustic: $\omega_u = \omega_k\sqrt{k\,d} = \sqrt{2\pi n e^2/d\,m}\;kd$, and even mode behaves as plasmon with doubled electron density: $\omega_g = \omega_k\sqrt{2 - k\,d}$.

The problem of electromagnetic coupling γ between two sphere possessing 2D electron gas (2DEG) has been considered in complete spherical harmonics $P_L(r)Y_{L,M}(\Omega)$ those form a complete set on a sphere. Evidently, for single sphere placed in coordinate origin one can omit radial part, but for sphere displaced along axis z from the first globe at $H = 2R + d$, intercenter distance, each $P_L(r')Y_{L,M}(\Omega')$, which centered at distance H from the origin, is expanded in a sum of harmonic centered at the origin. According to [6]:

$$\begin{aligned} &P_L(r')Y_{L,M}(\Omega') = \frac{1}{|\mathbf{r}-\mathbf{H}|}^{L+1} Y_{L,M}(\Omega') = \\ &\sum_{k=m}^{\infty} \delta_{M,m}\,(-1)^{k-m}\sqrt{\frac{2L+1}{2k+1}}\frac{(L+k)!}{\sqrt{(L+m)!(k+m)!(L-m)!(k-m)!}}\,H^{-(L+k+1)}r^k Y_{k,m}(\Omega)\end{aligned} \tag{4}$$

We use in [1,2,5] dimensionless harmonic $\mathcal{Y}_{L,M}(\Omega)$ which is usual spherical harmonic divided by $P_L(r = R)$, its radial part at globe radius. We expand spherical oscillations of electron density on a globe in $\mathcal{Y}_{L,M}$ harmonics as well as other quantities.

We define the couple through non-diagonal part of Hamiltonian for density oscillation operator, this energy is the energy of interaction between one globe and potential induced by the second is proportional to:

$$\int d\Omega\;\sigma^\dagger(1)\,e\varphi(2) = \sum_{l,m}\frac{4\pi e^2 R}{2l+1}\,\sigma^\dagger_{lm}(1)\int d\Omega\;\mathcal{Y}_{L,M}(\Omega)\sigma(2) \tag{5}$$

Substituting Eq.(4) into (5), including hermitian conjugated and exchange $(1) \to (2)$ terms, and making some algebra we find that spherical harmonics of density oscillation are mixed in a very symmetrical form:

$$\begin{aligned} &\sigma^{(1)}_{KM} \propto \gamma_{KLM}\,\sigma^{(2)}_{LM} = \sum_L (-1)^M \left(\tfrac{R}{H}\right)^{L+K+1}\frac{4\pi e^2 R}{\sqrt{(2L+1)(2K+1)}} \\ &\times\frac{(L+K)!}{\sqrt{(L+M)!(K+M)!(L-M)!(K-M)!}}\;\sigma^{(2)}_{LM}\;\frac{1+(-1)^{K+L}}{2}\end{aligned} \tag{6}$$

where last term results in vanishing of mixing for odd $L + K$ modes. It is natural for molecule with a reflection plane to have only even modes. In general, potential of $L^{\rm th}$ multipole $\varphi^{(1)}_{LM}(\omega)$ has infinite number of components with different K in harmonics of center (2), see Eq.(4). When sum $L + K$ rises, the couple diminishes according with Eq.(6) exponentially with the base $2R/H < 1$. It can be shown that coupling $\gamma(L, K, M)$ has maximum value either under $K = 1$ or $L = K$ amount, containing binomial coefficient. Also, we stress that M number is conserved that is due to axial symmetry of the problem.

In order to show the relation between coupled modes in two planes and SSQW plasmon with a coupling we have to find a limit of great radius of the sphere $R \to \infty$. Note that one should keep momentum of plasmon in the plane $q = L/R$ to be constant so angular momentum of spherical plasmon increases infinitely too. It let us use Stirling formula:

$$\begin{aligned} &\gamma_{LLM} = (-1)^M\left(\tfrac{R}{H}\right)^{2L}\frac{4\pi e^2 R}{(2L+1)}\,\frac{(2L)!}{(L+M)!(L-M)!} \simeq \\ &(-1)^M\left(\tfrac{R}{H}\right)^{2L}\frac{4\pi e^2 R}{2L+1}\exp[2L - (L+M) - (L-M)]\frac{(2L)^{2L}}{(L+M)^{L+M}(L-M)^{L-M}}\end{aligned} \tag{7}$$

Next condition should be considered to keep interglobes distance d finite under infinite increase of globe radius or equivalently distance between globe centers $H = 2R + d$, it corresponds finite distance between planes along z axis.

Also we demand the classical momentum vector to be pointed perpendicularly to z axis, due to that we consider only $L=\infty$, $M=0$ mode, which angular momentum has a zero z projection:

$$\lim_{R=q/L,\, L\to\infty} \gamma_{L,L,M=0} = \left(1-\frac{qd}{2Rq-qd}\right)^{2Rq} \frac{4\pi e^2 R}{2L+1} \simeq e^{-qd}\,\frac{2\pi e^2}{q} \tag{8}$$

We obtain classic formula for electromagnetic mixing of plane plasmon which gives Eq.(3) for plasmon energy.

Combining Eq.(1), (2) and adding a coupling (6), one obtains the equation system to solve for eigen mode of C_{119}:

$$\begin{cases} \sigma^{(1)} = \chi^{(1)}(\varphi^{ext} + \frac{4\pi R}{2L+1}\chi^{(1)}\sigma^{(1)} + \hat{\gamma}\,\sigma^{(2)}) \\ \sigma^{(2)} = \chi^{(2)}(\varphi^{ext} + \frac{4\pi R}{2L+1}\chi^{(2)}\sigma^{(2)} + \hat{\gamma}\,\sigma^{(1)}) \end{cases} \tag{9}$$

We stress that $\hat{\gamma}$ has nondiagonal matrix elements on different subspaces of angular momentum Eq.(6), but projection of angular momentum on z – intercenter axis still conserved, *i.d.* coupling $\gamma_{LM,KM}$ has three independent indexes L, K, M in doubled $L\otimes K$ angular momentum representation. Nontrivial solution of Eq.(9) in absence of external potential is obtained under condition of determinant of system is zero:

$$\det \begin{vmatrix} \left(1-\frac{4\pi R}{2L+1}\chi_L^{(1)}\right)\delta_{LK} & -\chi_L^{(1)}\,\gamma_{LK} \\ -\chi_L^{(2)}\,\gamma_{LK} & \left(1-\frac{4\pi R}{2L+1}\chi_L^{(2)}\right)\delta_{LK} \end{vmatrix} = 0 \tag{10}$$

here we omit third index M from $\hat{\gamma}$ matrix element due to the only plasmons with equal M are coupled. Diagonalization of this matrix (10) will bring energies of new modes with any accuracy. This is provided by exponential diminishing of γ with $L+K$ rising. Evidently coupling as electrical induction is weaker for higher multipole degree of potential. It can be compared with the join between planes, when electric field of plasmon has typical decrement k in z direction, which can be mapped onto L/R. That is why we can use perturbation theory on $L+K$ multipole power.

In our previous paper [3] we solve Eq.(10) within first order perturbation theory on $L+K$, when secular equation for even and odd plasmon modes becomes diagonal in LK indexes and has a quite simple result:

$$\omega^2_{g(u)} = \omega^2_L\left(1 \pm \gamma_{LL,M}\,\frac{2L+1}{4\pi R}\right) \tag{11}$$

This is approximation of coupling only between plasmons of equal L on both globes. The coupling mixes unperturbed spherical waves on single sphere and splits $2L+1$ degenerated modes in series on M and shifts the whole series up or down for two types of coupling. Zone mode with $M=0$ shifts as sign of coupling, but shifts of other tesseral modes alter sign and are less according to Eq.(6).

Then for dipole mode from Eq.(11) we obtain frequency of eigen mode:

$$\omega_{g(u)} = \omega_1\sqrt{1\pm\frac{3}{4\pi R}\,\gamma_{11,M}} = \omega_1\sqrt{1\pm\frac{1+3(-1)^M}{2}\left(\frac{R}{H}\right)^3} \tag{12}$$

where $\hbar\omega_1 \simeq 28$ eV – energy of dipole plasmon in C_{60}. Eq. (12) corresponds to dipole-dipole interaction between globes that does not mixed different angular momentum subspaces. Dipole-quadruplet coupling is prohibited and next order corresponds to $L=1\to L+3$ weak dipole-octuplet couple and we omit it.

Obtained two excitations have different symmetry. Even mode can be described as dipole of doubled charge. While potential induced by surface charge density of second, odd mode has only next quadrupole order in multipole expansion. First mode frequency is splitted into excitations of two polarizations – across and along the molecule axis. Longitudinal polarization with $M=0$ (z–type) is slightly, about 1.2 eV shifted from C_{60} plasmon position (28 eV), but x– and y–type ones are down about 0.6 eV.

III. TRANSVERSE PLASMON IN THE CHAIN

It is usual to think about collective oscillations as that has strongly longitudinal character being independent of geometry and dimension of the system.It is well known that in superlattice collective oscillations could be coupled and then mixed plasmons have some wave vector along the lattice axis. In the case of polymerized fullerene molecule the composed plasmon can be constructed from multipole plasma excitation of single molecule in tight-binding approximation with a cyclic boundary condition as:

$$\varsigma(k) = \sum_{n=0}^{N} e^{-iknH}\,\sigma(x-nH) \tag{13}$$

where $n = 0, \ldots N$ is the number of molecule in the chain, k is wave vector of composed plasmon.

Energy band for this plasmon is obtained from Eq.(11) in first order of coupling (diagonal approximation of γ):

$$\omega(k,L)^2 = \omega_L^2 \left(1 + cos(kH)\,\gamma_{LL,M}\,\frac{2L+1}{4\pi R}\right) \tag{14}$$

that gives for dipole plasmon two branches. First one is longitudinal mode, *i.e.* dipole momentum (and electric field) is directed along chain. It has $M = 0$. The second is transverse type and is degenerate (x- and y-polarizations), $M = \pm 1$:

$$\omega(k,1) = \omega_1 \sqrt{1 + cos(kH)\,\frac{1+3(-1)^M}{2}\left(\frac{R}{H}\right)^3} \tag{15}$$

In summary, we developed coupled spherical quantum well approach to calculate high frequency response of C_{119} molecule. We find C_{119} to have a dipole collective excitation series with energy slightly shifted from C_{60} molecule plasmon energy as dipole Coulomb interaction between two spheres and splitted into transverse and longitudinal polarizations. It corresponds to in phase oscillating both globe electron density. The transition to simple problem of two planes in the limit of large globe radius is followed. For polymerized chain of fullerenes composed plasma excitation is found to exist. It has interesting transverse type and can easily interact with light. Probably some kind of such collective excitations could be observed in photopolymerized films of fullerene.

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