

# Electron structure modelling and investigation of interaction processes for carbon-based-nanoclusters

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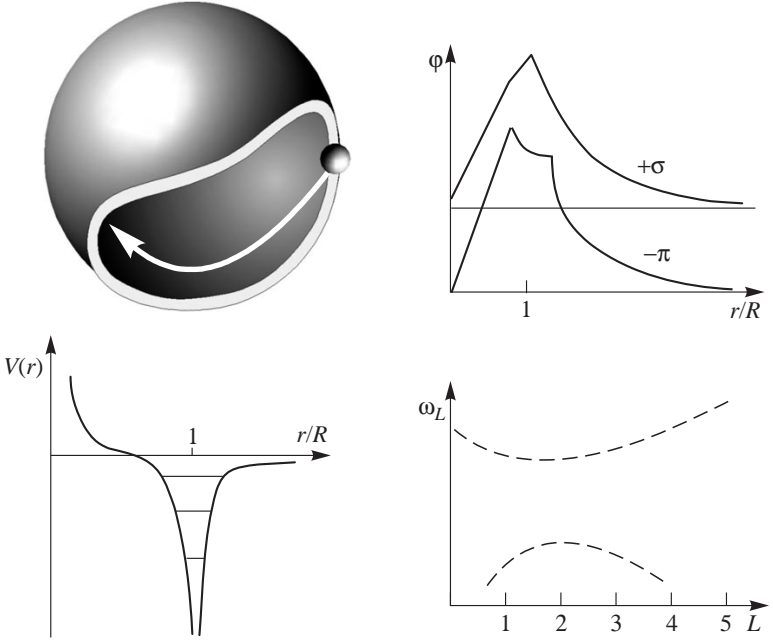
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The electronic structure of  $C_{60}$  has been in the focus of interest of physicists during the last decade. A variety of different theoretical approaches from purely phenomenological to *ab initio* calculations has been applied to find the electron energy structure and explain main experimental features. Among the experimental data, the high frequency peak ( $\sim 25$  eV) in the response of the cluster calls our attention owing to the self-evident collective nature of the corresponding excitation. It is clear now that the collective electronic excitation of  $C_{60}$  is the surface plasmon mode on the spherical cluster. Any Coulomb-including calculation has to reproduce this feature. However, it is rarely pointed out that mainly the global symmetry (SO(3) spherical topology of the cluster) influences the collective mode. The  $C_{60}$  electron structure symmetry reflects the local triangular symmetry of the graphite-like lattice distorted by the global homology of the curved closed surface. The first will be shown to be of small importance for the plasmon.

In relation to this we proposed a quantum mechanical model of spherical shell quantum well (SSQW) for the  $C_{60}$  cluster [1, 2]. We found that electrons freely moving within a thin spherical shell behave as a charged liquid at high enough frequency (see below); for example, the SSQW gives a quantum-mechanical description of the single cluster plasmon [1]. At high frequencies the spherical surface plasmon determines the optical response of the spherical nano-cluster or the spectrum of electron energy losses [3–5]. That is why it is of interest how the simple hydrodynamic picture accords with the multi-component nature of the  $\sigma$  and  $\pi$  electron system of the fullerene.

The spherical collective mode has a definite angular momentum, hence its electric field is the field of a definite charge multipole. Of course, this simplification fails in the case of a lower symmetry, for example, in a crystal. This means that all spherical single-cluster collective modes have to interact.

The plasmon frequency is the highest frequency of the dipole excitation of the total electron density of a quasi-spherical  $C_{60}$  molecule. This mode is triple



**Fig 1.** The spherical shell quantum well (upper left) has a radial potential well at the distance  $R$  from the coordinate origin (lower left). The energy levels of radial quantization are shown schematically over the well. Two components of the electron system correspond to two collective plasma modes. The dispersion law of plasma frequency on the angular momentum of excitation (lower right) of  $\sigma$ -upper branch is typical of the excitation of full symmetry, which is seen also in the potential radial distribution (upper right) with one maximum at  $R$ . In contrast, the potential of the  $\pi$ -lower plasmon has two maxima related to the shape of the  $\pi$ -electron wave function.

degenerate. Proper lowering of the  $SO(3)$  symmetry results in a splitting of the degenerate mode, and, in general, mixing with different angular modes occurs. When the dipole plasmon will interest us below, we will consider the dipole plasmon frequency splitting due to the interaction and drop the mixing with other excitations having higher multipole indices.

We discussed the particular problem of the collective excitation in the polymerized fullerene structures. We modelled the collective excitation in the chain and in the plane of the fullerene clusters, supposing that an individual cluster possesses a dipole plasma excitation. Then the excitation in the solid is a linear

combination of single cluster dipole modes. The algorithm is the same as in the case of formation of the Frenkel exciton in organic insulators, since no charge transfer from cluster to cluster occurs.

We calculated the RPA frequencies for a chain and a monolayer of fullerene molecules. It is well known that in these cases the dielectric function has a transverse excitation branch owing to the inhomogeneity in a single direction.

## 1. Spherical shell quantum well

Being extremely simple, the heuristic model of SSQW is able to reproduce the “closed shell” structure of  $C_{60}$ . Within the model only *three* possible one-electron configurations are ruled out in [2]. Moreover only the set which has 3 radial series is suitable for fullerene description.  $SO(3)$  symmetry allows one to resolve the RPA dynamic polarizability of cluster. We used the sum rule in the low-frequency limit to find the static polarizability of fullerene

$$\alpha(0) = R^3 \frac{1}{1 + a/4R} \quad (1)$$

where  $R$  and  $a$  are the shell quantum well radius and width (see Fig. 1). Contrariwise, the high frequency limit [1, 2] reveals the classical polarizability of the charged liquid [6] on the sphere surface

$$\alpha(\omega) = R^3 \frac{1}{1 - \omega^2/\omega_1^2} \quad (2)$$

where  $\omega_1$  is the plasmon frequency. This limit of the frequency, higher than all single electron transition frequencies, shows that the plasmon mode is insensitive to the local lattice symmetry. The small parameter of the model, the shell-width to shell-radius ratio, allows us to consider only the optical transitions within the single radial series of SSQW. Then the transition frequency within the model is the distance between two levels of orbital quantization for an electron revolving in an orbit with radius  $R \simeq 3.6 \text{ \AA}$

$$\hbar\omega_{f,i} = \frac{\hbar^2}{2mR^2} [L_f(L_f + 1) - L_i(L_i + 1)] \quad (3)$$

for a transition between levels with angular moments  $L_i$  and  $L_f$ , with  $m$  being the electron mass.

## 2. Interacting collective modes on the spheres

The SSQW system possesses some collective excitations like a conducting sphere. Their frequencies read as

$$\omega_L = \omega_p \sqrt{\frac{L(L+1)}{2L+1}} = \sqrt{\frac{4\pi n e^2}{mR}} \sqrt{\frac{L(L+1)}{2L+1}} \quad (4)$$

here  $\omega_p$  is the bare plasma frequency depending on the averaged surface electron density  $n$ , effective electron mass  $m$  and charge  $e$ ;  $L$  is the angular momentum of the excitation. The larger the radius of the  $C_{60}$  sphere, the closer the collective mode to the surface plasmon [7] of the 2D electron gas of the metal plane

$$\omega_L \rightarrow \sqrt{\frac{2\pi n e^2 L}{mR}} \propto \sqrt{k_{\parallel}} \quad (5)$$

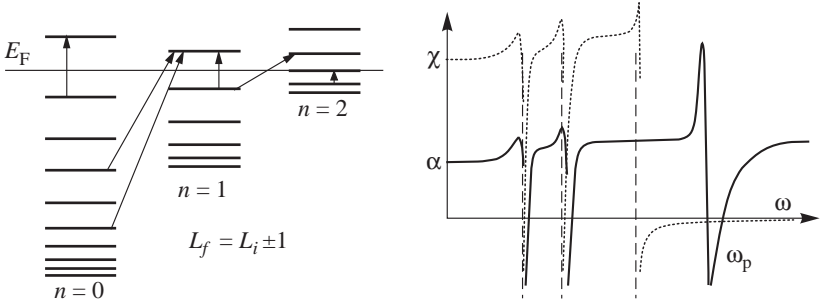
this limit  $R \rightarrow \infty, L \rightarrow \infty$  is traced for the SSQW model in [1].

Two conducting planes possess a pair of plasmon modes [8], owing to Coulomb interaction split depending on the mode wave number. A similar situation is shown to exist for the fullerene dimer. However, we argue that the picture is so simple only in the limit of infinitely large radius. For a dimerized molecule (two coupled SSQWs) we considered a Coulomb interaction between two spherical 2D-plasmons within the multipole expansion, showed numerically that it converges fast and obtained a new dipole excitation. Its frequency is split in the axial coupling field [9]

$$\omega_{\text{dim}} \simeq \omega_1 \sqrt{1 \pm \frac{1 + 3(-1)^M}{2} \left(\frac{R}{H}\right)^3} \quad (6)$$

here  $M = 0, \pm 1$  denotes 3 polarizations of the dipole mode,  $H \sim 8-10 \text{ \AA}$  is the center-to-center distance for dimer clusters. This analytical formula for splitting is given as the first non-vanishing term in the multipole series, expanded in the second power of the radius to the inter-cluster-distance ratio [10].

The high polarizability of the cluster leads to the coincidence of the quantum mechanical result and the simple classical calculation [2, 6] if one includes the interaction between electrons accurately, at least in RPA. It was suggested earlier [6] that the two-component plasma on the sphere surface can be described quantitatively with two phenomenological parameters: the restoring force for the  $\sigma$  electron liquid and the displacement of the electron density from the mean radius of the sphere. We point out that for the “empty lattice” the



**Fig 2.** Each radial quantization level in SSQW results in a series of orbital quantization levels (left). The selection rule for dipole-allowed transition leads to one strong optical transition within each series and some weaker ones between the series. With the weaker transitions neglected, the RPA polarizability  $\alpha$  is plotted as function of the excitation frequency  $\omega$  (right). The last pole corresponds to the plasmon.

restoring force is zero, so the resulting frequencies of plasma oscillations still depend only on the lattice potential strength, a meaningless parameter for the continuous charged fluid approximation used. Instead of that we proposed the Coulomb coupling between two plasma liquids with different radial symmetries as a new possible origin of the  $\sigma$ - $\pi$  plasmon splitting.

Within the SSQW model one gets a new parameter with a dimensionality of frequency,  $e^2/\hbar C$ , where  $e$  and  $\hbar$  are the electron charge and Planck constant, and  $C$  is the capacitance of the system. When one takes the whole  $\pi$  electron shell density to a distance  $\pm a/2$  away from the mean radius,  $R$ , where the  $\sigma$  electron density is located, the capacitance is  $R(4R/a)$  within a small parameter  $(a/2R)^2 \simeq 0.1$ . We stress that our model represents qualitatively the two-excitation-peak character of the plasma response of the fullerene as a result of the Coulomb mixing between plasmons, but it easily includes any additional terms. Hydrostatic pressure was considered in [11] as a simple example, which results in the dispersion of the plasma frequency with the angular momentum of excitation (see Fig. 2) like the volume plasma frequency disperses with the momentum of the plasmon.

### 3. Plasmon–Frenkel-exciton in the clustered solid

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 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 we described the excitation of the single cluster as a surface plasmon. For the solid, the Coulomb interaction between clusters should be taken into account. The problem has to be considered using the spherical symmetry approximation and multipole expansion. The approximation of a single oscillator strength holds, because all other dipole oscillator frequencies for the clustered solid are split of and lie far below our plasmon frequency.

It is enough to consider only the dipole-dipole interaction between the collective modes on different clusters, neglecting the dipole-octupole interaction and next-order terms. The one-dimensional-chain-plasmon was considered in [9]. The plasmon spectrum reads as

$$\omega(k) \simeq \omega_1 \sqrt{1 + \frac{1 + 3(-1)^M}{2} \left(\frac{R}{H}\right)^3 2 \sum_{n=1}^N \frac{\cos(kHn)}{n^3}} \quad (7)$$

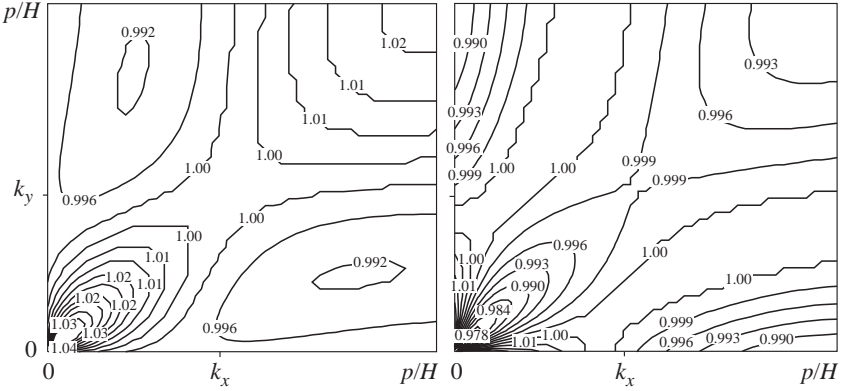
where  $k$  is the excitation wave number,  $M = \pm 1$  denotes double degenerate transverse branch naturally split off from the longitudinal excitation branch with  $M = 0$ . We ascribe such a linear structure to the orthorhombic polymerized phase of the fullerene. The plasmon band dispersion laws were obtained in the long-wave continuous limit  $kH \ll 1$  analytically

$$\omega(k) \simeq \omega_1 \left\{ 1 + \frac{1 + 3(-1)^M}{4} \left(\frac{R}{H}\right)^3 \left[ 2\zeta(3) - (kH)^2 \left( \ln \frac{1}{kH} + \frac{3}{2} \right) \right] \right\} \quad (8)$$

here the sum equals  $\zeta(3) \simeq 1.202$  at  $k = 0$ . The inhomogeneity of the system in a single direction results in the appearance of a transverse branch. This collective mode decays radiatively and can be excited by vacuum ultraviolet (VUV) light.

The monolayer of the fullerene, recently obtained by photopolymerization and by the vacuum deposition technique, is an interesting object for further discussion. We investigated the coupling between the optically active modes of the 2D-plane and the photons in the VUV region [12, 13]. Despite being localised on the surface of the clusters, the single cluster plasmons in the lattice are mixed via their electric field. This results in a new crystal excitation—plasmon–Frenkel-exciton (PFE) [14]. As usual, the dipole–dipole interaction calculation faces the lattice sum problem, hence we considered analytic asymptotes. For example the transverse-longitudinal splitting at  $k = 0$  is

$$\Delta\omega_{LT} = \omega_1 \left( \sqrt{1 + \frac{9}{4} \left(\frac{R}{H}\right)^3} - \sqrt{1 - \frac{3}{4} \left(\frac{R}{H}\right)^3} \right) \simeq \omega_1 \frac{3}{2} \left(\frac{R}{H}\right)^3 \simeq 1.6 \text{ eV} \quad (9)$$



**Fig 3.** The result of a numerical analysis of the dispersion law of 2D plasmon–Frenkel–exciton. Two polarizations of plasmon excitation are shown: the dipole is aligned with the wave vector of exciton (left) and the dipole is orthogonal to the wave vector and to the normal to the plane (right).

The characteristic wavelength is about  $400 \text{ \AA}$  which proves the continual dielectric function harnessing. The PFE band structure and the dielectric function calculation are very routine [15], excepting the excitation frequency region. Since in our case the Frenkel exciton is constructed on the base of the plasmon, the corresponding energy lies around 25–28 V.

#### 4. Summary

The SSQW model demonstrated a transition from the quantum mechanical description of the collective mode determined by the global topology of the 2D closed cluster surface to the phenomenological hydrodynamics. The proposed method of calculating the Coulomb interaction between the plasmon modes of two electron-liquids allows one to find consistently the single-cluster multi-component response as well as to follow the analogy with collective excitations in condensed matter. The longitudinal and optically-active transverse (for 1D and 2D systems) excitations in the lattice of clusters have the same description as the Frenkel exciton in an insulator. Their frequencies were computed using standard dielectric function formalism in the VUV region, thus simplifying significantly the VUV spectroscopy data analysis.

## References

- [1] V. V. Rotkin and R. A. Suris *Mol. Mat.* **4** 87 (1994).
- [2] V. V. Rotkin and R. A. Suris *Phys. Solid State* **36** 1899 (1994).
- [3] Ph. Lambin, A. A. Lucas and J.-P. Vigneron *Phys. Rev.* **B 46** 1794 (1992)  
A. A. Lucas, G. Gensterblum, J. J. Pireaux, P. A. Thiry, R. Caudano, J.-P. Vigneron,  
Ph. Lambin and W. Kratschmer *Phys. Rev.* **B 45** 13694 (1992).
- [4] M. T. Michalewicz and M. P. Das *Solid State Commun.* **84** 1121 (1992).
- [5] A. Bulgac and N. Ju *Phys. Rev. B* **46** 4297 (1992).
- [6] G. Barton and C. Eberlein *J. Chem. Phys.* **95** 1512 (1991).
- [7] A. V. Chaplik *Zh. Eksp. Teor. Fiz.* **60** 1845 (1971)  
A. V. Chaplik and M. V. Krashennikov *Surf. Sci.* **98** 533 (1980).
- [8] A. V. Chaplik *JETP Letters* **31** 275 (1980).
- [9] V. V. Rotkin and R. A. Suris *Proc. Int. Symp. Nanostructures: Physics and  
Technology* (St Petersburg, Russia) p. 210, 1995.
- [10] V. V. Rotkin and R. A. Suris *Solid State Commun.* **97** 183 (1995).
- [11] V. V. Rotkin and R. A. Suris *Proc. Symp. on Recent Advances in Chemistry and  
Physics of Fullerenes and Related Materials* eds K. M. Kadish and R. S. Ruoff  
(Pennington) p. 940, 1996.
- [12] V. V. Rotkin and R. A. Suris *Proc. Symp. on Recent Advances in Chemistry and  
Physics of Fullerenes and Related Materials* eds K M Kadish and R S Ruoff  
(Pennington) PV 97–14 p. 943, 1997.
- [13] V. V. Rotkin and R. A. Suris *Phys. Solid State* (1998, in press).
- [14] V. V. Rotkin and R. A. Suris *Mol. Mat.* (1998, in press).
- [15] V. M. Agranovich *Exciton theory* (Nauka: Moscow) 1968 (in Russian).