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MULTIPOLE EXCITATIONS OF TWO JOINT CONDUCTING SPHERES: APPLICATION TO C_{119} MOLECULE

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Model of coupled spherical shell quantum wells is applied to C_{119} molecule. In a frame of the model the frequencies of the collective excitation series are calculated. The lowermost excitation, which could be detected by optical methods, is founded to have essentially dipolar character. Two types of the coupled oscillations exist with a different parity, which frequencies shifted up and down from C_{60} molecule plasmon frequency. For a dipole mode the two plasmon peaks with a gap about 3.5 eV have different dipole polarization. A transition to the usual coupled plasmons in two metal planes is fulfilled.

Keywords: A. fullerene, A. quantum wells

1. Introduction: Coupling of 2DEG Plasmons

The problem of two-dimensional electron gas (2DEG) is in a focus of attention during last decades. Particularly, it was firmly stated that Coulomb coupling between two layers with 2DEG modifies the system response and leads to splitting between two 2D–plasmon branches[1,2]. We consider in this paper a problem of the coupling between 2D-plasmons on the surface of two conducting spheres. We suggest that the obtained result is applicable to recently discovered bispherical C_{119} macromolecule[3] and, probably, to some quantum dot system.

Electrons freely moving within a thin spherical shell behave as a charged liquid at the frequency higher than all single electron transitions. This system possesses some spherical collective excitations[4–6]. In frame of spherical shell quantum well (SSQW) model[7] we calculated plasmon frequency for quasi-spherical C_{60} molecule as lowermost dipolar excitation. This frequency is triply degenerated. For dimerized molecule we consider a coupling between two SSQW plasmons and get a new dipolar excitation which frequency is splitted in axial coupling field. At high frequency this excitation has to determine optical response of C_{119} or electron energy losses.

The physics of the Coulomb coupling of 2DEG plasmons is well understood[2]. To start with we remind some results concerning a simple problem of the plasma oscillation in 2DEG. We will introduce some terms to be used for the SSQW plasma coupling.

The local electron surface charge density undergoes deviation from its equilibrium value n at external potential φ. The density Fourier component, $\sigma(k,\omega)$, satisfies: $\sigma(k,\omega) = -k^2\chi(k,\omega)\varphi(k,\omega)$, where: χ is a response function of 2DEG[1]. In accordance with Gauss theorem, jump in electric field across the 2DEG plane is proportional to the surface density oscillation: $4\pi\sigma = E(z=0^+) - E(z=0^-) = 2k\,\varphi(\omega,k)$. These two expressions are solved together. Response could be simplified in a high frequency limit that yields the equation for eigenfrequency:

$$1 = -2\pi k\,\chi(k,\omega)\,|_{\,\omega\to\infty} = 2\pi n e^2\,k/m\omega^2 = (\omega_k/\omega)^2\,,$$

where e and m are the charge and the mass of electron respectively. 2DEG plasmon frequency ω_k is well known[2] to depend on square root of wave vector, k, of excitation: $\omega_k = \sqrt{2\pi n e^2 k/m}$.

Charge density waves in two parallel metal planes separated by a distance d are coupled via Coulomb interaction that results in the splitting of the frequencies of coupled modes. We do rewrite equation for $\sigma^{(1)}$, first plane density, induced by full acting potential, taken as a sum of $\varphi^{\rm ext}$, external potential, $\varphi^{(1)}$, induced potential from the same plane, and $g\,\varphi^{(2)}$, attenuated induced potential from the second plane. Here $g = e^{-kd}$ is a potential decay which plays a role of the coupling constant. In absence of external potential linear equation system for eigenmodes with coupling reads:

$$\begin{cases} \sigma^{(1)} = -2\pi k\, \chi^{(1)}(\sigma^{(1)} + g\, \sigma^{(2)}) \\ \sigma^{(2)} = -2\pi k\, \chi^{(2)}(\sigma^{(2)} + g\, \sigma^{(1)}) \end{cases} \tag{1}$$

When two 2DEGs have the same parameters, $\chi^{(1)}$ and $\chi^{(2)}$ are equal for two planes. This leads to simplest secular equation: $1 + 2\pi\, k\, \chi = \pm g\, 2\pi\, k\, \chi$, resolved for odd and even modes:

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

In a limit of weak coupling $g = 0$ it returns free plasmon frequencies. Under the condition $k\,d \ll 1$, the odd frequency becomes acoustic: $\omega_u = \omega_k \sqrt{k\,d} = \sqrt{2\pi n e^2/dm}\ kd$, and the even mode behaves as plasmon with doubled electron density: $\omega_g = \sqrt{2}\,\omega_k$. We point out that this result could be obtained by solving for poles of self-consistent polarizability of the whole system.

2. Plasmon in Two Coupled SSQWs

Now we will consider plasmon obtained in frame of spherical shell model of fullerene molecule[6–8]. The electric potential is the solution of Laplace equation for empty space inside, $\varphi^{\,\mathrm{in}}(r < R)$, and outside, $\varphi^{\mathrm{out}}(r > R)$, spherical shell of molecule. We wrote it in the multipole power expansion:

$\varphi^{\mathrm{in}}(r,\Omega) = \sum_{L,M} \frac{\varphi_{LM}}{R^L} |\mathbf{r}|^L\, Y_{L,M}(\Omega),$

$\varphi^{\mathrm{out}}(r,\Omega) = \sum_{L,M} \varphi_{LM} R^{L+1} \frac{1}{|\mathbf{r}|}^{L+1}\, Y_{L,M}(\Omega)$

In accordance with[8] we use spherical oscillation of electron density σ_{LM}. For central symmetry of each of the joined spheres we use expansion of all quantities in complete spherical harmonics $P_{\,L}(r) Y_{L,M}(\Omega)$ forming a complete set on a sphere. In spherical geometry a radial jump in electric field is given by:

$$\frac{2L+1}{R}\,\varphi^{i}_{\ LM} = 4\pi\sigma^{i}_{\ LM} \tag{3}$$

We get response of one globe in block-diagonal form[7] in subspace of angular momentum $L = \mathrm{const}$:

$$\sigma^{i}_{\ LM} = \chi^{i}_{\ L}\ \ \varphi^{act}_{\ LM} \tag{4}$$

where χ is a response function of single sphere, and $\varphi^{act} = \varphi^{ext}_{\ LM} + 4\pi\sigma_{\ LM} R/(2L+1)$ is an acting potential, L, M are multipole power indexes (or angular momentum and its projection onto z-axis), index $i = 1, 2$ is reserved for the first and second spheres of C_{119} molecule (see Fig. 1). In the same manner as for 2DEG we get eigenvalue equation for single sphere arising from Eqs.(4) and (3) at zero external potential. Alternatively, poles of the self-consistent polarizability, $\alpha_{\ LM}(\omega)$ are fixed by frequencies of molecular plasmon excitations with angular momentum L. It is easily seen[7] from explicit expression for the polarizability: $\alpha_{\ LM} = \chi_{\ L}/(1 - 4\pi R \chi_{\ L}/(2L+1))$. A frequency of plasmon of L^{th} multipole is proportional to square root of angular momentum $\omega^{(i)}_{\ L} \propto \sqrt{L/R}$ in a limit $L \gg 1$, similarly to 2D-plasmon frequency[8].

Coupling, $\widehat{\gamma}$, in the case of two spheres has more complicated form than for planes, because the two sets of

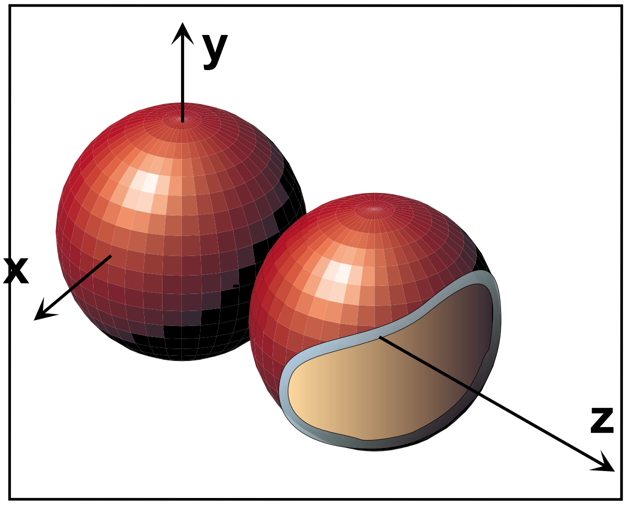

Fig. 1. The dumb-bell C_{119} molecule is described as a system of two coupled thin spherical shell quantum wells in our model. Each single molecule possesses a triply degenerated spherical dipole excitation with three, x-, y- and z-polarizations.

spherical harmonics centered at distinct points constitute overcomplete set. That is why we replace expansion of $\varphi^{(1)}$ in spherical harmonics centred on globe (1) with those centred at globe (2), which coordinate origin is displaced along axis z at $H = 2R + d$, intercentral distance. According to[9], potential of L^{th} multipole $\varphi^{(1)}_{\ LM}(\omega)$ has infinite number of components with different K :

$$P_L(r')Y_{L,M}(\Omega') = \frac{1}{|\mathbf{r}-\mathbf{H}|}^{L+1} Y_{L,M}(\Omega') = \sum_{K=m}^{\infty} \sqrt{\frac{2L+1}{2K+1}}$$
$$\times \frac{\delta_{M,m}\,(-1)^{K-m}(L+K)!}{\sqrt{(L+m)!(K+m)!(L-m)!(K-m)!}}\, H^{-(L+K+1)} r^{K} Y_{K,m}(\Omega) \tag{5}$$

We will consider here only a mixing through displacement current, having in mind a reason for tunneling to be negligible[10]. Substituting Eq.(5) into (4), including Hermitian conjugated terms, after some algebra we find out that spherical harmonics of density oscillation are mixed in a very symmetric form:

$$\sigma^{(1)}_{LM} \propto (\widehat{\gamma}\,\sigma^{(2)})_{LM} = \sum_{K} \left(\frac{R}{H}\right)^{K+L+1} \frac{4\pi e^2 R\ \sigma^{(2)}_{KM}}{\sqrt{(2K+1)(2L+1)}}$$
$$\times \frac{(-1)^M (K+L)!}{\sqrt{(K+M)!(L+M)!(K-M)!(L-M)!}} \frac{1+(-1)^{L+K}}{2} \tag{6}$$

Here the last term gives a vanishing of the mixing for odd $L + K$ modes. It is natural for molecule with a reflection plane. Also, we note that M number is conserved due to axial symmetry of the molecule. Then we write the equation system for eigenmodes of C_{119}:

$$\begin{cases} \sigma^{(1)}_{LM} = \chi^{(1)}_L(\varphi^{ext}_{LM} + \dfrac{4\pi R}{2L+1}\sigma^{(1)}_{LM} + (\widehat{\gamma}\,\sigma^{(2)})_{LM}\ ) \\ \\ \sigma^{(2)}_{LM} = \chi^{(2)}_L(\varphi^{ext}_{LM} + \dfrac{4\pi R}{2L+1}\sigma^{(2)}_{LM} + (\widehat{\gamma}\,\sigma^{(1)})_{LM}\ ) \end{cases} \tag{7}$$

We stress that operator $\hat{\gamma}$ has non-diagonal matrix elements on different subspaces of angular momentum, Eq.(6), but projection of angular momentum on z – intercentral axis is still conserved, *i.e.* coupling $\gamma_{LM,KM}$ has three independent indexes L, K, M. Below we will omit third index M from $\hat{\gamma}$ matrix element. Nontrivial solution of Eqs.(7) exists in the absence of the external potential when determinant of the system is equal to zero:

$$\det \begin{vmatrix} \left(1 - \frac{4\pi R}{2L+1}\chi_L^{(1)}\right)\delta_{LK} & -\chi_L^{(1)}\gamma_{LK} \\ -\chi_L^{(2)}\gamma_{LK} & \left(1 - \frac{4\pi R}{2L+1}\chi_L^{(2)}\right)\delta_{LK} \end{vmatrix} = 0 \tag{8}$$

When parameters of two electron systems are equal, χ is the same for both globes. Iterative diagonalization of this matrix (8) in doubled angular momentum representation space $L \otimes K$ will bring frequencies of new modes with any accuracy. This is provided by exponential diminishing of γ with $L + K$ rising. Evidently, the coupling as the electrical induction is weaker for higher multipole degree of potential. It can be compared with the coupling between planes[2], 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 resolve Eq.(8) within first order perturbation theory on small parameter $(R/H)^{L+K}$ when this equation is diagonal in $L = K$ indexes. Then simple variable transformation $S_{g(u)} = \sigma^{(1)} \pm \sigma^{(2)}$ divides Eq.(8) in two parts – secular equations for even and odd plasmon modes:

$$\omega_{g(u)}^2 = \omega_L^2 \left(1 \pm \gamma_{LL,M}\frac{2L+1}{4\pi R}\right). \tag{9}$$

Here we use high frequency limit of response $\chi_{LM}^{(i)}(\omega)\frac{4\pi R}{2L+1} = \left(\omega_L^{(i)}/\omega\right)^2$, where $\omega_L^{(i)} = \sqrt{\frac{L(L+1)}{2L+1}\frac{4\pi}{m}\frac{n\, e^2}{R}}$ is frequency of plasmon on $i^{\rm th}$ single sphere[8].

3. Dipole Plasmon in C_{119}

We restrict now ourselves to solution for dipole collective mode in C_{119}. Dipole excitations could be observed in optical measurements (unlike from 2DEG plasmon, but like an atomic dipole) or in experiments on scattering of charged particle on small angles.

From Eq.(9) we obtain frequencies of the odd and even modes in the first approximation:

$$\omega_{g(u)} = \omega_1\sqrt{1 \pm \tfrac{3}{4\pi R}\gamma_{11,M}} = \omega_1\sqrt{1 \pm \tfrac{1+3(-1)^M}{2}\left(\tfrac{R}{H}\right)^3} \tag{10}$$

where $\hbar\omega_1 \simeq 28$ eV – frequency of dipole plasmon in C_{60}. Eq. (10) corresponds to dipole-dipole interaction between globes which not mixes different angular momentum subspaces. Dipole-quadruplet coupling is prohibited and the next order corresponds to $L = 1 \rightarrow L + 2$ weak dipole-octuplet couple. It contains a factor $(R/H)^2$ and is neglected for analytical form of solution.

These two, odd and even, excitations have different symmetry. Even mode can be described as dipole of doubled charge. While potential induced by surface charge density of the second, odd, mode has only the next quadrupole order in multipole expansion. Each mode frequency is splitted into excitations of two polarizations – across and along the molecule axis, see Fig. 2. 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 ones ($M = \pm 1$) are shifted down twice less (about 27.2 eV).

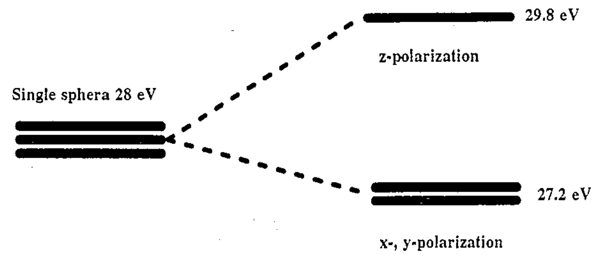

Fig. 2. The Coulomb coupling between two globes results in the splitting of the triply degenerated dipole collective excitation into even doubly degenerated x-, y-polarized excitations and even, non-degenerated, z-polarized one. The splitting between the frequencies of these two states is about 10 % of plasmon frequency (28 eV). 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 (8) up to 45×45 size to obtain 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 in[10] at length.

It is interesting to check how this result returns to the plane plasmon. In a limit of great radius of globe, R, when momentum of plasmon $k = L/R$ is constant so angular momentum of spherical plasmon increases infinitely too, we obtain from Eq.(8) the formula for 2DEG plasmon coupling. We stress that the plane plasmon has a momentum directed along the plane and perpendicular to former intercentral axis z. It means that the angular momentum should have a zero z projection $L = \infty$, $M = 0$:

$$\gamma_{LLM} = \left(\tfrac{R}{H}\right)^{2L+1}\tfrac{4\pi e^2 R}{(2L+1)}\tfrac{(-1)^M(2L)!}{(L+M)!(L-M)!} \simeq$$
$$\left(\tfrac{R}{d}\right)^{2L+1}\tfrac{4\pi e^2 R}{2L+1}\tfrac{(-1)^M(2L)^{2L}\,e^{[2L-(L+M)-(L-M)]}}{(L+M)^{L+M}(L-M)^{L-M}} \tag{11}$$

Using the Stirling formula, substituting of $L = Rk$, and changing of globe intercentral distance with $H = 2R + d$ we get:

$$\frac{2L+1}{4\pi e^2 R}\gamma_{Rk,Rk,M=0} = \left(1 - \frac{kd}{2Rk - kd}\right)^{2Rk} \simeq e^{-kd} \quad (12)$$

where d is the gap between surfaces of two spheres, staying finite under infinite large R and H, and last term is simply attenuation of potential from first Section to be compared with Eq.(2).

In summary, we developed coupled spherical quantum well approach to calculate high frequency response of C_{119} molecule. There is a splitting of frequency of composed plasmon of C_{119} of the order of the multipole Coulomb interaction between two spheres. We find C_{119} to have a lowermost excitation series centred at C_{60} molecule plasmon frequency. This series corresponds to in-phase (dipole) and contra-phase (quadrupole) oscillations of the electron density of both globes and consists of z- and x-, y-polarizations relatively to molecule axis. According to our estimation, there is a splitting of 3.5 eV between two dipole plasmon pikes of C_{119} molecule. Oscillator strength for lower pike is twice higher than for upper pike. We show that our result for two joined SSQWs reproduces 2DEG plasma behaviour in the limit of infinitely large sphere.

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