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LETTER TO THE EDITOR

Single-particle and collective degrees of freedom in C_{60}

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Abstract. The electromagnetic response of the fullerene C_{60} in the energy range $0 \leqslant E \leqslant 35$ eV, exhausting 84% of the Thomas–Reiche–Kuhn sum rule, has been worked out using the local density and random phase approximations. A detailed correspondence between the calculated π-plasmons and the peaks determined in optical/UV studies is found. The damping width (≈ 12 eV) of the Mie resonance observed at ≈ 20 eV is well reproduced, and is due to Landau damping. This resonance is found to be determined by $\sigma \to \sigma$ and, to a large extent, also by $\sigma \to \pi, \delta$ particle–hole transitions.

The basic elements needed for an accurate description of the response function of a many-particle system are: a proper treatment of ground state correlations, the fulfilment of energy weighted sum rules (EWSR), and the respect of the symmetries of the system. This has been the main scope of the work reported in the present paper, aimed at providing a quantitative microscopic understanding of the electromagnetic response of C_{60} [1–3].

Having to do with a system of delocalized electrons, we shall determine the mean field where the 240 valence electrons of C_{60} move, in the local density approximation (LDA, cf e.g. [4]). Because collective enhancements as well as screening effects are expected to be very important for the dipole response of this system, we shall calculate them making use of linear response theory within the random-phase approximation (RPA, cf. e.g. [5]), respecting both the icosahedral symmetry of the C_{60} molecule as well as the Thomas–Reiche–Kuhn (TRK) sum rule. In other words, no approximation has been introduced in solving the LDA plus RPA equations describing C_{60}. It will be concluded that a different quantitative picture concerning the distribution of dipole strength emerges from the present calculations as compared to previous calculations, in particular those based on the tight-binding approximation.

The Kohn–Sham equation for the valence electrons of C_{60} is

$$\left(T + U^{\mathrm{Loc}}(\boldsymbol{r}, [\rho])\right) \psi_k(\boldsymbol{r}) + U^{\mathrm{NL}}[\psi(\boldsymbol{r})] = E_k \psi_k(\boldsymbol{r}) \tag{1}$$

sum of the kinetic energy T, of a local potential displaying a functional dependence with the total density ρ of the electrons, $U^{\mathrm{Loc}}(\boldsymbol{r}, [\rho])$, and a non-local potential, $U^{\mathrm{NL}}[\psi(\boldsymbol{r})]$,

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characterized by a functional dependence with the wavefunction ψ describing the single-particle motion of the electrons. The local term can be written as

$$U^{\mathrm{Loc}}(\boldsymbol{r},[\rho]) = V_{\mathrm{ee}}(\boldsymbol{r},[\rho]) + V_{\mathrm{xc}}(\boldsymbol{r},[\rho]) + V_{\mathrm{ext}}(\boldsymbol{r}) \tag{2}$$

where V_{ee} is the Coulomb potential acting among the electrons. For the exchange-correlation potential $V_{\mathrm{xc}}(\boldsymbol{r},[\rho])$ we use the parametrization of [6]. In equation (2), the quantity $V_{\mathrm{ext}}(\boldsymbol{r}) = \sum_{i=1}^{N_a} v_{\mathrm{pseudo}}^{\mathrm{Loc}}(|\boldsymbol{r}-\boldsymbol{R}_i|)$, represents the 'external' potential felt by the electrons due to the $N_a = 60$ positive carbon ions disposed on the truncated icosahedron. Here, the $\boldsymbol{R}_i$ are the equilibrium positions of the carbon nuclei, referred to the centre of the molecule. The nearest neighbour distances between carbon ions used were 1.453 Å on pentagons and 1.369 Å between pentagons. Then, the radius of C_{60}, $R = |\boldsymbol{R}_i|$ results 3.5256 Å. The function $v_{\mathrm{pseudo}}^{\mathrm{Loc}}(r) = v_{\mathrm{core}}(r) + v_2(r)$, is the local part of the pseudo-potential caused by the two tightly bound 1*s* core electrons on the four 2*s*, 2*p* valence electrons of each carbon atom. The expressions used are those of [7] and the term v_2 is connected with the non-local part of the pseudo-potential (see below). The contribution of the non-local part of the pseudo-potential, $U^{\mathrm{NL}}(\boldsymbol{r}) \equiv \sum_{i=1}^{N_a} v_{\mathrm{pseudo}}^{\mathrm{NL}}(|\boldsymbol{r}-\boldsymbol{R}_i|)$, was calculated† from the expression $v_{\mathrm{pseudo}}^{\mathrm{NL}}(r) = (v_0(r) - v_2(r))|0\rangle\langle 0| + (v_1(r) - v_2(r))|1\rangle\langle 1|$, where $|\ell\rangle\langle\ell|$ is a projection operator on single-particle eigenstates of angular momentum ℓ, and $v_\ell(r)$ are parametrized functions [7]. Note that the pseudo-potentials are referred to the centre of mass of each of the ions.

We next expand the external potential $V_{\mathrm{ext}}(\boldsymbol{r})$ in spherical harmonics obtaining $V_{\mathrm{ext}}(\boldsymbol{r}) = \sum_{L,M} S_{L,M} V_L(r) Y_{L,M}(\hat{r})$, where $S_{L,M} = \sum_{i=1}^{N_a} Y_{L,M}^*(\hat{\boldsymbol{R}}_i)$. The radial functions are given by $V_L(r) = 2\pi \int_{-1}^{1} \mathrm{d}x\, v_{\mathrm{pseudo}}^{\mathrm{Loc}}(y) P_L(x)$, where $y^2 = r^2 + R^2 - 2rRx$ and $P_L(x)$ is a Legendre polynomial. Due to the icosahedral symmetry of C_{60}, the coefficients $S_{L,M} = (-)^M S_{L,-M}$ are different from zero for selected values of the angular momentum $L = 0, 6, 10, 12, 16, 18, 20, 22$, etc. For instance, $S_{0,0} = 16.9257$, $S_{6,0} = 1.4123$ and $S_{6,\pm 5} = \mp 1.1267$. Particularly large are $S_{10,\pm 5} = \mp 11.3725$, $S_{18,0} = 20.2541$, $S_{18,\pm 15} = \mp 18.0509$ and $S_{18,\pm 5} = \mp 11.4227$ (cf also [8, 9]).

Because of the nearly spherical symmetry of C_{60}, it is convenient to use the spherical harmonics expansion $\psi_k(\boldsymbol{r}) = \sum_{n\ell m} C_{n\ell m}^k \phi_{n\ell m}(\boldsymbol{r})$, where $\phi_{n\ell m}(\boldsymbol{r}) = R_{n\ell}(r) Y_{\ell,m}(\hat{\boldsymbol{r}})$. The radial functions $R_{n\ell}(r)$ of the basis wavefunctions $\phi_{n\ell m}(\boldsymbol{r})$ are solutions of equation (1) taking into account only the spherical ($L = M = 0$) component of U^{Loc} and disregarding U^{NL}.

For the solution of the full Kohn–Sham equation (1), one needs to calculate matrix elements of the pseudo-potential $v_{\mathrm{pseudo}}^{\mathrm{NL}}(\boldsymbol{r}')$ in the spherical basis $\phi_{n\ell m}(\boldsymbol{r})$. These matrix elements are simple (one-dimensional) integrals, with exception made for the fact that the wavefunctions $\phi_{n\ell m}(\boldsymbol{r})$ are referred to the centre of mass of the fullerene, while the pseudo-potential is referred to the centre of each ion. This is testified by the relation $\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{R}_i$, where $\boldsymbol{r}'$ is the vector position measured from the ion, while $\boldsymbol{R}_i$ is the position of the ith carbon ion. There is a simple solution to this technical problem which amounts to transforming $\phi_{n\ell m}(\boldsymbol{r})$ to the reference frame of each of the ions, an operation which leads to $\phi_{n\ell m}(\boldsymbol{r}) = \sum_{m'} D_{mm'}^{\ell *}(\hat{\boldsymbol{R}}_i) \sum_{\ell'} \tilde{R}_{n\ell}^{\ell'|m'|}(r', R_i) Y_{\ell' m'}(\hat{\boldsymbol{r}}')$. This relation expresses the fact that in the transformation process one has both to rotate the reference frame of the molecule to make its z-axis coincide with the $\boldsymbol{R}_i$ vector (D-function), as well as to shift the origin of the molecule to coincide with that of each of the ions, a translation which leads to the 'effective' radial wavefunction (see e.g. [10]) $\tilde{R}_{n\ell}^{\ell'|m'|}(r', R_i) = 2\pi \int_{-1}^{1} \mathrm{d}x\, R_{n\ell}(r) \Theta_{\ell,|m'|}(x') \Theta_{\ell',|m'|}(x)$.

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† Note that a term proportional to v_2 was added and subtracted with projection on $\ell = 0$ and $\ell = 1$ states. In this way, a completeness summation could be carried out leading to the v_2 term in the expression of $v_{\mathrm{pseudo}}^{\mathrm{Loc}}$.

Here, $r = (r'^2 + R_i^2 + 2r'Rx)^{1/2}$, $x' = (R_i + r'x)/r$ and $\Theta_{\ell m}(\theta) = \exp(-\mathrm{i}m\phi)Y_{\ell m}(\theta, \phi)$. The matrix elements of the pseudo-potential are then proportional to integrals of the type $\int_0^\infty \mathrm{d}r' r'^2 \tilde{R}(r', R_i) v_{\mathrm{pseudo}}^{\mathrm{NL}}(r') \tilde{R}(r', R_i)$.

The diagonalization of the Hamiltonian (1) in the spherical basis discussed above, is performed, for each iteration, by including moments of V_{ext} up to $L = 20$ and all the spherical wavefunctions with eigenenergies up to 40 eV. This means that spherical wavefunctions having angular momenta in the range $0 \leqslant \ell \leqslant 20$ and number of nodes $n = 0, 1, 2, \ldots, 15$, denoted as σ, π, $\delta, \ldots$ orbitals, were considered. The energy gap between the highest-occupied and the lowest-unoccupied molecular orbital states (HOMO-LUMO gap) is predicted to have a value of 1.91 eV as compared to the value of 1.86±0.1 eV measured experimentally [11]. These states have $n = 1$ character ($\approx 70\%$) and have no components with $n = 0$. Consequently, one can identify these states with π electrons whose orbitals are mainly concentrated perpendicularly to the surface of the hollow sphere. Important contributions to this gap arise from the very large $S_{10,M}$ ($M = 0, \pm 5, \pm 10$) term in V_{ext}. This is due to the fact that the angular momentum of the levels defining the gap is mainly $\ell = 5$. The band width is predicted to be $\cong 21$ eV. This number is controlled, to a large extent, by the non-local part of the pseudopotential, as well as by the large $S_{18,M}$ term of the local part. This is because the highest bound state with $n = 0$ character (σ orbital) arises predominantly from $\ell = 9$ states.

Making use of the single-particle basis discussed above, the dipole response of C_{60} has been worked out in the random phase approximation (RPA). The basic quantity to be calculated is the free density–density correlation function (cf e.g. ch 6 of [4] and ch 4 of [5]

$$G^{(0)}(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \sum_{ph} \Psi_{ph}(\boldsymbol{r}) g_{ph}(\omega + \mathrm{i}\eta) \Psi_{ph}^*(\boldsymbol{r}') \tag{3}$$

where $g_{ph}(\omega + \mathrm{i}\eta) = [1/(\Delta E_{ph} - \hbar\omega - \mathrm{i}\eta) + 1/(\Delta E_{ph} + \hbar\omega + \mathrm{i}\eta)]$, $\Delta E_{ph} = E_p - E_h$, $\eta > 0$, and $\Psi_{ph}(\boldsymbol{r}) = \psi_p^*(\boldsymbol{r})\psi_h(\boldsymbol{r}) = \sum_{\lambda\mu} \Phi_{ph,\lambda\mu}(r) Y_{\lambda\mu}(\hat{\boldsymbol{r}})$. The induced density within RPA is given by

$$\delta n(\boldsymbol{r}) = \delta n^{(0)}(\boldsymbol{r}) - \int \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 G^{(0)}(\boldsymbol{r}, \boldsymbol{r}_1; \omega) V(\boldsymbol{r}_1, \boldsymbol{r}_2) \delta n(\boldsymbol{r}_2) \tag{4}$$

where $V(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1/|\boldsymbol{r}_1 - \boldsymbol{r}_2| + \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)\mathrm{d}V_{\mathrm{xc}}/\mathrm{d}n$, and where

$$\delta n^{(0)}(\boldsymbol{r}) = -\int \mathrm{d}^3 r' G^{(0)}(\boldsymbol{r}, \boldsymbol{r}'; \omega) D(\boldsymbol{r}) \tag{5}$$

with $D(\boldsymbol{r}) = D(r)Y_{10}(\hat{\boldsymbol{r}})$, $D(r) = e\sqrt{\frac{4}{3}\pi}\, r$, for the dipole field. Making use of the multipole expansion of the Ψ_{ph}, equation (3) becomes

$$G^{(0)}(\boldsymbol{r}_1, \boldsymbol{r}_2; \omega) = \sum_{\ell_a m_a, \ell_b m_b} G^{(0)}_{\ell_a m_a, \ell_b m_b}(r_1, r_2) Y_{\ell_a m_a}(\hat{\boldsymbol{r}}_1) Y_{\ell_b m_b}(\hat{\boldsymbol{r}}_2) \tag{6}$$

where

$$G^{(0)}_{\ell_a m_a, \ell_b m_b}(r_1, r_2) = \sum_{ph} \Phi_{ph,\ell_a m_a}(r_1) g_{ph}(\omega + \mathrm{i}\eta) \Phi_{ph,\ell_b m_b}(r_2). \tag{7}$$

Expanding δn and V in spherical harmonics, the relation (4) transforms into a set of coupled linear equations in r-space. In the case of a dipole field,

$$\delta n_{10}(r) = \delta n_{10}^{(0)}(r) - \sum_{L'M'} \int \mathrm{d}r_1 dr_2\, r_1^2 r_2^2\, G^{(0)}_{10,L'M'}(r, r_1; \omega)\, V_{L'M'}(r_1, r_2)\, \delta n_{L'M'}(r_2). \qquad (8)$$

We have found that the main contribution arises from the term with $L' = 1$ and $M' = 0$. Once the induced density is obtained, the dynamic polarizability can be calculated through the relation $\alpha(\omega) = \int_0^\infty \mathrm{d}r r^2 \delta n_{10}(r) D(r)$ and the associated strength function is given by the relation $S(\omega) = -(1/\pi)\mathrm{Im}\alpha(\omega)$. The dipole response function is then obtained as $d(\omega) = \omega S(\omega)$. The unperturbed strength function, $S^{(0)}(\omega)$, is obtained by replacing in the expression of $\alpha(\omega)$, δn by $\delta n^{(0)}$. For the static polarizability of the system we obtain $\alpha(0) = 88.6$ Å^3. There are at present no direct measurements of $\alpha(0)$ for a single molecule. However, we can compare our result with estimates from the solid phase (fullerites). Using the Clausius–Mossotti relation between the dielectric constant of the solid and $\alpha(0)$ estimates of the polarizability range from 78 to 92 Å^3 (cf e.g. [12]).

The results for both the unperturbed particle–hole and RPA strength functions $S(\omega)$ of C_{60} are displayed in figure 1 in the range $0 \leqslant \omega \leqslant 35$ eV, in comparison with the experimental findings [1, 2]. Within this range of energy, the theoretical strength functions $S^{(0)}$ and S exhaust 95% and 84% of the TRK sum rule, respectively. Although the RPA results show strong mixing of individual particle–hole excitations, it is still possible to identify the different peaks below ≈6 eV with π–π transitions, while for increasing energies transitions connecting σ orbitals with π and δ orbitals dominate the response. To be noted is that the tail of $S(\omega)$ ($\omega \geqslant 30$ eV) is not very accurate. This is due to the energy cutoff at 40 eV used for the particle–hole basis states.

As seen from figure 1, theory provides an overall account of the experimental findings. In particular of the width of the Mie resonance. Consequently, single-particle decay (Landau damping) can be viewed as the main relaxation mechanism of this collective mode. A clear test of this result is provided by including in the calculation only the particle–hole excitations which contribute more than 0.1% to the EWSR. As compared with the calculation in the full basis, there is a shift of the peak of the Mie resonance of about 4–5 eV, and a reduction by a factor ≈3 in the damping width (i.e., from 12 eV to 4.5 eV, see figure 1(*b*)). This is a consequence of the fact that at the lowest energy of the shifted centroid, the density of unperturbed particle–hole excitations is 50 eV^{-1} while around 20 eV is 200 eV^{-1} (cf inset figure 1(*a*)). A further check of the Landau damping mechanism is provided by taking into account in the solution of equation (8) the coupling of the Mie resonance not only to the monopole component of the external field (as shown in figure 1(*b*)) but also to the higher multipolaritites ($L' = 5, 7, M' = 0, \pm 5$; $L' = 9, M' = 0, \pm 5$; $L' = 11, M' = 0, \pm 5, \pm 10$, etc). The results essentially coincide with those displayed in figure 1(*b*). This is gratifying, also in view of the fact that the effect of the coupling between the Mie resonance and the thermal fluctuations of the cluster surface, which have been found to be very important in explaining the spreading width of the plasmon in alkali clusters (cf e.g. [13]) leads, in the present case, to negligible contributions to the damping width [14, 15].

The experimental data at low excitation energy corresponds to the optical/UV absorption spectra of C_{60} in hexane solution, at room temperature [1]. Nine transitions below 6.4 eV have been observed displaying the following energies (oscillator strength): 3.04 eV (0.005), 3.30 eV (–), 3.78 eV (0.37), 4.06 and 4.35 eV (0.10), 4.84 eV (2.27), 5.46 eV (0.22), 5.88 eV (3.09) and 6.36 eV (–). Theory predicts 3.4 eV (0.048), 3.91 eV (0.59), 4.38 eV (0.041), 5.05 eV (0.50), 5.30 eV (0.14), 5.42 eV (0.21), 5.70 eV (0.084), 5.92 eV (0.95) and 6.35 eV

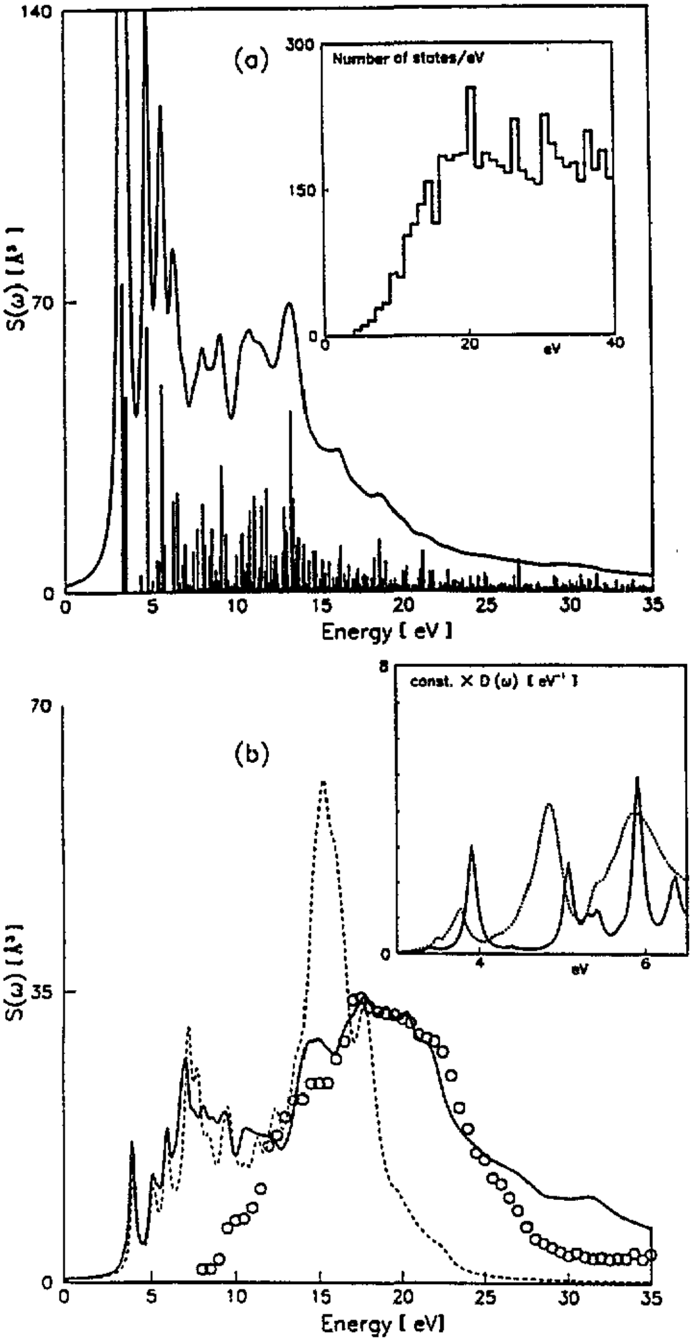

Figure 1. Dipole strength function of the C_{60} molecule. (*a*) The free response $S^{(0)}(\omega)$. Making use of this result, the density of states has been calculated and is displayed in the inset. Also shown is the unperturbed strength function averaged with Lorentzian functions having widths $\Gamma = 0.06\omega$ (full curve). (*b*) The RPA response (full curve), $S(\omega)$, is displayed and compared with experimental data [2] (circles). The RPA results have been averaged with Lorentzian functions having widths $\Gamma = 0.06\omega$. The broken curve represents the RPA result obtained by keeping only those particle–hole transitions which contribute more than 0.1% to the EWSR. In the inset details are given of the optical/UV response of the system (const $= 2m/\hbar^2e^2$) in comparison with the experimental findings [1] (broken curve).

(0.48). There is an overall correspondence between the calculations and the experimental findings . However, theory leads to too strong a screening. In fact, while the observed summed oscillator strength below 6.4 eV amounts to 6.07, the RPA prediction is 3.1. To be noted is that the value associated with the unperturbed response function in the same energy interval is 33.4.

During recent years a number of calculations concerning the collective properties of C_{60} have been reported in the literature [3, 9, 16–19]. The assumption of spherical symmetry made in a number of papers has important consequences for the whole response function, but in particular for the width of the Mie resonance which in this approximation becomes very narrow (cf [3, 18, 19]) and much smaller than the experimental value [2].

The calculations based on the tight-binding approximation and linear response [3, 17] lead also to a Mie resonance which is still noticeably narrower than the one displayed in figure 1. Furthermore, while the present calculation predicts this mode to carry an oscillator strength of ≈ 160, the results reported in [3] display half this value. This difference implies a factor of 2 in the associated photoabsortion cross section, a prediction that can be tested experimentally. Moreover, in the calculations of [3, 17] most of the oscillator strength lies above 40 eV, while we find, within the range 0–40 eV about 90% of the oscillator strength. This prediction has important consequences, in particular for the photoionization process, and can be again tested experimentally.

Concerning the low-lying states, there is an overall agreement between the present results and those of [3]. As already mentioned above, the lowest observed state [1] has an energy of 3.04 eV and oscillator strength $f = 0.005$. These results are very accurately reproduced by Bertsch *et al* [3]. Our results are more in line with those of [16], which predict the lowest optical transition at ≈ 3.4 eV with an oscillator strength of 0.08. On the other hand, the integrated oscillator strength below 6.4 eV which can be read from figure 2(*b*) of [3] is ≈ 1.8 compared to the experimental value of 6.07 and our value of 3.1.

In conclusion, we have found that the optical/UV part of the dipole response of C_{60} is dominated by particle–hole transitions among π orbitals, while the Mie resonance observed at ≈ 20 eV arises not only from σ–σ transitions but also, and to a large extent, from particle–hole excitations connecting σ with π and δ orbitals, as well as final states with a higher number of nodes. The inclusion of these transitions is essential to fulfil the energy weighted sum rule. The width of the Mie resonance is due to the decay of the plasmon into single-particle configurations. To obtain a quantitative account of the experimental findings the icosahedral symmetry of the mean field has to be respected to a high degree of accuracy.

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