On the Plasmon-like Excitations of Atomic Clusters with Application to Fullerene

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Abstract

We present here a modified hydrodynamical model which can be used to investigate in a easy way the collective electronic excitations of spherical atomic clusters. The model is then applied to the case of the giant-dipole plasmon mode of the free fullerene molecule.

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Collective electronic excitations of small metallic particles or atomic clusters like fullerites may be and in fact are currently [1-6] of great interest with the goal to bridge the gap between our description of atom and solid. A part the polarization propagator response method [8] within RPA a good tool to investigate theoretically the plasmon-like collective behaviour of the nearly free or valence electrons in such systems is certainly the hydrodynamical model which date back to pioneering work by Bloch [9, 10]. It was early used [11] eventually in refined version, as for instance in the investigation of photoabsorption of a Thomas-Fermi atom [12]. More recently such an approach was successfully used investigating the excitation of plasmons by energetic electrons in small spheres [13] and photon bombardment of a plasma slab [14]. Since then the model has been refined, [15] and now leads to very sophisticated equations for the density fluctuations around the equilibrium distribution of a inhomogeneous electron gas [16]. In spite of that, this approach seems not so widely used, probably because the necessary equations are very cumbersome to handle unless the equilibrium density distribution can be considered constant. Thus I propose in this note a way to simplify these difficulties in the case of a problem with spherical symmetry, which will be presented within the more simple Bloch’s original scheme. It consists on the idea to consider the equilibrium electronic density $\rho_0(r)$ which is isotropic for a problem with spherical symmetry, to assume constant values $\rho_0^{(i)}$ within each shell of a given thickness $\Delta_i$ by which the space around the origin can be subdivided. I will also consider the quantity above to be zero outside a certain distance $R$ from the origin. The case of $\rho_0(r)$ being continuous is of course recovered if the shell’s thickness goes to zero and $R$, if necessary, to infinity. But all that amounts to present an approximate method to solve the continuous case, with no less difficulties than before if you like to approach more and more the limit. Instead, also in view of the validity of the approximation leading to $\rho_0(r)$ both the set of values $\rho_0^{(i)}$ as well $R$ and the $\Delta_i$ will be considered as parameters referring to a model equilibrium density. The net result
will be a kind of multi-shell or onion model.

The starting point in the Bloch’s approach is a Lagrangian $L_2$. It comes as the second order (quadratic) contribution in the development around equilibrium of the full Lagrangian $L$ for an irrotational fluid of electrons in which only the Coulomb interaction with the positive background, the Coulomb interaction among the electrons and the kinetic energy term are considered. The first variation of $L$ in the static case leads to the Thomas-Fermi equation. The equations of motion (written in atomic units to be used in the following) result to be:

$$\begin{align*}
\dot{\phi}(r, t) &= \frac{C[\rho_0(r)]}{\rho_0(r)} n(r, t) + \int \frac{n(r', t)}{|r-r'|} dr' \\
\dot{n}(r, t) &= \nabla \cdot [\rho_0(r) \nabla \phi(r, t)] \quad (1)
\end{align*}$$

where $n(r, t)$ and $\phi(r, t)$ are perturbations in the electronic density and velocity potential, respectively, in the electron gas. As already indicated $\rho_0(r)$ is the electronic density in the undisturbed state so that $\rho_0(r) \nabla \phi(r, t)$ represents at this order of development the current density of the fluctuations. $C[\rho_0(r)]$ is the quantity $\pi^2/3(3/\pi)^{2/3} \rho_0(r)^{2/3}$. Assuming:

$$\begin{align*}
\phi(r, t) &= f(r) \begin{cases} 
- \cos \omega t \\
\sin \omega t
\end{cases} \\
n(r, t) &= g(r) \begin{cases} 
\sin \omega t \\
\cos \omega t
\end{cases}
\end{align*} \quad (2)$$

we have:

$$\begin{align*}
\omega f(r) &= \frac{C[\rho_0(r)]}{\rho_0(r)} g(r) + \int \frac{g(r')}{|r-r'|} dr' \\
\omega g(r) &= -\nabla \cdot [\rho_0(r) \nabla f(r)] 
\end{align*} \quad (3)$$

In the case that $\rho_0(r)$ assumes a constant value $\rho_0$ and using both the Eq. (3) one see that $g(r)$ satisfies the equation:

$$\begin{align*}
\triangle g(r) + \left( \frac{\omega^2 - 4\pi \rho_0}{C[\rho_0]} \right) g(r) &= 0 
\end{align*} \quad (4)$$

which is easy solvable after separation of the angular dependence. In the present case it is convenient to do so using the real, normalized spherical harmonics $Y_{m,l}^s(\Omega)$ [17] where $s$ means even or odd, in order to easily obtain $f(r)$ and $g(r)$ as real
functions as it should be. Let \( F = (\omega^2 - 4\pi \rho_0)/C[\overline{\rho}_0] \) and \( \mu = \sqrt{|F|} \). The general solution of Eq. (4) is of the type:

\[
g_{s,m}^s(r) = [a \ A_l(\mu r) + b \ B_l(\mu r)] Y_{m,l}^s(\Omega)
\]

where \( a, b \) are numerical coefficient and \( A_l(\mu r), B_l(\mu r) \) indicate the couple \( j_l(\mu r) \) and \( \eta_l(\mu r) \) of independent Bessel functions of order \( l \) when \( F \) is positive or their analytical extension in terms of hyperbolic sinus and cosinus otherwise. Consider now a isotropic equilibrium density distribution which is zero outside the sphere of radius \( R \) and let \( R \) be subdivided for simplicity in \( N \) equal intervals of length \( \Delta = R/N \). The sphere is thus subdivided in \( N \) shells, the \( i^{th} \) among them having \( r_{i-1} \) and \( r_i \) as internal and external radius respectively with \( r_i = i\Delta \quad (i = 1, N) \) and let the quantity \( \rho_0^{(i)} \) be the constant value of the equilibrium density within the \( i^{th} \) shell. The solutions for \( g(r) \) will be:

\[
g_{s,m}^s(r) = \sum_{i=1}^{N} [a_i^{(i)} A_l(\mu_i r) + b_i^{(i)} B_l(\mu_i r)] Y_{m,l}^s(\Omega) \chi^{(i)}(r)
\]

where \( \chi^{(i)}(r) \) is the step function which is equal to one inside the \( i^{th} \) shell and zero otherwise, and the meaning of the quantities indexed with \( i \) is obvious. The corresponding solution for the velocity potential is obtained from Eq. (3) using the first equation in Eq. (3). It is required that both \( f(r) \) and \( g(r) \) be regular at the origin and as usual that the normal component of the fluctuation current density at the surface \( r = R \) be zero. Besides these boundary conditions also the matching conditions at the separating surfaces of the shells are required. For that we have at disposal the values of the fields \( \phi \) and \( n \) and of their derivatives at such places. As \( \rho_0(r) \) is considered discontinuous I see no need to impose continuity conditions on the fluctuation density. So we can concentrate on \( \phi \) requiring the continuity of the velocity potential and of the fluctuation density current \( \rho_0(r) \nabla \phi(r, t) \). The regularity of the fields at \( r = 0 \) requires that the coefficient of the non regular Bessel function referring to the first shell around the origin be zero. The boundary condition at \( r = R \) and the \( 2N - 2 \) conditions at the separation walls then give rise to \( 2N - 1 \) homogeneous
linear equations for the remaining \(2N - 1\) unknown coefficients and we are left with an eigenvalue problem. Let \(\omega_n\) be an eigenvalue and \(f_n(r)\) \(g_n(r)\) the couple of corresponding solutions for \(f(r)\) and \(g(r)\). It is easy to show [18] that thanks to the conditions imposed the integral of the product \(f_m(r)g_n(r)\) over the volume \(|r| < R\) is zero unless \(m = n\), that is the result which holds when \(\rho_0(r)\) is continuous [9, 12] is recovered. The solution will then be normalized with the following choice:

\[
\int f_n(r) g_m(r) dr = \delta_{nm} \omega_n .
\] (7)

I notice that a choice of an orthogonal set of harmonic functions for the angular part was already made, so the degeneracy connected with the spherical symmetry does not cause trouble in this respect.

To illustrate the method outlined above I applied the onion model to the collective electronic excitations of fullerene, since this recently produced macromolecule is the subject of many investigation both on experimental and theoretical side. The \(C_{60}\) is considered with good approximation [19] as a neutral system composed of nearly-free electrons with the background positive charge uniformly distributed over the surface of a sphere of radius \(r_b\). As a starting point the Thomas-Fermi equilibrium distribution \(\rho_{0TF}(r)\) of the valence electrons, whose number was fixed to be 240 following the Ref. [25], was computed. Then the following quantities were considered for each shell:

\[
\overline{\rho}_{0i} = \frac{1}{V_i} \int \rho_{0TF}(r) dV_i
\] (8)

where \(V_i\) is the volume of the \(i^{th}\) shell. The required constant quantities \(\rho_0^{(i)}\) were then obtained as \(\overline{\rho}_{0i}\) time a normalization factor with the aim to ensure that the total number of electrons contained in the volume \(|r| < R\) be exactly 240. The eigenvalue problem was solved numerically for three different values of the fullerene radius \(r_b\) in the only case for which \(l = 1\). The interval of explored frequencies ranges from 7 to 32 eV, in order to explore the discovered high-energy giant-dipole plasmon mode
of the free molecule \[20\]. We know that it exists a lower limit of distance given by \(1/Z\) where \(Z\) is the charge, for the applicability of Thomas-Fermi equation near a charged nucleus (in the present case the carbon nucleus screened by the two inner s-electrons) \[21\], and therefore the detailed behaviour of the resulting equilibrium electronic density at shorter distance can be ignored. We also know that the ground state electronic distribution of a Thomas-Fermi atom has a tail going wrong \[22\], i.e. it goes too much slowly to zero at infinity, and as a crude remedy we can cut off the obtained \(\rho_{\text{TF}}(r)\) at some finite radius. Taking into account the considerations above the values \(\Delta = 0.2\) and \(R = 14.2\) were adopted as sensible. The last figure is about two time the value of \(C_{60}\) radius i.e. 3.5 Å \[23\] and so the equilibrium distribution ends at fairly the same radial distance from the positive charged surface. After the eigenvalues and the related eigenfunctions are known the next step is to build up the Hamiltonian which using these normal mode will look of course like a collection of non interacting harmonic oscillator hamiltonians. Let us restrict to the space of functions whose angular dependance is that of the usual \(l = 1, m = 0\) harmonic. Indicating with \(s_k(r)\) and \(w_k(r)\) the \(k^{th}\) solution with the above angular part for \(f(r)\) and \(g(r)\) respectively and expanding with such a basis the fields \(\phi\) and \(n\) it is easy to build up the contribution to the total Hamiltonian as coming from the subspace considered. It is also easy to write down the dipole interaction term when an external electric field \(E\) directed along the polar axis is considered. At last one see that the oscillator strength \(x_k\) of the \(k^{th}\) dipole mode is \(x_k = y_k^2\) where

\[
y_k = \int r \cos \vartheta \, w_k(r) \, dr .
\]

I recall that the functions \(s_k(r)\) and \(w_k(r)\) are normalized as indicated previously.

The results of computations are collected in Table 1. One may see that the contribution of the dipole strength within the range 7-32 eV to the total figure of 240 electrons required by the dipole sum rule is quite large. After the inspection of other solutions below this range and above up to 42 eV it appear that the sum rule is satis-
fied in defect within about then percent. So it is very probably satisfied exactly taking into account larger frequencies and the computing errors as well. The contribution of the modes listed to the static polarizability of a free $C_{60}$ give a somewhat large figure, in agreement with the quantum-chemical result of reference [24]. The imaginary part of the dynamic polarizability for a free fullerene molecule was recently determined indirectly from photoionisation data on gaseous $C_{60}$ [20]. The authors concluded for the presence of absorption peaks at about 7.8, 10, 13, 17 and 21 eV. The plasmon collective excitation modes are presumably strongly coupled to the single electron states and so the absorption line width can be very large. Referring to the middle column of the Table 1 we could thus suppose that the experimental maxima near 13 and 17 eV are due to the two couples of resonances here found at 12.14, 14.37 eV and at 16.41, 18.17 eV respectively. We may then conclude that the prediction of our calculations in that of the three cases for which the fullerene radius $r_b$ is the nearest to the indicated value of 3.5 Å [23] is in a good accordance with the experiments. I stress however that the aim was especially to present here the model and not to present very refined predictions. The conclusion above still seems to indicate that the method outlined does work well. It can be useful to look at other multipoles than the simple dipole and then investigate such things like the inelastic electron scattering and the behaviour of Van der Waals interaction at large distance to which large multipoles may contribute appreciably [25, 26]. As a concluding remark I observe that of course the present method can be improved further. First such terms like exchange and correlation energies must be included in the Lagrangian of departure. And on the mathematical side it would be useful to correlate the shells thickness to the rapidity of variation of $\rho_0^{(i)}$.

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Table 1: The frequencies $\omega$ and the oscillator strengths $x$ for three values of $r_b$ as result from the present calculation in the frequency range 7-32 eV. The cases where $x < 0.25$ are omitted.

| $r_b = 6.4$ | $r_b = 6.6$ | $r_b = 6.8$ |
|------------|-------------|-------------|
| $\omega$ (eV) | $x$ | $\omega$ (eV) | $x$ | $\omega$ (eV) | $x$ |
| 7.23 | 9.76 | 7.60 | 11.26 | 8.00 | 13.11 |
| 9.44 | 10.44 | 9.92 | 12.46 | 10.43 | 15.25 |
| 11.57 | 14.34 | 12.14 | 18.00 | 12.71 | 21.98 |
| 13.70 | 18.03 | 13.85 | 1.41 | 12.95 | 1.39 |
| 14.89 | 0.69 | 14.37 | 22.32 | 14.99 | 33.62 |
| 15.77 | 25.19 | 16.41 | 36.73 | 16.88 | 37.40 |
| 17.71 | 35.55 | 18.17 | 29.75 | 17.61 | 5.79 |
| 19.38 | 28.30 | 18.92 | 7.76 | 18.95 | 32.81 |
| 20.28 | 4.66 | 20.20 | 27.08 | 20.85 | 7.51 |
| 21.40 | 23.54 | 22.09 | 6.36 | 22.24 | 5.78 |
| 23.20 | 6.84 | 23.76 | 2.82 | 23.21 | 4.59 |
| 25.82 | 7.83 | 24.42 | 6.32 | 26.87 | 4.94 |
| 27.39 | 1.00 | 26.46 | 0.36 | 27.88 | 0.37 |
| 30.94 | 4.38 | 28.50 | 1.50 | 30.15 | 0.25 |
| 31.74 | 0.58 | 29.06 | 3.60 | 31.51 | 4.18 |