Electronic interactions in fullerene spheres

F. Guinea*

The Harrison M. Randall Laboratory of Physics, The University of Michigan, Ann Arbor, Michigan 48109-1120

J. González

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

M. A. H. Vozmediano

Departamento de Física Teórica, Facultad de Ciencias Físicas, Universidad Complutense,
Avenida Complutense s/n 28040 Madrid, Spain
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The electron-phonon and Coulomb interactions in C_{60} and larger fullerene spheres are analyzed. The coupling between electrons and intramolecular vibrations give corrections $\sim$ 1–10 meV to the electronic energies for C_{60}, and scales as R^{-4} in larger molecules where R is the radius of the fullerene sphere. The energies associated with electrostatic interactions are of order $\sim$ 1–4 eV in C_{60} and scale as R^{-1}. Charged fullerenes show enhanced electron-phonon coupling, $\sim$ 10 meV, which scales as R^{-2}. Finally, it is argued that not only $C_{60}{}^-$, but also $C_{60}{}^{2-}$ are highly polarizable molecules. The polarizabilities scale as R^3 and R^4, respectively. The role of this large polarizability in mediating intermolecular interactions is also discussed.

I. INTRODUCTION

Fullerene molecules are being discovered in an astonishing variety of sizes and shapes. The most frequently studied fullerene, C_{60} shows a number of unexpected electronic properties, most notably the fact that, when combined with many metallic elements, it gives rise to superconducting compounds. Recently, a number of other spherical shaped carbon molecules have been found.[1,2] In the present work, we discuss the most relevant interactions which influence the highest occupied electronic states in these molecules.

The analysis is based on earlier work[3,4] (hereafter referred to as I and II), which proposed a continuum scheme to analyze the properties of these molecules. The method makes use of the fact that simple, long-wavelength approximations to the electronic spectrum of graphite planes can be made. We showed that it is possible, in this way, to write down analytical expressions for the highest occupied and lowest unoccupied states of C_{60}. Moreover, the method is more accurate for larger molecules. In I, a brief outline of its usefulness for the study of the coupling between electrons and lattice vibrations was also sketched.

In Sec. II, we describe the most relevant features of the electronic states of C_{60}. The next section deals with the main properties of the coupling between electrons and phonons in *neutral* molecules. Section IV analyzes the electrostatic coupling between the electrons. Section V describes the electron-phonon couplings which appear in *charged* molecules. In Sec. VI we discuss the electronic polarizability of these molecules, and the interactions which may be relevant in a crystalline structure. The main conclusions are analyzed in Sec. VII.

II. THE ELECTRONIC STATES OF C_{60}

The electronic properties of conjugated carbon compounds are determined by the states derived from the unsaturated π orbitals at each carbon atom. The very successful Hückel model[5] uses this fact to describe a large variety of such materials, from benzene to conjugated polymers, like polyacetylene, to graphite. The most important parameter in the model is the hybridization energy between orbitals placed at nearest-neighbor carbons, which we will take as $t \sim 2.2$ eV. Longer-range hybridizations are neglected. The remaining three valence electrons in each C atom give rise to covalent σ bonds. These bonds give rigidity to the lattice. Their spring constant, K, is also well known, which allows a simple approximation to the vibration spectra of materials with only carbons, like graphite. We will assume for the highest frequency, $\omega_{opt} = 3\sqrt{K/M} = 0.20$ eV (M is the mass of a C atom). The electronic states derived from π orbitals are affected by the lattice vibrations, because they modify the distance between nearest atoms. This coupling is described by the variation of the hybridization t with distance. We will take $\partial t/\partial l = 4.5$ eV Å^{-1}. There is a greater controversy about the value of the on-site Coulomb repulsion, when two electrons occupy the same π orbital. In isolated fullerene molecules, metallic screening is absent, and the long-range electrostatic interactions dominate. We expect also no metallic screening at distances shorter than the intermolecule distance in C_{60} crystals. In contrast, screening effects will be significant in onionlike compounds, where the spheres are stacked inside each other.

The Hückel model, when applied to a plane of graphite, gives rise to two electronic bands which intersect at two

inequivalent points of the Brillouin zone. Near these points, the spectrum can be written as $\epsilon_k = \hbar v_F |\mathbf{k}|$, where $v_F = 3ta/\hbar$, and a is the distance between nearest carbon atoms. As discussed in I and II, this dispersion relation can be seen as arising from an effective long-wavelength equation, which is nothing but the Dirac equation in (2+1) dimensions. The two inequivalent points of the Brillouin zone lead to two independent equations. The components of each spinor correspond to the amplitude of the wave function in each of the two sublattices in which the honeycomb structure can be divided.

This long-wavelength approximation can be extended to spherical fullerenes. Naively, one would expect that the electronic states will be given by the solutions of the (2+1) Dirac equation on the surface of a sphere. The presence of pentagons in the lattice modifies this picture. When going around one of them, the two sublattices are interchanged. One of the components of the spinor associated with one point of the Brillouin zone is changed into the other component of the spinor associated with the second point. This effect can be included by means of an auxiliary gauge potential, whose magnetic flux threads each of the pentagons. Because of the mixing of the two electron spinor components, this field is non-Abelian. However, as discussed in II, a transformation is possible, which changes the two coupled Dirac equations into two decoupled ones, which include an Abelian monopole of opposite charge, $Q = \pm 3/2$.

These equations can be solved analytically, by means of suitably defined angular momentum operators. The resulting spectrum has two degenerate triplets at $\epsilon = 0$, and a succession of higher multiplets, with degeneracies $2 \times (2j + 1), j = 2, 3, \ldots$ and energies $\epsilon_j = \pm v_F/R\sqrt{j(j+1) - 2}$. R is the radius of the molecule. The wave functions described by this long-wavelength approximation correspond to the envelope of the real wave functions. In order to recover the tight-binding states, one has to multiply the continuum wave functions by a rapidly fluctuating phase, determined by the Bloch states of a plane of graphite at the corners of the Brillouin zone. This phase can be obtained by inverting the procedure discussed in II: The atomic sites of C_{60} can be thought of as the sites of a honeycomb lattice wrapped over the surface of an icosahedron. The surface of the icosahedron can be unfolded, and projected onto a plane. Then, the initial atomic positions fill sites of an extended, planar, honeycomb lattice. The phases of each spinor at each site can be described in terms of the phases of the Bloch states from the corners of the Brillouin zone of planar graphite. The phase change between two nearest equivalent sites is $\pm 2\pi/3$.

As extensively analyzed in I and II, this spectrum is a reasonably good approximation to spherical carbon fullerenes, becoming more accurate as the number of atoms in the molecule increases. In particular, for C_{60}, the two degenerate triplets at $\epsilon = 0$ mentioned above can be identified with the lowest low-lying molecular orbitals in the molecule. The fact that these two triplets are split in C_{60}, and that they are not strictly at $\epsilon = 0$, can be understood as arising from the next leading cor-

rections to the Dirac equation. These corrections modify the spectrum of graphite away from the Fermi points. They contain additional derivatives. When included into our effective Dirac equation for the spherical fullerenes, they give rise to a coupling between the two triplets, and an overall shift. The fact that this interpretation is correct can be seen from the way in which these terms scale with the radius of the molecule. The splitting of the two triplets shows the expected R^{-2} dependence for all sizes, including C_{60}. The behavior of the average energy is more involved, and the proposed scaling seems to set in only for large sizes (C_{540} and beyond).

In this way, we complete our description of the two lowest unoccupied triplets in C_{60} and related molecules. In lowest order, they correspond to the states at zero of the Dirac equation on the surface of a sphere, with an additional monopole of charge $Q = \pm 3/2$. Their wave functions are

$$
\begin{aligned}
\Psi^\alpha_{+1,a} &= \sqrt{\tfrac{3}{8\pi}}\sin^2(\tfrac{\theta}{2})e^{i\phi}, & \Psi^\beta_{+1,a} &= 0, \\
\Psi^\alpha_{0,a} &= \sqrt{\tfrac{3}{4\pi}}\sin(\tfrac{\theta}{2})\cos(\tfrac{\theta}{2}), & \Psi^\beta_{0,a} &= 0, \\
\Psi^\alpha_{-1,a} &= \sqrt{\tfrac{3}{8\pi}}\cos^2(\tfrac{\theta}{2})e^{-i\phi}, & \Psi^\beta_{-1,a} &= 0, \\
\Psi^\alpha_{+1,b} &= 0, & \Psi^\beta_{+1,b} &= \sqrt{\tfrac{3}{8\pi}}\cos^2(\tfrac{\theta}{2})e^{i\phi}, \\
\Psi^\alpha_{0,b} &= 0, & \Psi^\beta_{0,b} &= -\sqrt{\tfrac{3}{4\pi}}\sin(\tfrac{\theta}{2})\cos(\tfrac{\theta}{2}), \\
\Psi^\alpha_{-1,b} &= 0, & \Psi^\beta_{-1,b} &= \sqrt{\tfrac{3}{8\pi}}\sin^2(\tfrac{\theta}{2})e^{-i\phi}.
\end{aligned}
\tag{1}
$$

The superscripts α and β refer to the two components of each spinor, and the subscripts label each of the six different wave functions.

The residual interactions described earlier can be projected onto the subspace spanned by these six states. There is a global shift, which scales as $k_1 t(R_0/R)^2$, and a hybridization between spinors of type a and b with the same angular momentum. It can be written as $k_2(R_0/R)^2$. R_0 is the radius of C_{60}, and the dimensionless coefficients k_1 and k_2 can be deduced from the spectrum of C_{60}. Their values are 1.53 and 0.09, respectively.

III. ELECTRON-PHONON INTERACTION IN NEUTRAL MOLECULES

We now describe the influence of the various lattice vibrations in the states given in Eq. (1). It is interesting to note first that the hopping t, and any modulation of it, couple orbitals in different sublattices. To lowest order, the orbitals given by (1) represent electronic states which combine wave functions derived from one point in the Brillouin zone and one sublattice, and wave functions from the other point and the other sublattice. The hopping does not mix them, and that is why their energies are at zero. Thus, the only electron-phonon interactions possible, *for these triplets*, arise from the modification, by the phonons, of the next-order terms, which were described before. This effect was not properly included in I.

The states in Eq. (1) are delocalized throughout the

sphere, and change little from site to site. Hence, they will only couple to long-wavelength phonons. The graphite planes, which we use as a starting point, have two acoustic and two optical branches near the center of the Brillouin zone, which we will consider separately.

The acoustical modes are well described by the elastic theory of spherical shells, as mentioned in I. They can be parametrized in terms of fields which give the lattice displacements at each point in the sphere: $\mathbf{u} = [u_r(\theta, \phi), u_\theta(\theta, \phi), u_\phi(\theta, \phi)]$. On general grounds, we can classify them using vector spherical harmonics for the functions u_θ and u_ϕ, and ordinary spherical harmonics for u_r. For each value of l and m, the calculation of the eigenmodes is reduced to the diagonalization of a 3×3 matrix. The simplest vibration is the breathing mode, $l = m = 0, u_r = u, u_\theta = u_\phi = 0$. This mode simply changes the radius of the sphere. We know that the lowest-order coupling possible is through the modification of the electronic interactions within the triplets which decay like R^{-2}, as discussed in the previous section. Thus, it is straightforward to describe the coupling of the breathing mode to the lowest-lying triplets given in Eq. (1). To leading order in u/R, their mean energy and splitting depend on u as

$$\bar{\epsilon} = k_1 \frac{\partial t}{\partial l} u \frac{R_0^2}{R^2},$$

$$\Delta \epsilon = k_2 \frac{\partial t}{\partial l} u \frac{R_0^2}{R^2}. \tag{2}$$

For a general mode, the coupling to the electrons can only depend on the strain tensor, given by

$$u_{\theta,\theta} = u_r + \partial_\theta u_\theta,$$

$$u_{\phi,\phi} = u_r + \frac{\partial_\phi u_\phi}{\sin(\theta)} + \frac{\cos(\theta)}{\sin(\theta)} u_\theta,$$

$$u_{\theta,\phi} = \partial_\theta u_\phi + \frac{\partial_\phi u_\theta}{\sin(\theta)} - \frac{\cos(\theta)}{\sin(\theta)} \mu_\phi. \tag{3}$$

We now make the assumption that the way the strain tensor changes the electronic levels is through its only scalar contraction, $u_{\theta,\theta} + u_{\phi,\phi}$. Physically, this quantity describes the local variation in the area of the sphere. Generalizing the coupling to the breathing mode, discussed before, and particularizing in the changes in $\bar{\epsilon}$, which is the largest effect, we write

$$\mathcal{H}_{\text{el-phon(acc)}} = 2k_1 \frac{\partial t}{\partial l} \sum_{\alpha, i} \int (u_{\theta,\theta} + u_{\phi,\phi}) \Psi_i^{\alpha *} \Psi_i^{\alpha}. \tag{4}$$

For an elastic vibration with a given l and m, $u_{\theta,\theta} + u_{\phi,\phi} \propto Y_l^m(\theta, \phi)$. Given the shape of the wave functions [Eq. (1)], this result implies that only modes with $l = 0, 1, 2$ couple to them.

We can now estimate the change in the electronic levels due to each lattice mode, using second-order perturbation theory. From $\langle u^2 \rangle = \hbar/(2M\omega)$ (M is the mass of the molecule) the characteristic energy shift induced by a mode of frequency ω is $(k_1 \partial t/\partial l)^2/(2M\omega^2)$. For C_{60}, typical phonon frequencies are in the range 500–1000 cm^{-1}. The associated shifts are of order 1–5 meV. The dimensionless electron-phonon coupling parameter,

λ, is ≤ 0.1 per mode.

In larger molecules, $M \sim R^2$ and $\omega \sim R^{-1}$. Hence, the shifts will decay as R^{-4} and $\lambda \sim R^{-3/2}$. Note that the number of acoustic modes which couple to the states studied here does not scale with the size of the molecule, because the characteristic dimension of the electronic wave function is always proportional to the radius of the sphere.

The estimates discussed before point to a weak coupling between the acoustical modes and the lowest-lying electronic states of spherical fullerenes. This effect can be traced back to the low density of states of graphite near the Fermi level. For instance, the lowest-order coupling between the triplets in Eq. (1) and phonons vanishes, but is finite for other multiplets at higher energies. Furthermore, the extended nature of these wave functions implies that few modes can couple to them.

In molecules with one or two electrons in these states, another effect may arise. As discussed in I, the degeneracy of the allowed states gives rise to a Berry phase which modifies the quantization rules for the lattice vibrations. The combined electron and phonon wave function changes its symmetry with respect to the case of no electron degeneracy. As a consequence, Raman and infrared modes are exchanged, an effect which can be verified experimentally.

Finally, we discuss the coupling to optical modes. At each point in the sphere they can be characterized by its polarization, longitudinal or transverse, which can be defined as a two-dimensional vector field, $\mathbf{n}(\theta, \phi)$. We will neglect the out-of-the-sphere modes. It is simple to calculate the coupling between this field and the spinors which describe the electronic states in planar graphite. It gives rise to a term in the Hamiltonian,

$$\mathcal{H}_{\text{el-opt}} = \int \bar{\psi} \boldsymbol{\sigma} \mathbf{n} \psi, \tag{5}$$

where the σ's are the Pauli matrices. As in the case of the acoustical modes, this term does not modify, to lowest order, the triplets given in Eq. (1).

We can estimate the residual coupling by explicitly changing the hoppings in the discrete Hamiltonian which describes C_{60}, simulating the presence of an optical phonon. The simplest such mode alters the pentagon-hexagon and the hexagon-hexagon bonds in opposite directions. In order for the area of the sphere to stay constant, the pentagon-hexagon bond deformation should be close to one-half that of the hexagon-hexagon bonds. The change in the average energy of the lowest triplets, with respect to such a modification of the hoppings, is $\partial \bar{\epsilon}/\partial t = 0.9$. On general grounds we can expect this derivative to be of order unity. In our continuum formulation, such coupling can be incorporated into the formalism by a term

$$\mathcal{H}_{\text{el-phon(opt)}} = 2k_3 \frac{\partial t}{\partial l} \sum_{\alpha, i} \int \left(\partial_\theta n_\theta + \frac{\partial_\phi n_\phi}{\sin(\theta)} \right.$$
$$\left. + \frac{\cos(\theta)}{\sin(\theta)} n_\theta \right) \Psi_i^{\alpha *} \Psi_i^{\alpha}, \tag{6}$$

where $k_3 = 0.9$. As in the case of acoustical phonons,

this expression makes clear that only modes with small l, m values couple to the triplets considered here.

The change in the energy of the electronic states is $\sim (k_3 \partial t/\partial l)^2/(2M\omega_{\text{opt}}^2)$. Taking $\omega_{\text{opt}} = 0.20$ eV, this energy is ~ 40 meV. The dimensionless coupling λ is $\sim 0.2 - 0.3$ per mode. These values for the energies and dimensionless couplings should be independent of the size of the molecule. Note that ω_{opt} does not scale with R, and $M \sim R^2$.

The combined coupling to all phonons compares well with more detailed calculations for C_{60}.[6-8] Our definition of the dimensionless coupling λ is $\partial t/\partial l \sqrt{\hbar/(M\omega^2)}/(\hbar\omega)$, where ω is the frequency of the mode under consideration. This is equivalent to the formulas used in Refs. 6–8, in the limit when the coupling is local and the electronic bandwidth tends to zero.

IV. COULOMB INTERACTIONS IN CHARGED FULLERENES

From Eq. (1) it is simple, although tedious, to calculate the different Coulomb integrals between orbitals. The needed integrals are discussed in the Appendix. A variety of estimates are available in the literature, and our results come close to those reported in Ref. 9. In fact, if we neglect the splitting between the two triplets, we obtain, for $C_{60}{}^{2-}$, exactly the same succession of multiplets as in that reference, in what is called also *the continuum approximation*. We believe that the scheme used in Ref. 9 is equivalent to ours, in that the same wave functions are used. Thus, for $C_{60}{}^{2-}$ the lowest configurations are two $^1s_+$ and $^1s_-$ singlets at $3e^2/5R_0$, followed by two $^3p_+$ and $^3p_-$ triplets, at $7e^2/10R_0$. The splitting between these two sets of configurations is generated by the second-order term which couples the one-electron triplet states, discussed after Eq. (1). An effective Hamiltonian which describes each symmetry (^1s and ^3p) is given in the Appendix. These terms are also responsible for the splitting of the triplets in $C_{60}{}^-$. In the doubly ionized molecule, however, this term induces a much weaker effect. The coupling of the two degenerate singlets is through an intermediate state at $8e^2/5R_0$, and the coupling between the triplets is mediated by another triplet at $6e^2/5R_0$. In both cases, the splitting goes like $\Delta\epsilon^2/(e^2/R_0)$. For large fullerenes, $\Delta\epsilon \sim R^{-2}$, and this splitting decays like R^{-3}. Further details can be found in the Appendix.

Our method is sufficiently simple to allow us to calculate electrostatic energies of molecules with higher charge. For $C_{60}{}^{3-}$, we find, at low energies, two ^4s multiplets. The electrostatic energy is $21e^2/10R_0$. The splitting between these two configurations is even smaller than in $C_{60}{}^{2-}$, and goes like $\Delta\epsilon^3/(e^2/R_0)^2$. For large fullerenes, this value scales as R^{-4}. In molecules with higher ionization, the splittings grow again.

Finally, our simple form for the wave functions (1) allows us to characterize the charge distribution of the molecule. The two orbitals with angular momentum in (1) carry an electric dipole, $eR_0/2$. It is easy to show that the two ^3p multiplets discussed for $C_{60}{}^{2-}$ carry the same dipole. The existence of these large dipoles is an amusing consequence of the fact that the orbitals given in (1) sim-

ulate the state of electrons in a fictitious magnetic field, described by the monopole. These orbitals are not chiral invariant. A given angular momentum also induces an electric dipole. The terms responsible for the mixing of these orbitals restore the chiral symmetry. As mentioned before, the influence of these terms is significantly reduced in $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$, and in larger fullerenes. The relevance of these dipoles for intermolecular interactions will be discussed in Sec. VI.

The scale of electrostatic energies, given the radius of C_{60}, $R_0 \sim 3.5$ Å is large, ~ 3 eV. We have not investigated the extent to which the level structure of the spheres needs to be modified. For larger fullerenes, both the separation between one-electron levels and the Coulomb energies scale in the same way, $\sim R^{-1}$, so both remain comparable for all sizes.

An alternative method, used to classify the multiplets of the C_{60} molecule, is to use spherical harmonics and crystal-field terms.[10,11] This scheme is equivalent to using a continuum approximation for the bottom of the graphite band (the point $\mathbf{k} = 0$ in the Brillouin zone), and filling all the levels up to the required charge state. Our method has the right multiplicity and symmetry for the relevant orbitals near the neutral state, as it starts from an approximation which describes graphite near its Fermi energy. Moreover, the separation between levels, which in other schemes arises from crystal-field effects, appears in a natural way, and its scaling as a function of size can be easily investigated. In that respect, we differ somewhat from the assumptions about scaling in Ref. 11.

In onion-shaped materials, the energy levels are affected by the tunneling between contiguous layers. The energy of these processes is, in graphite, ~ 0.3 eV.[12] The Coulomb interactions will be more drastically changed by the appearance of screening effects.

V. ELECTRON-PHONON INTERACTION IN CHARGED FULLERENES

In charged fullerenes, the deformations of the lattice-induce rearrangements in the charge distribution, which modify the Coulomb energies. As discussed in the previous section, these energies are important, so that this effect needs to be taken into account. This effect is unique to systems like the doped fullerenes, which combine localized electronic states and inhomogeneous charge distributions. Hence, other conjugated compounds, like graphite intercalates, offer no clue to the strength of this coupling.

These modifications in the charges over scales comparable to the size of the molecule can only be induced by long-wavelength acoustical phonons. Optical modes redistribute the charge within each unit cell, but do not alter the overall charge distribution.

The leading effect of a deformation of the lattice is to change locally the area element. The charge density in that region is then modified. Again, we can discuss this effect by taking the simplest lattice vibration, the breathing mode, as an example. The area of the sphere is expanded or contracted, and the Coulomb energies change due to the variation in the radius of the sphere. There is no effect in $C_{60}{}^-$. In $C_{60}{}^{2-}$, the change of energy as-

sociated with a vibration of amplitude u is $\sim e^2 u/R_0^2$. For a general mode, the charge density at a given place decays as the area element increases. The local expansion induced by a given mode is $u_{\theta,\theta} + u_{\phi,\phi}$. Thus, we have to insert this expression in the Coulomb integrals between different orbitals. As in the case of the standard coupling to acoustical phonons, this result implies that only vibrations with $l \le 4$ can couple to the triplets given by Eq. (1).

We can make an estimate of the energy shift in the electronic levels in the same way as in the case of the modification in the hybridization due to the vibration. The only difference is that the factor $(k_1 \partial t/\partial l)^2$ has to be replaced by $(e^2/R_0^2)^2$. The second factor is larger by a factor of 8–10. Thus, the energy scales at which this coupling can play a role are ~ 20–40 meV. The values of the dimensionless constant λ will become $\sim 0.8 - 1$. These interactions are significantly larger than the standard electron-phonon couplings. The energies should scale as R^{-4} for large molecules, and the values of λ as $R^{-3/2}$.

VI. INTERACTIONS BETWEEN DIFFERENT FULLERENE MOLECULES

So far, we have discussed the various electronic interactions within a given fullerene molecule. It is interesting to analyze which ones may play a role when different molecules are close to each other. As the most important influence that we have found is due to the Coulomb interaction, we will analyze further its role in this case.

We will assume that charge that the fullerenes may have is compensated by some neutralizing background, so that the only residual interaction is due to the van der Waals forces. Then, the relevant magnitude is the electrical polarizability of the molecules. As mentioned in Sec. IV, C_{60}^- is highly polarizable, a result also discussed in Ref. 9. Also, C_{60}^{2-} has a large polarizability, if the molecule is in a ^3p state. An estimate of the polarizabilities of various charged states of fullerenes is given in Table I. These polarizabilities are due to the extra electrons which are present in charged C_{60} molecules. The polarization of the closed shell in neutral C_{60} has been estimated[13] to be ~ 80 Å$^3 \sim 300$ a.u., that is, significantly smaller than the values we find for C_{60}^- and C_{60}^{2-}.

The high polarizability of C_{60}^{2-} can play a role, if the interaction between neighboring molecules overcomes the energy difference between the ^1s and the ^3p configurations. This difference is $e^2/(10R_0) \sim 0.5$ eV, as discussed in Sec. IV. The van der Waals interaction between two molecules at distance D is $\sim e^4 R_0^4/(4D^6 \epsilon_p)$, where ϵ_p is the splitting between the two ^3p configurations, $\sim 2\Delta\epsilon^2/(e^2/R_0)$ (see the Appendix for details of the calculation). Hence, the van der Waals energy is $\sim 5e^6 R_0^3/(4D^6 \Delta\epsilon^2)$, where $\Delta\epsilon \sim 0.40$ eV, as discussed in Sec. II. Even for $D = 4R_0$, this energy is ~ 0.2 eV, and increases rapidly at shorter distances. Thus, it is not inconceivable that C_{60}^{2-} will exist in its ^3p state in a doped crystal, and neighboring molecules will interact strongly through their mutual dipoles.

VII. CONCLUSIONS

We have investigated the various interactions which may influence the electronic properties of a fullerene molecule. The relevant energies and the scaling as a function of molecule size are given in Table II.

Our results suggest that the most relevant effects will arise from the Coulomb interactions. The weakness of the electron-phonon coupling can be related to a similar effect in graphite, due to the vanishing density of states near the Fermi *points*. Phonons can only play a significant role in charged molecules, where they modify the charge distribution.

On the other hand, long-range Coulomb interactions have no counterpart in other conjugated compounds. The most studied charged (through doping) carbon systems, graphite intercalation compounds and polyacetylene, do not show these features. In both cases, the relevant electronic states are delocalized, and are not susceptible to charging effects.

We have pursued further the role of Coulomb interactions in crystalline systems. The most striking effect that we have found is the extremely high polarizability of C_{60}^{2-} molecules. This property leads to significant intermolecular interactions at distances $\sim 3 - 4$ times the radius of the molecule. The scale of these couplings, ~ 0.3–3 eV, can easily overcome most other efffects in a doped C_{60} crystal, and may be even responsible for the unusual dipolar moments found in neutral C_{60}.[14] Its role in other properties, like superconductivity, is being further investigated.

TABLE I. Typical energy scales associated with the various interactions discussed in the text, for C_{60}, and scaling of each of them as function of molecule radius, for larger fullerenes.

Interaction	Energy	Scaling
Electron-phonon (acoustic)	0.004 eV	R^{-4}
Electron-phonon (optical)	0.04 eV	R^0
Coulomb	3–6 eV	R^{-1}
Electron-phonon (in charged molecules)	0.1 eV	R^{-4}

TABLE II. Polarizability (of the valence electrons) in different charge states of C_{60} (in atomic units), and scaling behavior for larger molecules.

Charge state	Polarizability (in a.u.)	Scaling
Neutral (^1s)	0	R^0
1 e^- (^2p)	10^3	R^4
2 e^- (^1s)	0	R^0
2 e^- (^3p)	10^5	R^5
3 e^- (^4s)	0	R^0

APPENDIX: CALCULATION OF COULOMB INTEGRALS

The Coulomb integrals required to evaluate the energies of the various configurations of charged C_{60} can be obtained from the wave functions given in Eq. (1). We denote the six orbitals in that equation as $|a, +1\rangle$, $|a, 0\rangle$, $|a, -1\rangle$, $|b, +1\rangle$, $|b, 0\rangle$, and $|b, -1\rangle$, where we are omitting spin indexes. The Coulomb potential can be expanded in spherical harmonics, $1/|\mathbf{r}_1 - \mathbf{r}_2| = 4\pi \sum_l 1/(2l + 1) \sum_m Y_l^{-m}(\hat{r}_1) Y_l^m(\hat{r}_2)$, where we are using the fact that $|\mathbf{r}_1| = |\mathbf{r}_2| = 1$, and we use units such that $R_0 = 1$. Then, the seven different Coulomb integrals are (in units of e^2/R_0):

$$v_{a+1,a+1;a+1,a+1} = v_{a+1,a+1;b-1,b-1} = \frac{63}{50},$$

$$v_{a+1,a+1;a0,a0} = v_{a+1,a+1;b0,b0} = \frac{49}{50},$$

$$v_{a+1,a+1;a-1,a-1} = v_{a+1,a+1;b+1,b+1} = \frac{19}{25},$$

$$v_{a+1,a0;a+1,a0} = \frac{7}{25}, \qquad \text{(A1)}$$

$$v_{a+1,a0;b+1,b0} = -\frac{11}{50},$$

$$v_{a+1,a-1;a+1,a-1} = \frac{3}{50},$$

$$v_{a0,a0;a0,a0} = v_{a0,a0;b0,b0} = \frac{26}{25}.$$

The remaining integrals can be obtained by exchanging the a and b indices.

As mentioned in Sec. IV, this procedure leads to the multiplet energies for $C_{60}{}^{2-}$ discussed in Ref. 9. The wave functions with ^1s symmetry are

$$|1\rangle = \frac{1}{\sqrt{3}}(|a + 1 \uparrow, a - 1 \downarrow\rangle - |a0 \uparrow, a0 \downarrow\rangle$$
$$+ |a - 1 \uparrow, a + 1 \downarrow\rangle),$$

$$|2\rangle = \frac{1}{\sqrt{6}}(|a + 1 \uparrow, b - 1 \downarrow\rangle - |a + 1 \downarrow, b - 1 \uparrow\rangle$$
$$+ |a - 1 \uparrow, b + 1 \downarrow\rangle - |a - 1 \downarrow, b + 1 \uparrow\rangle$$
$$- |a0 \uparrow, b0 \downarrow\rangle + |a0 \downarrow, b0 \uparrow\rangle), \qquad \text{(A2)}$$

$$|3\rangle = \frac{1}{\sqrt{3}}(|b + 1 \uparrow, b - 1 \downarrow\rangle - |b0 \uparrow, b0 \downarrow\rangle$$
$$+ |b - 1 \uparrow, b + 1 \downarrow\rangle).$$

These three states are mixed by the term in the C_{60} Hamiltonian which gives rise to the splitting of the two triplets, $\Delta\epsilon$. Thus, we end up with the matrix

$$\mathcal{H}_{1_s} = \begin{pmatrix} \frac{3e^2}{5R_0} & \frac{\Delta\epsilon}{\sqrt{2}} & 0 \\ \frac{\Delta\epsilon}{\sqrt{2}} & \frac{8e^2}{5R_0} & \frac{\Delta\epsilon}{\sqrt{2}} \\ 0 & \frac{\Delta\epsilon}{\sqrt{2}} & \frac{3e^2}{5R_0} \end{pmatrix}. \qquad \text{(A3)}$$

Similarly, the states with ^3p symmetry are

$$|1\rangle = |a + 1 \uparrow, a0 \uparrow\rangle,$$

$$|2\rangle = \frac{1}{\sqrt{2}}(|a + 1 \uparrow, b0 \uparrow\rangle + |b + 1 \uparrow, a0 \uparrow\rangle), \qquad \text{(A4)}$$

$$|3\rangle = |b + 1 \uparrow, b0 \uparrow\rangle,$$

and the corresponding effective Hamiltonian is

$$\mathcal{H}_{3_p} = \begin{pmatrix} \frac{7e^2}{10R_0} & \frac{\Delta\epsilon}{\sqrt{2}} & 0 \\ \frac{\Delta\epsilon}{\sqrt{2}} & \frac{6e^2}{5R_0} & \frac{\Delta\epsilon}{\sqrt{2}} \\ 0 & \frac{\Delta\epsilon}{\sqrt{2}} & \frac{7e^2}{10R_0} \end{pmatrix}. \qquad \text{(A5)}$$

For the purposes of the discussion in Sec. VI, it is important to realize that the states $|1\rangle$ and $|3\rangle$ in (A4) carry an electric dipole, $\pm eR_0/2$.

*On leave from Instituto de Ciencia de Materiales, CSIC, Cantoblanco, 28049 Madrid, Spain.

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