

Energies of Higher Multipole Vibrations of Fullerenes in a Semi-Classical Approach.

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Abstract

Starting with a brief description of the local current approximation (LCA) as previously applied to the photoionization cross section of C_{60} , we discuss the results of higher multipole resonances of fullerene molecules. The comparison to data obtained from electron scattering experiments reveals the adequacy of the semi-classical approach as well as the collective nature of even high L resonances. Similar to the results of the dipole case, the coupling of surface and volume plasmons mode in C_{60} molecules is seen to shift the peaks slightly towards lower energies.

1 INTRODUCTION

The focus of the present work is an extension of previous work [1] using the local current approximation (LCA) to study the higher collective modes of C_{60} . The ion structure consisting of sixty carbon nuclei with their innermost electrons is treated as a positively charged jellium shell in the potential field of which the 240 valence electrons move essentially freely. When stimulated, the valence electrons tend to respond collectively to the external source leading to collective oscillations. Collective properties of a many-body system have played an important role in the early years of nuclear physics and are always of utmost interest to physicists because they are often the source of macroscopic effects. The collective dynamic response of delocalized valence electrons in metal clusters to external perturbations has been studied for a long time.

The work on nuclear collective motion has been summarized by Rowe [2]. Quite similar ideas have been applied to metal clusters and fullerenes. In particular, two classical models suggested by Goldhaber and Teller [3] and Steinwedel and Jensen [4] describing the physics of giant dipole resonances (GDR) in terms of surface and volume oscillations are used also for clusters and general finite

fermion systems. Such resonances occur when a nucleus is electromagnetically excited by photons. When a photon hits a nucleus, protons will move due to the electric field thus destroying the ideal mixture of protons and neutrons. After the incident, the proton fluid due to the attractive nucleon-nucleon interaction begins to oscillate against the neutron fluid trying to reconstitute locally the optimal mixture of the two nucleons.

More recently, the technique to manufacture fullerenes has opened the door to analyze this new and interesting form of carbon. At the end of the 20th century, the electronic structure of solid fullerene has been studied using Auger electron spectroscopy, UV and X-ray photoelectron spectroscopy, UV and X-ray emission and absorption spectroscopy.

For the purpose of the present study the experimental results of [5] are particularly relevant. J. W. Keller and M.A Coplan investigated the spectrum of the gaseous form of C_{60} using electron energy loss spectrum (EELS), and compared their results to the spectrum of solid C_{60} and to optical absorption measurements of solutions of C_{60} . They presented EELS data of C_{60} in the gas phase from 1 to 30 eV. Their spectrum is similar to spectra of the solid fullerene, with shifts in the mutually observed bands seen only for the previously identified plasmon features. On the theoretical side, Garibel and Claudia [6], by using so-called hydrodynamic model, predicted the presence of π plasmons in the range between 6 and 8 eV and σ plasmons near and above 25 eV. Ju et al [7] presented theoretical and experimental electron-energy-loss spectroscopy results illustrating the excitation of collective plasmon states in gas phase fullerene targets with higher L values.

Most prominently, C_{60} is known to have a plasmon excitation: 240 delocalized valence electrons oscillating relative to the ion core, produce a giant dipole resonance (GDR) at an excitation energy of 20 eV. S. W. J. Scully et al, from their experimental work at the Lawrence Berkeley National Laboratory light source, reported the existence of an additional resonance near 40 eV in photoionization of C_{60} ions [8]. Their experimental data together with the time dependent local density functional (TDL) results from the Berlin-Dresden collaboration [9] motivated the present authors to attempt a macroscopic interpretation of the phenomena with a semi-classical approach (LCA), coupling the surface and volume dipole oscillations in C_{60} molecules. This semiclassical approach for strongly collective excitations in finite Fermion systems has been applied to metal clusters before by one the present authors [10]. Here it elucidates the coupling of the pure translational mode (surface plasmon) with compressional volume modes. The agreement between the semiclassical LCA and the microscopic TDL calculations [1] is surprisingly good.

Volume plasmons can not be excited directly by photoabsorption. Because of the longitudinal nature of volume plasmons and transversal nature of light, the photoexcitation of volume plasmons is forbidden in classical electrodynamics. But this is relevant only for extended systems. In recent times V.Kresin [11], however, identified a broad structure which may be interpreted as a volume plasmon absorption peak centered slightly above 4 eV in photodepletion measurements of Na_{20} and Na_{92} , thus, revealing the possibility of optical excita-

tion of volume plasmons in a confined metallic system (nanocluster). Recently, Höfllich et al [12], for the special geometry of a nanoshell, consisting of a dielectric core surrounded by a metallic shell, in a photoexcitation spectrum, a structure at 3.8 eV which they interpreted as a volume plasmon. Such structures can appear in a photoexcitation process only because of the coupling to the surface oscillation.

The present work is focused on the calculation of the energies of higher multipole excitations of the 240 valence electrons in C_{60} molecules and comparison to experimental data [7], [5], extending the approach used recently by Brack et al [1].

The present article is organized as follows: section 2 introduces the main aspects of the equation of motion method (EOM), which is the tool of choice to formulate the "local current approximation" (LCA), including both fluid-dynamical and sum rule approaches. In section 3 we describe the LCA. Section 4 summarizes the theoretical description. Section 5 discusses the results of this work, with special emphasis on coupling of surface and volume plasmon oscillations in C_{60} molecules.

2 Equation of Motion Approach

The equation of motion approach has been widely used in studying the collective degrees of freedom in nuclei [2], but it is general enough to be applied to most many-body systems. So we find a wide spectrum of applications also in theoretical chemistry from early calculations of electron affinities [13] and photodetachment energies [14] of molecules to more recent and more comprehensive representations of theories of general electronic excitations [15] to [18].

Here we consider a many-body system described by a Hamiltonian \hat{H} with a ground state $|0\rangle$ of energy E_0 . Suppose the states $|\nu\rangle$, with $\nu \neq 0$, are the excited states with energies $E_0 + \hbar\omega_\nu$. The stationary Schrödinger equation $\hat{H}|\nu\rangle = (\hat{H}_0 + \hat{V})|\nu\rangle = E_\nu|\nu\rangle$ can be rewritten as the following equations of motion

$$\langle 0 | \hat{O}_\nu [\hat{H}, \hat{O}_\nu^\dagger] | 0 \rangle = \hbar\omega_\nu \langle 0 | \hat{O}_\nu \hat{O}_\nu^\dagger | 0 \rangle \quad (1)$$

$$\langle 0 | \hat{O}_\nu [\hat{H}, \hat{O}_\nu] | 0 \rangle = \hbar\omega_\nu \langle 0 | \hat{O}_\nu \hat{O}_\nu | 0 \rangle = 0 \quad (2)$$

where the operators $\hat{O}_\nu, \hat{O}_\nu^\dagger$ are defined as the creation and annihilation operators of the excited states of the system:

$$\hat{O}_\nu^\dagger |0\rangle = |\nu\rangle, \quad \hat{O}_\nu |\nu\rangle = |0\rangle \quad \text{and} \quad \hat{O}_\nu |0\rangle = 0 \quad \text{and} \quad \hbar\omega_\nu = E_\nu - E_0 \quad (\nu > 0)$$

are the excitations energies.

The exact solution of the equations (1) and (2) is unknown for most systems. Approximate methods have to be devised. One of these, the local current approximation, will be described in the next section.

3 Local Current Approximations (LCA).

In the local current approximation [19] the displacement field \vec{u} of fluid elements is studied using the theoretical framework of the Rayleigh-Ritz variational principle. The response of the system to suitable external perturbations leads to collective vibrations with associated frequencies

$$\omega^2 = \frac{C}{B}$$

with C as a restoring force constant and B as the inertia parameter. This will be the actual vibrational mode if its frequency has been determined as the minimum ω with respect to variations in \vec{u} . In appendix A, a simple mechanical oscillator model is considered which has two resonant frequencies corresponding to systems with different ratios of the constants C/B .

It has been shown that solving the equation of motions (1) and (2) for the lowest excited state is equivalent to solving the variational equation

$$\frac{\delta E_3 [\hat{Q}]}{\delta Q(\vec{r})} = 0$$

where E_3 is defined by

$$E_3 [\hat{Q}] = \sqrt{\frac{m_3[\hat{Q}]}{m_1[\hat{Q}]}}$$

where the moments m_1 and m_3 are defined as the multiple commutators

$$m_1(\hat{Q}) = \frac{1}{2} \langle 0 | [\hat{Q}, [\hat{H}, \hat{Q}]] | 0 \rangle \quad (3)$$

$$m_3(\hat{Q}) = \frac{1}{2} \langle 0 | [[\hat{H}, \hat{Q}], [\hat{H}, [\hat{Q}, \hat{H}]]] | 0 \rangle \quad (4)$$

The exact operator \hat{Q} is not known. It has to be Hermitean and will in general be nonlocal. It can be viewed as a generalized coordinate. The values of the moments, however, depend on an explicit form of \hat{Q} . So we need a convenient set of approximate operators $Q_p(\vec{r})$ which are defined below.

The excitation spectrum can be produced by successive orthogonalization of \hat{Q} . In the fluid dynamical approach, one approximates the collective excitation energies $\hbar\omega_\nu$ by the energy $E_3[\hat{Q}_\nu]$ with ν pointing to a particular excitation

energy. In the LCA one starts from the uncorrelated Hartree-Fock (or Kohn-Sham) ground state $|0\rangle$ and takes the operator \hat{Q} as a local function $Q(\vec{r})$, to calculate the following moments:

$$m_1(\hat{Q}) = \frac{1}{2} \left\langle 0 \left| \left[\hat{Q}, \left[\hat{H}, \hat{Q} \right] \right] \right| 0 \right\rangle = \frac{m}{2\hbar^2} \int u(\vec{r}) \cdot u(\vec{r}) \rho(\vec{r}) d^3r \quad (5)$$

with

$$u(\vec{r}) = -\frac{\hbar^2}{m} \nabla Q(\vec{r})$$

where $u(\vec{r})$ is a local displacement field to be determined by the Rayleigh-Ritz variational principle. It is proportional to the collective current

$$\vec{j}_\alpha(\vec{r}, t) = \rho_\alpha(\vec{r}, t) \vec{v}_\alpha(\vec{r}, t)$$

with

$$\vec{v}_\alpha(\vec{r}, t) = \alpha_p(t) \vec{u}(\vec{r})$$

which obey the continuity equation:

$$\frac{\partial}{\partial t} \rho_\alpha(\vec{r}, t) + \nabla \cdot \vec{j}_\alpha(\vec{r}, t) = 0$$

Here $\rho_\alpha(\vec{r}, t)$ are "scaled" time dependent densities. Note that if $\nabla^2 Q(\vec{r}) = 0$ and thus $\vec{\nabla} \cdot \vec{u}(\vec{r})$ vanishes, then one has incompressible collective flow; otherwise the collective motion incorporates also local compressions of the fermi fluid.

As an illustration, we consider the the displacement field for a multipole surface vibration. This is obtained by having a field of the form $\vec{\nabla} r^L P_L(\cos \theta)$, with P_L a Legendre function of angular momentum L . The incompressibility then follows from the relation

$$\vec{\nabla} \cdot \vec{u}(\vec{r}) = \nabla^2 r^L P_L(\cos \theta) = 0$$

Any flow generated by such a potential field is also irrotational. The moment $m_3(\hat{Q})$ defined as

$$m_3(\hat{Q}) = \frac{1}{2} \left\langle 0 \left| \left[\left[\hat{H}, \hat{Q} \right], \left[\hat{H}, \left[\hat{Q}, \hat{H} \right] \right] \right] \right| 0 \right\rangle \quad (6)$$

is a more complicated functional of $\vec{u}(\vec{r})$, of the spatial density $\rho(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2$ and the kinetic energy density $\tau(\vec{r}) = \sum_{i=1}^N |\nabla \phi_i(\vec{r})|^2$ in terms of the ground state HF or KS wave functions $\phi_i(\vec{r})$.

For an intuitive understanding how $\frac{\delta E_3[Q]}{\delta Q(\vec{r})} = 0$ can be solved approximately, it helps to recall the scaling model of nuclear physics [20], [21] and references therein. In this model, the energy $E_3[\hat{Q}] = \sqrt{\frac{m_3[\hat{Q}]}{m_1[\hat{Q}]}}$ is interpreted corresponding to a scaling transformation

$$|\phi_n\rangle = e^{-i\eta S} |\phi_0\rangle \quad (7)$$

with respect to the collective Hamiltonian

$$H_{\text{col}} = \frac{1}{2} \sum (B_{pp'} \dot{\eta}_p \dot{\eta}_{p'} + C_{pp'} \eta_p \eta_{p'}) \quad (8)$$

where η is a harmonically oscillating arbitrary scalar parameter and the scaling operator is defined by

$$\hat{S} = [\hat{H}, \hat{Q}_{ext}] .$$

Then

$$m_3 = \frac{1}{2} \frac{\partial^2}{\partial \eta^2} \left[\langle \phi_n | \hat{H} | \phi_n \rangle \right]_{\eta=0}$$

The energy weighted moment m_3 measures the change of the energy of the nucleus when the ground state wavefunction is deformed according to expression (7). It is a finite quantity, given by the expectation value of a one-body operator and, thus, quite model independent. For clusters, it depends only on the total electronic density at the origin. For instance, if \hat{Q}_{ext} stands for the dipole operator $\hat{Q} = z$, the scaling transformation is just a translation along the z-axis. The variation $\frac{\delta E_3[Q]}{\delta Q(\vec{r})} = 0$ leads to fluid dynamical eigenvalue equations:

$$\frac{\delta m_3[\vec{u}]}{\delta u_j(\vec{r})} = (\hbar\omega_\nu)^2 \frac{m}{\hbar^2} \rho(\vec{r}) \vec{u}_j(\vec{r}) \quad (9)$$

yielding the spectrum $\hbar\omega_\nu$ and eigenmodes \vec{u}_ν . A practical way to solve (9) approximately consists in representing the operator function $Q(\vec{r})$ in terms of a finite set of known basis functions $\{Q_\lambda(\vec{r})\}$:

$$Q(\vec{r}) = \sum_{\lambda=1}^N c_\lambda Q_\lambda(\vec{r}) \quad \text{with } Q_\lambda = r^\lambda Y_{L0}(\theta), \quad \lambda = L, L+1, \dots, N \quad (10)$$

The first two multipole operators exciting surface vibrations are the dipole operator $Q_d = r \cos \theta = z$ describing a purely translational mode and the quadrupole operator $Q_2 = r^2 Y_{20}$ with a more structured oscillation pattern. The monopole operator $Q_0(r) = r^2 Y_{00}$ effects a breathing mode but not a surface phonon. It is density changing mode. Other density changing modes can be obtained also for higher multipoles when by setting the power λ of the radial variable r^λ to values higher than L . (see [1] appendix).

The variational principle yields then a set of M secular equations with

$$\det \left| C_{pp'} - (\hbar\omega_\nu)^2 B_{pp'} \right| = 0, \quad (p, p', \nu = 1, 2, \dots, M) \quad (11)$$

as the characteristic equation. Here

$$B_{pp'} = \left\langle 0 \left| \left[Q_p, \left[\hat{H}, Q_{p'} \right] \right] \right| 0 \right\rangle \quad (12)$$

$$C_{pp'} = \frac{1}{2} \left\langle 0 \left| \left[\left[\hat{H}, Q_p \right], \left[\hat{H}, \left[Q_{p'}, \hat{H} \right] \right] \right] \right| 0 \right\rangle \quad (13)$$

By solving equation (11), one can find the excitation energies $\hbar\omega_\nu$ of the system and can evaluate its response to an external excitation operator Q_{ext} . Details can be found in appendix [1].

The dipole mode describes the collective translational motion of the electrons relative to the ion core. The displacement field vector can be as simple as a uniform displacement field, rendering dipole modes which are relatively simple to construct and rather collective. The collectivity of the response causes a concentration of a large fraction of the oscillator strength in a small frequency interval. This gave the mode the name "giant dipole resonance" in nuclear physics, a term that is now applied to a corresponding bump that appears in the optical absorption spectrum of atoms as well [22].

The quadrupole mode $L = 2$ and higher modes are not excited by a single photon but in collision processes or multiphoton absorption.

It is easy to see that different moments m_k of the strength function $S(E)$ corresponding to different values of k satisfy a chain of inequalities obtainable from Schwartz's inequality

$$\int f(E)^2 \rho(E) dE \int g(E)^2 \rho(E) dE \geq \left(\int f(E) g(E) \rho(E) dE \right)^2 \quad (14)$$

where $\rho(E)$ is a positive definite function, $\rho(E) dE$ is a positive measure and f and g are arbitrary real functions. The strength function $S(E)$ is defined for positive values of E , so that

$$\rho(E) = E^k S(E)$$

is a density function (positive definite and assumed normalizable). Therefore using expression (14) with $\rho(E)$ and $f(E) = E$ and $g(E) = 1$ we get

$$m_{k+2} m_k \geq m_{k+1}^2$$

or

$$\frac{m_{k+2}}{m_{k+1}} \geq \frac{m_{k+1}}{m_k}$$

and finally one can write

$$\dots \geq \frac{m_{k+2}}{m_{k+1}} \geq \sqrt{\frac{m_{k+2}}{m_k}} \geq \frac{m_{k+1}}{m_k} \geq \sqrt{\frac{m_{k+1}}{m_{k-1}}} \geq \dots$$

These ratios are all homogeneous functions of an energy variable. This fact suggests to define energy variables E_3 and E_1 as

$$E_3 = \sqrt{\frac{m_3}{m_1}}, \quad E_1 = \sqrt{\frac{m_1}{m_{-1}}}$$

It is thus possible to estimate the position and the width of a resonance mode, whose collective strength is concentrated in one peak, by calculating the sum rules (3) and (4). We use the following general expressions to write down the different moments:

$$m_k = (-1)^t (i)^k \langle 0 | Q_s Q_t | 0 \rangle \quad (15)$$

with

$$Q_s = [iH, [iH, \dots, [iH, Q] \dots]] \quad (16)$$

where s indicates the number of times that H appears and s and t are integers such that $s + t = k$. Thus, with the ground state wavefunction known, all positive moments can be computed from it. It is interesting to notice that among the odd and even moments, only the odd moments appear in a natural way in a dynamical description of the system. Clearly high k moments are very sensitive to the form of the potential and attention will be required when making approximations leading to simple interactions if a realistic behavior of the high k moments is to be described [20].

4 Theoretical Description

We determine multipole excitation energies of C_{60} using the same electron density which had previously been used to obtain the dipole resonances of C_{60} [1] and originated from the Berlin-Dresden collaboration [9]. It is shown in figure one

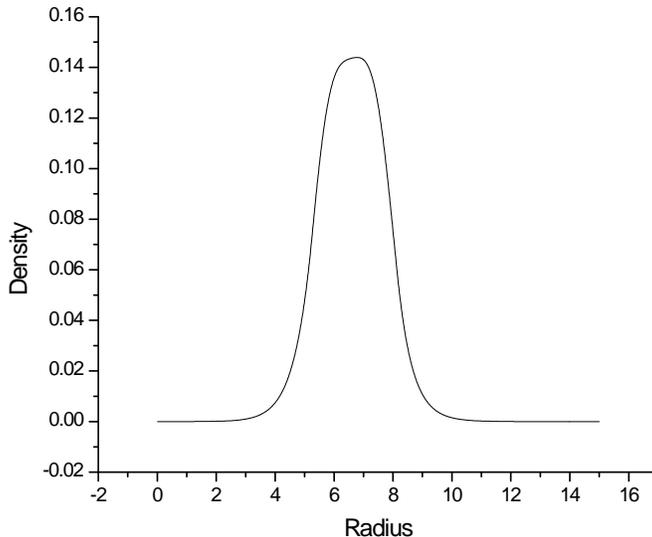


Figure 1: Electron density in the fullerene molecules C_{60}

This density is matched to an ionic density expressed by step functions

$$\rho_I(r) = \rho_0 [\Theta(R_2 - r) - \Theta(r - R_1)] \quad (17)$$

where $R_1 = R - \frac{\Delta}{2}$, $R_2 = R + \frac{\Delta}{2}$ are the inner and outer radii of the shell with the constants $R = 0.354 \text{ nm}$ and $\Delta = 0.153 \text{ nm}$. The uniform ion density ρ_0 is chosen such that the integrated ion charge is equal but of opposite sign to that of the valence electrons. We hold the ionic charge fixed and unaffected by the oscillations of the valence electrons (jellium model).

The next highest multipole beyond the dipole is the quadrupole mode with energy $E_3(Q_2)$ and operator $Q_2(\vec{r}) = r^2 Y_{20}$. The calculation yields its surface plasmon at

$$E_3(Q_2) = \sqrt{\frac{2}{5}} \sqrt{\frac{\hbar^2 N e^2}{m R^2 \Delta}} = 23.4 \text{ eV} \quad (18)$$

Extending the operator basis by adding higher functions $Q_P(r) = r^P Y_{L0}(\theta)$ with $L = 2$ and $P = 3, \dots, M$, includes compressional modes which couple to the translational surface plasmon. The element of the mass parameter $B_{PP'}$ and of the restoring force parameter $C_{PP'}$ for the quadrupole case are given as

$$B_{PP'} = \left(\frac{\hbar^2}{2m} \right) \frac{PP' + 6}{5} N R^{P+P'-2} \quad (19)$$

$$C_{PP'} = \left(\frac{\hbar^2}{m} \right)^2 \frac{N^2 e^2}{5} \left(R^{P+P'-5} \right) \left[\frac{R}{2\Delta} PP' + \frac{3}{5} (12 - P - P' - 2PP') \right] \quad (20)$$

They are required to set up the secular equation (11). Higher multipole modes for $L = 3$ and 4 have been calculated by the same procedure. The results are presented and discussed in the next section.

5 Results and Discussion

The sixty carbon atoms of the fullerene molecule C_{60} provide four valence electrons each, so that 240 valence electrons oscillate collectively against the ionic structure which is assumed static. A noticeable dipole resonance peak around $20 - 22 \text{ eV}$ has early on been predicted, measured and in the framework of the jellium model interpreted as a Mie surface plasmon. This picture was refined by later research performed at lower energies which showed that there is also a vibrational mode around 5 eV ascribed to the sixty weakly bound π -electrons [11]. The electron density used in this work provided to us by, Berlin-Dresden group, however, does not distinguish between σ - and π -electrons. Hence, we can not reproduce any low energy structure which would be mainly due to the

resonant response from the weakly bound π electrons. We focus on the experimental data above 10 eV. In the formation of the giant resonance peak all electrons are involved.

Table 1: The optic dipole response of fullerene molecules C_{60} .

pure surface Plasmon	coupled surface plasmon	coupled volume plasmon
22.1 ^a	21.4 ^a	37 ^a
—	20 ^b	—
—	22 ^c	42 ^c
—	20 ^d	—
—	22 ^e	40 ^e
—	19 ^f	—

a: LCA theoretical data [1], *b*: Theoretical data [23]

c: TDLDA calculation [9], *d*: Experimental data [24], (data exhibits a flat structure from 15 to 25eV), *e*: Experimental data [8], *f*: Experimental data [7]

From table 1 it is not difficult to conclude that the the giant dipole surface plasmon resonance of 240 delocalized valence electrons in the C_{60} molecules can be excited by an external electromagnetic field of $\hbar\omega = 20-22$ eV. However, the experimental result presented by Ju et al [7] is lower than 20 eV. A first experimental result of such a dipole resonance [24] reported a strong broad resonance centered near 20 eV (see figure 2). From the careful comparison between the experimental data reported by different experimentalists, it is found that the reported experimental results differ by ± 2 eV in the case of the dipole translational mode. The experimental uncertainty is higher for the compressional dipole mode.

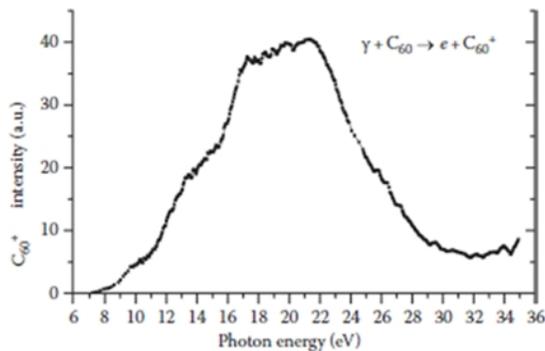


Figure 2: Photoionization experiments have been performed with C_{60}^+ ions [24] and lead to excitation of the giant plasmon resonance.

It is noteworthy to mention that recent theoretical work on the optic response of C_{60} molecules studied at higher energies found a broad shoulder around 30–45 eV which is interpreted as a volume plasmon. As an example of exploration of higher energy regime the theoretical LCA calculation of the volume plasmon along with surface plasmon of C_{60} molecules for the dipole mode is reported in

figure 3 below. This feature is not seen as clearly in experimental data because of the broadness of the underlying structure. But its existence can be deduced by the observed shift of the resonance peak to lower energy which is a consequence of the coupling of volume and surface plasmons.

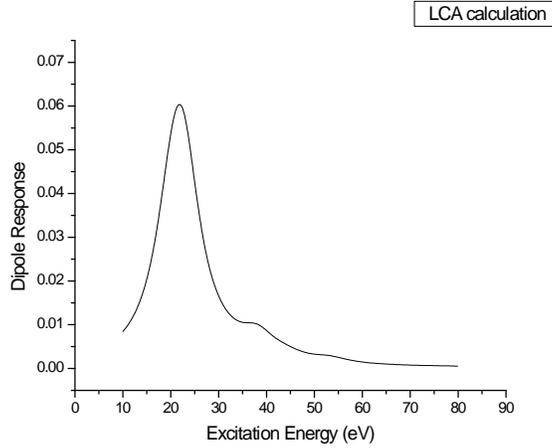


Fig. 3. Optic response of C_{60} molecules : LCA calculation

The strong collective nature of the dipole plasmon in fullerene C_{60} molecules suggests the study of higher multipoles as well.

Table 2: The LCA multipole response of fullerene molecules C_{60} .

Multipole Order	Operator	Pure Surface Plasmon	Coupled Surface Plasmon	Experiment	Volume Plasmon
$L = 2$	$r^2 Y_{20}$	25 eV ^(a)	22.5 eV ^(a)	21 eV ^(b)	41 eV ^(a)
$L = 3$	$r^3 Y_{30}$	29 eV ^(a)	26 eV ^(a)	21.5 eV ^(b)	42 eV ^(a)
$L = 4$	$r^4 Y_{40}$	32 eV ^(a)	28.5 eV ^(a)	22 eV ^(b)	42 eV ^(a)

a : Present LCA calculation

b : Experimental data [7]

The results in column three represent the energies in eV of the surface modes calculated with the operators given in column two. Columns four and five are obtained by augmenting the operators with the volume changing contributions discussed in section 3: This change effects the appearance of the volume plasmon and also shifts both peaks to slightly lower energies. The volume plasmon which has experimentally been verified for the dipole case but so far not for higher multipoles. Compressional effects seem to be less pronounced both in our calculations and obviously also in experimental work which does not report such features. The comparison of our results to experimental data by Bulgac is therefore restricted to the results given in columns four and five of table 2.

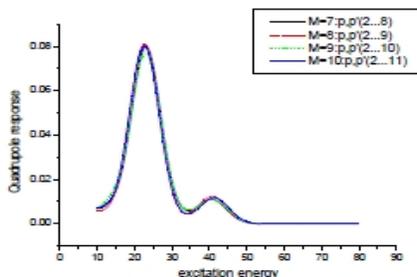


Figure 4: Convergence of the sum- rule weighted quadrupole response of C_{60} molecules in the LCA with respect to the number M of coupled modes with $p, p' = 2, \dots, M$.

In agreement with Ju et al [7] measurement the present LCA calculation shows that the translational quadrupole mode is around $22.5 eV$, however, the higher multipole computed in LCA regime are higher than experimental result. We do not have as much as necessary experimental result to compare with the present higher multipole calculations. To the best of our knowledge the only experimental results available for multipole excitation ($L \geq 2$) of fullerene molecules is [7]. The work presented by Bulgac et al does not include a discussion of experimental uncertainty. It is noteworthy to report that in higher multipole motion of C_{60} molecules besides the surface plasmon an extra peak due to the volume plasmon has been found in our computations around $40 - 50 eV$, which is not reported in [7]. Experimentally [7] it has been established that the states with higher angular momentum show no collective behavior. In contrast to this measurement we found that 240 delocalized valence electrons in fullerene molecules show the collective nature.

In figure four it has been shown that in quadrupole mode for $M \geq 7$ the LCA spectrum is converged. Higher multipole also show the consistency of this quadrupole feature. In contrast to the experimental results our LCA calculation shows that except for the monopole and dipole responses in fullerene molecules C_{60} , the states with higher angular momenta have a similar structure, the translational mode around $22 - 30 eV$ and a high energy compressional mode around $40 - 50 eV$, however, LCA curves are blue shifted by $5.5 eV$

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6 Appendix

6.1 Appendix:A

To compute the commutators in equations (12) and (13) and consequently equation (19) and (20) we start with the operators

$$Q_L^p = r^p Y_{L0}(\theta)$$

Assume that for a given Hamiltonian with kinetic energy \hat{T} and potential energy \hat{V}

$$\hat{H} = \hat{T} + \hat{V}$$

one has scaling operator

$$\hat{S} = [\hat{H}, \hat{Q}_L^p] = [\hat{T}, \hat{Q}_L^p]$$

For the local operator \hat{Q} which commutes with the potential energy \hat{V} in the total hamiltonian $\hat{H} = \hat{T} + \hat{V}$ the scaling operator \hat{S} and the moments m_1 and m_3 have a simple physical meaning. We can the scaling operator \hat{S} by

$$\hat{S}_L^p = [\hat{H}, \hat{Q}_L^p] = [\hat{T}, \hat{Q}_L^p] = \frac{1}{2} (\nabla \cdot \mathbf{u}_L^p) + \mathbf{u}_L^p \cdot \nabla \quad (\text{A1})$$

where \mathbf{u} is a displacemen field given by

$$\mathbf{u}_L^p(\mathbf{r}) = -\frac{\hbar^2}{m} \nabla Q_L^p(\mathbf{r})$$

The operator \hat{S} creates a scaled state by means of a unitary transformation

$$|\alpha\rangle = e^{-\alpha \hat{S}_L^p} |0\rangle$$

where the real variable α is scaling parameter and is also understood as a collective variable $\alpha(t)$. One write the time dependent one body density

$$\rho(\mathbf{r}, t) = \rho(\mathbf{r}, \alpha(t)) = \sum_{i=1}^A |\psi_i(\mathbf{r}, \alpha)|^2 = \exp(-\alpha((\nabla \cdot \mathbf{u}) + \mathbf{u} \cdot \nabla)) \rho(\mathbf{r})$$

Now the velocity field

$$\mathbf{v}(\mathbf{r}, t) = \dot{\alpha}(t) \mathbf{u}(\mathbf{r})$$

and the local current

$$\mathbf{j}_\alpha(\mathbf{r}, t) = \rho_\alpha(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)$$

which satisfies the continuity equation

$$\frac{\partial}{\partial t} \rho_\alpha(\mathbf{r}, t) + \nabla \cdot \mathbf{j}_\alpha(\mathbf{r}, t) = 0$$

From equation (A1) we can see that the moment m_1 is proportional to the mass parameter:

$$B_{PP'} = \frac{m}{2\hbar^2} \int \vec{u}_L^P(\vec{r}) \cdot \vec{u}_L^{P'}(\vec{r}) \rho(\vec{r}) d^3r$$

with

$$\vec{u}_L^P(\vec{r}) = -\frac{\hbar^2}{m} \nabla Q_L^P(\vec{r}), \quad Q_L^P(\vec{r}) = r^P Y_{L,0}(\theta, \phi)$$

$$B_{PP'} = \frac{\hbar^2}{2m} \frac{PP' + L(L+1)}{2L+1} (4\pi) \int_0^\infty r^{P+P'} \rho(r) dr$$

$$\text{or } B_{PP'} = \frac{\hbar^2}{2m} \frac{PP' + L(L+1)}{2L+1} \frac{4\pi N}{\frac{4\pi}{3}(R_2^3 - R_1^3)} \int_{R_1}^{R_2} r^{P+P'} dr$$

where $R_1 = R - \frac{\Delta}{2}$ and $R_2 = R + \frac{\Delta}{2}$ so that upon integration

$$\text{or } B_{PP'} = \frac{\hbar^2}{2m} \frac{PP' + L(L+1)}{2L+1} \frac{3N}{P+P'+1} \frac{(R + \frac{\Delta}{2})^{P+P'+1} - (R - \frac{\Delta}{2})^{P+P'+1}}{(R + \frac{\Delta}{2})^3 - (R - \frac{\Delta}{2})^3}$$

$$B_{PP'} = \left(\frac{\hbar^2}{2m} \right) \frac{PP' + L(L+1)}{2L+1} N R^{(P+P'-2)}$$

The restoring force parameter defined in equation (12) can be rewritten as

$$\begin{aligned} C_{pp'} &= \frac{1}{2} \left\langle 0 \left| \left[S_L^p, \left[S_L^{p'}, \hat{H} \right] \right] \right| 0 \right\rangle \\ &= \frac{d^2}{d\alpha d\alpha'} \left[\left\langle 0 \left| e^{\alpha S_L^p} \hat{H} e^{-\alpha' S_L^{p'}} \right| 0 \right\rangle \right]_{\alpha=\alpha'=0} \\ &= \frac{d^2}{d\alpha d\alpha'} \left[\left\langle \alpha \left| \hat{H} \right| \alpha' \right\rangle \right]_{\alpha=\alpha'=0} \end{aligned} \quad (\text{A2})$$

where

$$|\alpha\rangle = e^{-\alpha S_L^p} |0\rangle$$

is the scaled ground state. Now one can write

$$C_{pp'} = C_{pp'}^{kin} + C_{pp'}^{xc} + C_{pp'}^{Coul} + C_{pp'}^{Vi}$$

Note that \hat{S}_L^p and $\hat{S}_L^{p'}$ even do not commute, $C_{pp'}$ in equation (A2) would be symmetric as long as $|0\rangle$ is eigenstate of \hat{H} . The kinetic energy term for $L = 1$ is

calculated analytically (please see [25]) and for $L > 1$ involves complicated angular momentum algebra and is very cumbersome to evaluate in general. It has been evaluated in the local density approximation, which for the kinetic energy means using the Thomas-Fermi functional. The exchange-correlation contribution has been evaluated in the local density approximation. The following formula is used for any part of energy that is just a spatial integral over a function f of the density $\rho(r)$. The energy functional E_f is given by

$$E_f = E_f[\rho] = \int f(\rho(r)) d^3r$$

Then the symmetrized contribution to E_f (A2) is found to be

$$\begin{aligned} C_{PP'}^f &= \frac{1}{2} \left(\frac{\hbar^2}{m} \right)^2 \frac{4\pi}{(2L+1)} \int_0^\infty r^{p+p'-2} [(p+p'-1) \\ &\quad \{p[p'(p'+1) - L(L+1)] + p'[p(p+1) - L(L+1)]\} \times \left[f(\rho) - \rho \frac{df(\rho)}{d\rho} \right] \\ &\quad + 2[p(p+1) - L(L+1)][p'(p'+1) - L(L+1)] \rho^2 \frac{d^2f(\rho)}{d\rho^2} \Big] dr \quad (A3) \end{aligned}$$

The symmetrized Hartree-Coulomb contribution to $C_{PP'}^{coul}$ is

$$\begin{aligned} C_{PP'}^{coul} &= \left(\frac{\hbar^2}{m} \right)^2 \frac{(4\pi e)^2}{2(2L+1)} \int_0^\infty \rho(r) \left[-\frac{1}{2} [(P+P)L(L+1) + PP'(P+P'-6)] \right. \\ &\quad \left. \int_0^r r^{\mathcal{L}+P} \rho(r') dr' + \left\{ (L-P)(P+L+1) r^{P-L-1} \int_0^r r^{\mathcal{L}+P} \rho(r') dr' + \right. \right. \\ &\quad \left. \left. (L-P)(P+L+1) r^{P-L-1} \int_0^r r^{\mathcal{L}+P} \rho(r') dr \right\} \frac{L(L+1)}{(2L+1)} \right] dr \quad (A4) \end{aligned}$$

$$C_{PP'}^{coul} = \frac{1}{2} \left(\frac{\hbar^2}{m} \right)^2 \frac{N^2 e^2}{(2L+1)} \frac{L(L+1)}{(2L+1)} \frac{N^2}{4\pi R^2 \Delta} (2L^2 + 2L - P - P' - 2PP') R^{P+P'-5}$$

The contribution from any external jellium potential $V_{ion}(r)$ is

$$\begin{aligned} C_{PP'}^{V_{ion}} &= \left(\frac{\hbar^2}{2m} \right)^2 \frac{4\pi}{(2L+1)} \int_0^\infty V_{ion} r^{p+p'-2} [(P+P-1)[(P+P+2)PP' - (P+P)L(L+1)] \rho(r) \\ &\quad \left[(3P+3P'-2)PP' - (P+P)L(L+1) \right] r \frac{d\rho(r)}{dr} + 2r^2 PP' \frac{d^2\rho(r)}{dr^2} \Big] dr \quad (A5) \end{aligned}$$

After some algebra, we get

$$C_{PP'}^{V_{ion}} = \left(\frac{\hbar^2}{2m} \right)^2 \frac{4\pi}{(2L+1)} 2PP' \int_{R_1}^{R_2} \nabla^2 V_{ion}(r) r^{P+P'} \rho(r) dr$$

$$C_{PP'}^{V_{ion}} = \left(\frac{\hbar^2}{2m} \right)^2 \frac{4\pi}{(2L+1)} \frac{4\pi e^2 N^2}{(16\pi^2 R^4 \Delta^2)} \frac{2PP'}{(P+P'+1)} \left(R_2^{(P+P'+1)} - R_1^{(P+P'+1)} \right)$$

$$C_{PP'}^{V_{ion}} = \left(\frac{\hbar^2}{m} \right)^2 \frac{N^2 e^2}{(2L+1)} \frac{R}{2\Delta} PP' \left[R^{(P+P'-5)} \right]$$

Now

$$C_{PP'} = C_{PP'}^{coul} + C_{PP'}^{V_{ion}}$$

so that

$$C_{PP'} = \left(\frac{\hbar^2}{m} \right)^2 \frac{N^2 e^2}{(2L+1)} \left(R^{(P+P'-5)} \right) \left[\frac{R}{2\Delta} PP' + \frac{L(L+1)}{2(2L+1)} (2L^2 + 2L - P - P' - 2PP') \right]$$

For quadrupole motion, $L = 2$ and $P, P' = 2$, then

$$C_{PP'} = \left(\frac{\hbar^2}{m} \right)^2 \frac{N^2 e^2}{5} \frac{2}{\Delta}$$

$$B_{PP'} = \left(\frac{\hbar^2}{m} \right) NR^2$$

The energy E_3 discussed in section three is written as

$$E_3 [\hat{Q}] = \sqrt{\frac{m_3 [\hat{Q}]}{m_1 [\hat{Q}]}} = \sqrt{\frac{C_{PP'}}{B_{PP'}}$$

$$E_3 [Q_2] = \sqrt{\frac{2}{5}} \sqrt{\frac{\hbar^2 N e^2}{m R^2 \Delta}}$$

If we set $p = p' = L$, and using equation (A3), (A4), and (A5) we can recover the following equations:

$$m_1 [Q_L] = \frac{\hbar^2}{m} \frac{L}{2} \int r^{2L-2} \rho(r) d^3r$$

$$m_3^{Coul} = - \left[\frac{\hbar^2}{m} \right]^2 \frac{L^2 (L-1)}{2L+1} (4\pi e)^2 \times \int_0^\infty r^{2L-3} \rho(r) dr \int_0^r (r')^2 \rho(r') dr'$$

$$m_3^{VI} = \left[\frac{\hbar^2}{m} \right]^2 \frac{L^2}{2(2L+1)} \times \int_0^\infty V_I(r) r^{2L-4} [r^2 \rho''(r) + 2rL\rho'(r)] d^3r$$

where $\rho'(r)$ and $\rho''(r)$ are radial derivatives. Note that the exchange-correlation energy in LDA, does not contribute to $m_3(Q_L)$ like any part of the total energy which is only a function of $\rho(r)$, [25]