Electrostatic screening in fullerene molecules.

J. González
Instituto de Estructura de la Materia.
Consejo Superior de Investigaciones Científicas.
Serrano 123, 28006-Madrid. Spain.

F. Guinea
Instituto de Ciencia de Materiales.
Consejo Superior de Investigaciones Científicas.
Cantoblanco. 28049-Madrid. Spain.

M. A. H. Vozmediano
Escuela Politécnica Superior.
Universidad Carlos III.
Avda. Mediterráneo 20.
Leganés. 28913 Madrid. Spain.

Abstract

We study the Coulomb interactions in fullerene molecules within a continuum formalism. The model gives rise to a renormalizable field theory, which has many similarities to standard quantum electrodynamics. The effective electric charge at low energies is reduced by screening processes. The associated renormalization of the one electron Green’s function leads to the vanishing of the quasiparticle pole. It implies the disappearance of coherent one particle excitations, in close analogy to the one dimensional Luttinger liquid. The relevance of these results for C_{60} and related molecules is discussed.

75.10.Jm, 75.10.Lp, 75.30.Ds.
I. INTRODUCTION.

The localization of the electrons within the C$_{60}$ spheres implies that electrostatic interactions cannot be neglected in fullerene crystals. The simplest estimate for the charging energy of a C$_{60}$ molecule, $e^2/R$, where $R$ is the radius, gives a rather large value, $\approx 4eV$. Moreover, the low density of states at the Fermi level in graphite reduces metallic screening (see below). In general, the intermediate size of the molecule puts it in a regime different from that for an isolated atom or a bulk system. Different approaches have been used in the study of electrostatic effects [1–7]. It has also been proposed that they can be the origin of superconductivity in doped systems [8,9].

In the present work, we use a simple model for the long wavelength electronic properties of fullerene molecules [10,11], to analyze the screening properties. It has been shown that it gives a reasonable approximation to the electronic levels of C$_{60}$. Furthermore, the scheme is sufficiently general to describe other systems with similar topology, like nanotubes and fullerene 'onions'. The model can also be used to study other features, like the electron-phonon interaction with reasonable accuracy, a shown in a previous work [12].

Calculations based on this model for the electrostatic interactions between the highest occupied orbitals (in doped systems) are in good agreement with more detailed calculations [9].

In the next section, we discuss how to incorporate the Coulomb interaction into this model. It will be shown to lead to a renormalizable field theory in (2+1) dimensions. Then, we analyze in detail the leading divergent diagrams in the theory, and show how to deal with these divergences by defining appropriate renormalized couplings. The flow of these couplings, and its implication for some quantities of physical interest, is discussed in the next section. Finally, in the conclusions, we discuss the applicability of our results to C$_{60}$ and related systems, as well as the changes induced by the finite curvature and doping expected in these systems.

II. THE MODEL.

The low lying electronic states of an isolated graphitic sheet are well approximated by an effective Dirac equation in (2+1) dimensions, using Hückel’s theory of conjugated carbon compounds. This description plays the same role as the effective mass theories used for the study of the long wavelength properties in other materials. The existence of rings with an odd number of atoms in C$_{60}$ leads to additional complications, which require the introduction of a fictitious gauge field, to account for the frustration that these rings induce in the electronic states.

We use the preceding scheme to analyze first the screening properties of an isolated graphite plane. The single sheet, in the absence of interactions, is semimetallic, with a vanishing density of states at the Fermi level. Hence, the screening properties are expected to differ significantly from those typical of standard metals, as no screening length, $k_{FT} = \sqrt{4\pi e^2N(\epsilon_F)}$, can be defined.

Within the approximation described above, we can write the total hamiltonian, including the Coulomb interaction, as:
\[ H_{\text{Coulomb}} = \frac{3}{2} t a \int d^2 r \ \overline{\Psi}(r) \gamma \cdot \nabla \Psi(r) + \frac{e^2}{2} \int d^2 r_1 \int d^2 r_2 \frac{\overline{\Psi}(r_1) \sigma_3 \Psi(r_1) \overline{\Psi}(r_2) \sigma_3 \Psi(r_2)}{4\pi |r_1 - r_2|} \]  

where the first part describes the independent electron Hamiltonian by means of the Dirac equation. The \( \gamma \)'s are Dirac matrices, \( t \) is the hopping between nearest neighbor orbitals, \( \sim 2.2 \text{eV} \) and \( a \) is the interatomic distance, \( \sim 1.4 \text{Å} \). The Fermi velocity is given by \( 3 \tau a/(2\hbar) \). The second part is the standard electrostatic interaction.

We can now try to analyze the interaction term perturbatively. To lowest order, we have the exchange term, depicted in figure (1). Note that what we define as Coulomb interaction is not the same as what is traditionally assumed for 2D charges, which is a logarithmic potential. We suppose that the electronic charge, although localized within a plane, gives rise to a 3D electrostatic potential, which decays as \( r^{-1} \). This difference is crucial to the cutoff dependence of the diagrams that we will encounter. For instance, the exchange contribution to the self energy, figure (1), can be written as:

\[ \Sigma_{\text{xc}}(\vec{k}) \propto e^2 \gamma \cdot \vec{k} \int_0^{\omega_c} \frac{d^2 k'}{k'^3} \]  

where \( \omega_c \) is an upper cutoff, above which the linearization we use ceases to be valid. The integral in (2) diverges logarithmically as function of its upper and lower limits.

This divergence is an indication of the need of some kind of renormalization procedure. The possibility of logarithmic corrections to the physical quantities can also be inferred from standard power counting. If we choose units such that velocities are dimensionless, then the coupling constant, \( e^2 \), is also dimensionless. In fact, this power counting is identical to that in standard quantum electrodynamics.

In the following, we will account for the divergence in equation (2), and those other divergences which appear at higher orders in \( e^2 \), by renormalizing the terms in the initial Hamiltonian. A proof that it can be done, and a detailed explanation of most technical steps, can be found in [13]. Thus, many intermediate steps will be omitted in this paper, although we will discuss in full the physical implications.

In order to simplify the calculations of the divergences, we will couple the 2D Dirac equation in our theory to 3D photons, which then induce the Coulomb interaction, eq. (1). This step is not simply a technicality, as it also allows us to discuss retardation effects. Retardation due to the finiteness of the velocity of light is relevant at sufficiently large distances. This is a well known effect in the study of Van der Waals forces, for instance. If the typical separations, \( l \), are of the order of \( \Delta \epsilon/(\hbar c) \), where \( \Delta \epsilon \) is a typical energy splitting, and \( c \) the velocity of light, then the dependence of the interaction on \( l \) changes. We study the generalization of these interactions to graphite planes, and, as we will see, similar effects appear.

To include the 3D electromagnetic field, we generalize the Hamiltonian, eq. (1), to:

\[ H = \frac{3}{2} t a \int d^2 r \ \overline{\Psi}(r) \gamma \cdot \nabla \Psi(r) - e \int d^2 r \ j_\mu A^\mu \]  

where we are using units such the velocity of light, \( c = 1 \), and we are omitting the term associated to the free electromagnetic field. It is important to realize that this model,
although formally similar to QED, does not exhibit Lorentz invariance. We have two dimensionless velocities, \( v_F = 3ta/(2\hbar) \), and \( c \). Initially, \( v_F/c \ll 1 \), which corresponds to the nonrelativistic limit.

The interaction of the field \( A_\mu \) and the electrons in the layer is described in the standard fashion, by coupling to the conserved current:

\[
j_\mu \sim (i \overline{\Psi} \gamma_0 \Psi, i v \overline{\Psi} \gamma \Psi)
\]

(4)

This poses some technical problems since the electromagnetic field propagates in three-dimensional space while we want the dynamics of the electrons to be confined to the two-dimensional layer. Although this may not be achieved in general, it turns out to be possible by specializing to the Feynman gauge, which enforces the constraint:

\[
\nabla_\mu A^\mu = 0
\]

(5)

In order to proceed perturbatively, we need to know the propagator of the \( A_\mu \) field in this gauge, which is:

\[
\langle TA_\mu(t, \mathbf{r})A_\nu(t', \mathbf{r}')\rangle = -i\delta_{\mu\nu} \int \frac{d^4k}{(2\pi)^4} \frac{e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')}}{-\omega^2 + k^2 - i\epsilon} e^{-i\omega(t-t')}
\]

which then couples to the 2 + 1 dimensional current. The nonrelativistic limit of any quantity is obtained by expanding in powers of \( v_F/c \). As mentioned above, we may expect differences between treatments based in Hamiltonian (1) and Hamiltonian (3), when retardation effects become relevant.

III. CALCULATION OF THE LEADING DIVERGENCES.

We expect logarithmic divergences to all orders in a perturbation expansion in powers of \( e^2 \). To facilitate the computation, we use a dimensional regularization procedure [13,14].

The bare parameters in the Hamiltonian undergo multiplicative renormalization:

\[
\begin{align*}
v_{\text{bare}} &= Z_v v_R \\
e_{\text{bare}} &= Z_e e_R \\
\Psi_{\text{bare}} &= Z^{1/2}_\Psi \Psi_R \\
A^\mu_{\text{bare}} &= Z^{1/2}_A A^\mu_R
\end{align*}
\]

(7)

A detailed calculation of the leading divergences in each of these factors can be found in [13]. As an example, to lowest order in \( e^2 \), we find the following contributions:

\[
\begin{align*}
Z_\Psi &= 1 + \frac{e^2}{8\pi^2} \left(1 - 2v^2\right) \int_0^1 dx \frac{\sqrt{1-x}}{1-x + v^2 x} \frac{1}{\varepsilon} + O(e^4) \\
Z_v &= 1 - \frac{e^2}{8\pi^2} \int_0^1 dx \frac{\sqrt{1-x}}{(1-x + v^2 x)^2} \frac{1}{\varepsilon} \\
&\quad - \frac{e^2}{8\pi^2} \left(1 - 2v^2\right) \int_0^1 dx \frac{\sqrt{1-x}}{1-x + v^2 x} \frac{1}{\varepsilon} + O(e^4)
\end{align*}
\]

(8)
where \(v\) stands for the Fermi velocity in dimensions where \(c = 1\). In the nonrelativistic limit, \(v \to 0\), we can write an expansion in terms of \(v\). The leading term in \(Z_v\) is:

\[
Z_v = 1 - \frac{1}{16\pi^2} e^2 \left\{ \frac{1}{v} F \left( \frac{1}{2}, \frac{3}{2}; \frac{1}{2}; v^2 \right) - 2\pi v \left( 1 - 2v^2 \right) F \left( \frac{3}{2}, \frac{3}{2}; \frac{3}{2}; v^2 \right) \right. \\
+ 4 \left( 1 - 2v^2 \right) F \left( 1, 1; \frac{1}{2}; v^2 \right) - 4F \left( 1, 2; \frac{3}{2}; v^2 \right) \left. \right\} \frac{1}{\varepsilon} + O \left( e^4 \right) \quad (9)
\]

This expression is written in terms of hypergeometric functions.

The model exhibits gauge symmetry, which is not broken by our choice of regularization scheme. That imposes constraints on the values of the \(Z\)'s. The renormalized Lagrangian can be written as:

\[
S_{\text{bare}} = Z_{\text{kin}} \int dt d^2r \overline{\Psi} \left( -\gamma_0 \partial_0 + Z_v v \gamma \cdot \nabla \right) \Psi \\
- Z_{\text{int}} ie \int dt d^2r \overline{\Psi} \left( -\gamma_0 A_0 + Z_v v \gamma \cdot A \right) \Psi \quad (10)
\]

and the gauge invariance implies that \(Z_{\text{kin}} = Z_{\text{int}}\). This, in turn, implies that \(Z_e = Z_{A}^{-1/2}\). Furthermore, we can infer from the structure of vortex diagrams, figure (2), that the electric charge is not renormalized. The reason is the insertion of a \(\gamma\) operator at each vortex, which makes the diagram tend to zero as the momentum transferred, \(q \to 0\). We have checked that these requirements are satisfied to order \(e^4\).

**IV. RENORMALIZATION FLOW.**

Once the multiplicative constants, eq. (8) are known, we can analyze the dependence of the propagators upon a change in the cutoff:

\[
\left( \Lambda \frac{\partial}{\partial \Lambda} + \beta_v(v, e^2) \frac{\partial}{\partial v} + \beta_e(v, e^2) \frac{\partial}{\partial e} - \gamma(v, e^2) \right) G(\omega, k; \Lambda; v, e^2) = 0 \quad (11)
\]

where

\[
\beta_v(v, e^2) = \Lambda \frac{\partial Z_v}{\partial \Lambda} v_R \\
\beta_e(v, e^2) = \Lambda \frac{\partial Z_e}{\partial \Lambda} e_R \\
\gamma(v, e^2) = \Lambda \frac{\partial}{\partial \Lambda} \log Z_\Psi \quad (12)
\]

The well-known solution to this equation takes the form

\[
G(\omega, k; \rho \Lambda; v, e^2) = \exp \left\{ \int_0^\rho \frac{d\rho'}{\rho'} \gamma \right\} \quad G(\omega, k; \Lambda; v_{\text{eff}}(\rho), e_{\text{eff}}^2(\rho)) \quad (13)
\]

and the effective parameters are given by
\[ \rho \frac{\partial}{\partial \rho} v_{\text{eff}}(\rho) = -\beta v_{\text{eff}}(v_{\text{eff}}, e_{\text{eff}}^2) \]

\[ \rho \frac{\partial}{\partial \rho} e_{\text{eff}}(\rho) = -\beta e_{\text{eff}}(v_{\text{eff}}, e_{\text{eff}}^2) \] (14)

Increasing the scale \( \rho \) of the cutoff is equivalent to measure the observables of the theory at large distance scale. From the one-loop order results of the previous section we see that \( e_{\text{eff}} \) remains constant, while \( v_{\text{eff}} \) does not. We expect, therefore, the effective coupling of the electronic interaction \( e^2/(4\pi v) \) to have a nontrivial renormalization group flow in the infrared regime. Actually, from equations 7 and 12,

\[ \rho \frac{\partial}{\partial \rho} v_{\text{eff}}(R) = \frac{1}{16 \pi} e^2 + O \left( \frac{e^4}{v_{\text{eff}}^2} \right) \] (15)

so that the asymptotic behaviour of the coupling is:

\[ \frac{1}{4\pi v_{\text{eff}}} (\Lambda/\Lambda_0) = \frac{1}{4\pi v_0} e^2 \left( 1 - \frac{1}{8\pi v_0} \log \frac{\Lambda}{\Lambda_0} \right)^{-1/2} \] (16)

Here, \( \Lambda \) is the energy at which the effective parameters are defined.

The behavior of the coupling constants as function of energy, eq. (13), is a consequence of the screening processes which take place within the graphite sheet. The effective coupling is reduced at low energies and long distances. The increase in the Fermi velocity leads to a reduction in the density of states near the Fermi points, which can be thought of as the tendency towards the formation of a Coulomb gap. A true gap, however, does not exist.

The fact that the electromagnetic interaction becomes comparatively weaker at long distances implies that our results, although perturbative, are qualitatively correct at low energies. The initial coupling is large in dimensionless units (see below), but is reduced as the renormalization proceeds. Hence, below a given scale, our results, which have been calculated to order \( e^4 \), are valid. We can not predict quantitatively, however, the relation between the coupling at that scale and its bare value.

The flow of the parameters towards the weak coupling fixed point resembles the flow in QED. In fact, even a "Landau pole" appears, if the equations are iterated towards the ultraviolet. This pole is not too far above the bare parameters. It probably signals a phase transition for sufficiently large initial couplings. We should also remark that the flow of the Fermi velocity towards large values is bounded by the velocity of light. At this point, the model becomes Lorentz invariant. This symmetry should be preserved by the subsequent renormalization flow.

The fact that the propagators acquire non trivial exponents should be reflected in all physical properties. For instance, the temperature dependence of the specific heat will differ from the \( T^2 \) law expected in this semimetal, and the exponent will no longer be an integer.

The one electron propagator is of special importance, as it measures the coherence of the quasiparticles, and also governs the hopping processes to other molecules or planes away from the one being considered. The local density of states in the non interacting case is \( \text{Im}G(\omega) \sim |\omega| \). This power law is changed to \( \text{Im}G(\omega) \sim |\omega|^{1 + O(e^4/(\hbar a)^2)} \). This appearance of anomalous exponents resembles closely the features of a one dimensional Luttinger liquid. It reflects the same physical processes, namely, the absence of a coherent quasiparticle pole.
near the Fermi level. Thus, the system is not truly metallic, although it does not exhibit a gap either. This result implies, among other things, a significant reduction in the effective hopping elements to an external system, as discussed extensively in connection to Luttinger liquids [16].

V. APPLICATION TO FULLERENE MOLECULES.

In fullerene molecules, a number of factors not considered so far play a role:
- The initial value of the coupling constant, $e^2/(\tau a) \sim 4$ is large, although in a perturbative scheme it appears divided by numerical factors greater than unity. As mentioned earlier, the existence of a large initial coupling does not change qualitatively the low energy features of the model. Screening processes reduce this values, until a scale is reached below which perturbation theory is applicable. The actual exponents associated to physical quantities, however, will depend on the value of the coupling at this scale, which cannot be obtained perturbatively.
- In a finite system, the typical dimensions act like an infrared cutoff, below which scaling is not applicable. This is a severe restriction for the $C_{60}$ molecule, whose radius, $R \sim 3.2\text{Å}$ is close to the distance between carbon atoms, which is the initial cutoff. Thus, the renormalization scheme is only a qualitative guide to the role of electron-electron interactions in this molecule. It suffices, however, to rule out models based on the existence of strong metallic screening beyond the C-C separation, like the Hubbard model. The renormalization flow, on the other hand, should be more precise for the larger fullerene molecules, which may exhibit the unconventional features reported here.
- In doped systems, the finite density of states at the Fermi level allows for metallic screening. The best known cases are the family of alkali doped $C_{60}$, $A_3C_{60}$, where $A$ stands for an alkali metal. Then, the doping concentration is 1/40 electrons per site and per spin. That means that the Fermi is equal to $k_F = a^{-1}\sqrt{4\pi/(15\sqrt{3})} \sim 2\text{Å}$. Using the density of states for a linear dispersion relation, we can define a screening length: $k_F^{-1} \sim 3.4\text{ Å}$. This number is similar than the radius of the molecule, so that metallic screening should not play a significant role. Alternatively, we can use the density of states of $K_3C_{60}$ from band structure calculations [15]. Its value is 25 eV$^{-1}$ per $C_{60}$ molecule. This number is higher than the estimate given above. Hence, we find $k_{FT} \sim 1\text{Å}$. However, as discussed in [15], the high density of states is due to the hybridization of a single orbital from each $C_{60}$ molecule. The charge transfer between $C_{60}$ molecules in the presence of an electric field does not imply the existence of local, intramolecular rearrangements of the charge distribution, because the charge remains in this triply degenerate orbital.

These points restrict the application our results, obtained for infinite graphite sheets, to the $C_{60}$ compounds. However, some qualitative conclusions remain valid:
- The long range effects of the Coulomb interaction are significant, and cannot be neglected. From the preceeding sections, we can conclude that there is no screening length in isolated sheets of graphite. The inclusion of finite size effects, and of the doping does not change this result. The new length scales which appear when these phenomena are taken into account are of the order of the $C_{60}$ radius. Thus, the effective range of the Coulomb interaction is, at least, comparable to the size of each $C_{60}$ unit.
The absence of coherent quasiparticles implies the existence of strong shake up effects when electrons tunnel into the molecule. The behavior of the C$_{60}$ spheres resemble that of finite 1D Luttinger liquids. As discussed above, the flow of the coupling constants is towards a fixed point with no quasiparticle pole. Coherent quasiparticles cannot be defined at this fixed point. Finite size effects halt this flow before this situation is reached. However, its effects will be manifested in a variety of physical processes. The most relevant of them is, possibly, the reduction of the effective tunneling matrix between neighboring spheres. This is a consequence of the strong shake-up effects which are induced when a single electron is transferred between spheres [17–19]. The ration between the bare intermolecular tunneling element, $t_{\text{inter}}$, and the effective tunneling at low energies, $t_{\text{eff}}$, goes as $t_{\text{eff}}/t_{\text{inter}} \sim (\omega/\omega_c)^g$, where $\omega_c$ is the initial ultraviolet cutoff, proportional to the $\pi$ bandwidth, and $g$ is the exponent which characterizes the anomalous scaling of the density of states at low energies. As mentioned earlier, this scaling low cannot be continued to energies below a given cutoff. This cutoff is of the same order of magnitude as $ta/R$, where $t$ is the hopping between nearest neighbor $\pi$ orbitals on the same sphere, $a$ the interatomic distance, and $R$ the radius of the molecule. Thus, $\omega/\omega_c \sim a/R \sim 1/3$. From the fact that we are in the strong coupling regime, $e^2/(at) > 1$, we infer that $g$ is of order unity. Hence, these effects play a significant effect in renormalizing the effective hopping between C$_{60}$ molecules. Note that shake up effects cannot be studied within conventional band structure calculations.

VI. ACKNOWLEDGEMENTS

This work has been partially supported by the CICyT, Spain (grant MAT91-0905).
REFERENCES

[1] R. L. Hettich, R. N. Compton and R. H. Ritchie, Phys. Rev. Lett. 67, 1242 (1991).
[2] R. Saito, G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. B 46, 9906 (1992).
[3] V. P. Antropov, O. Gunnarson and O. Jepsen, Phys. Rev. B 46, 13647 (1992), see also
O. Gunnarson and G. Zwicknagl, Phys. Rev. Lett. 69, 957 (1992).
[4] G. N. Murphy and A. Auerbach, Phys. Rev. B 46, 331 (1992), G. N. Murphy and A.
Auerbach, Europhys. Lett. 19, 103 (1992).
[5] R. L. Martin and J. P. Ritchie, Phys. Rev. B 48, 4845 (1993).
[6] V. P. Antropov, O. Gunnarsson and A. I. Liechtenstein, Phys. Rev. B 48, 7651 (1993).
[7] S. Krummacher, M. Biermann, M. Neeb, A. Liebsch and W. Eberhardt, Phys. Rev. B 48,
8424 (1993).
[8] S. Chakravarty, M. Gelfand and S. Kivelson, Science 254, 970 (1991).
[9] R. Friedberg, T. D. Lee and H. C. Ren, Phys. Rev. B 46, 14150 (1992).
[10] J. González, F. Guinea and M. A. H. Vozmediano, Phys. Rev. Lett. 69 (1992) 172.
[11] J. González, F. Guinea and M. A. H. Vozmediano, Nucl. Phys B406, 771 (1993).
[12] F. Guinea, J. González and M. A. H. Vozmediano, Phys. Rev. B, 47, 16576 (1993).
[13] J. González, F. Guinea and M. A. H. Vozmediano, preprint.
[14] P. Ramond, Field Theory. A Modern Primer. (Benjamin/Cummings, London, 1981).
[15] R. P. Gupta and M. Gupta, Phys. Rev. B 46, 11835 (1993).
[16] X. G. Wen, Phys. Rev. B 42, 6623 (1990).
[17] C. L. Kane and M. P. A. Fisher, Phys. Rev. Lett. 68, 1220 (1992).
[18] M. Ueda and F. Guinea, Zeits. für Physik, 85, 413 (1991).
[19] M. Sasetti and U. Weiss, preprint.
FIGURES

Figure 1. Lowest order correction to the electron propagator (exchange term)

Figure 2. Lowest order correction to the electronic charge.