Continuum Approximation to Fullerene Molecules

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(Received 17 March 1992)

The electronic and elastic properties of large fullerene molecules are studied. The low-lying electronic levels are described by the Dirac equations in (2+1) dimensions, and the intramolecular modes are given by the theory of elasticity. Coupling between electrons and phonons can also be written in a simple way. The quantum dynamics of the ions is modified by the appearance of nontrivial Berry's phases. The qualitative features of fullerenes with elliptical and cylindrical geometries, and minimal surfaces with negative curvature are also studied.

PACS numbers: 75.10.Jm, 75.10.Lp, 75.30.Ds

Newly discovered large carbon molecules [1] have attracted a great deal of attention because of their unusual properties, the most widely studied being C_{60}. Many other structures have been synthesized or proposed [2-6]. They share the fact that they resemble locally graphite planes.

In the present work, we present a systematic approach to quasi-two-dimensional sheets of carbon atoms with threefold coordination and arbitrary geometry. We exploit the fact that the electronic and elastic properties of a single graphite plane have simple descriptions in the continuum limit: The electronic spectrum coincides with that of the Dirac equation in (2+1) dimensions. The elastic properties can be analyzed within the continuum theory of elasticity [7]. Thus, it seems reasonable to try a similar approach for systems which closely resemble curved graphite planes. While the resulting electronic states and atomic vibrations are always an approximation limited by finite-size effects, the scheme is general and applies to any large fullerene molecule. We will illustrate the utility of our method by using it to analyze the electron-phonon coupling in the C_{60} molecule. The degeneracies induced by the symmetries of this molecule give rise to a number of interesting effects, like the appearance of a Berry phase when quantizing the lattice degrees of freedom. This approximation also gives interesting insights into the nature of the frustration induced by fivefold rings inserted in the honeycomb lattice. These rings, which are required to close the C_{60} sphere, introduce fictitious monopole fields, when analyzed within a continuum framework.

We assume that the electronic properties of fullerenes are well described in terms of three σ bonds per atom, and one unpaired π state. In the neutral state, there is one electron per π bond. This is the standard Debye-Hückel model used for graphite and many other unsaturated organic compounds. Only hopping between nearest neighbors will be taken into account. The macroscopic elastic constants are mostly due to the stiffness of the σ bonds. The coupling between the ionic vibrations and the π electrons takes place through the modulation in the hopping terms induced by the motion of the lattice. We take as typical parameters, $t=2.5$ eV for the π-π hopping, $\partial t/\partial l=4.5$ eV/Å for the derivative of the hopping with respect to the interatomic distance, and the bond stiffness is defined such that the top of the acoustic band coincides with the observed frequency of the optical phonon, $\omega_{\mathrm{opt}}=1600\ \mathrm{cm}^{-1}$.

It is well known that the bands of a graphite plane, linearized around the corners of the hexagonal Brillouin zone reduce to the solutions of two independent Dirac equations in 2+1 dimensions [8]. This is the region of energies where the Fermi surface (more precisely, points) lies at half filling.

The local lattice structure of the fullerenes synthesized or proposed resembles closely that of graphite. Each atom has threefold coordination, and most of the cage is tiled by rings of six atoms. As we create new fullerenes by inflating the old ones, we should recover the electronic structure of graphite [1]. On the other hand, all the fullerenes grown from the C_{60} have twelve pentagons, placed always at the same relative positions. The spinors acquire a nontrivial phase when rotated around each of the pentagons which is a reflection of the fact that the intrinsic curvature of the lattice is accumulated in the pentagon sites. These transformation properties can be reproduced by an effective magnetic monopole field of half-integer charge. The complete description of the electronic structure leads to the study of the Dirac equation in the presence of a monopole field, on the geometry of the sphere.

The Dirac equation on the sphere with a magnetic gauge field is [9] $i\gamma^\mu \nabla_\mu \psi = \epsilon\psi$, γ^μ being two-dimensional Dirac matrices satisfying $\{\gamma^\mu,\gamma^\nu\}=2g^{\mu\nu}$ and ∇_μ being covariant derivatives including spin and gauge connections. Taking the monopole field as $A_\theta=0$, $A_\phi=l/2\cos(\theta)$, the resulting Dirac equation reads

$$A^+\psi_\uparrow=\left[i\partial_\theta-\frac{1}{\sin(\theta)}\partial_\phi+\frac{i(1+l)\cos(\theta)}{2\sin(\theta)}\right]\psi_\uparrow=R\epsilon\psi_\downarrow\,,$$
$$A\psi_\downarrow=\left[i\partial_\theta+\frac{1}{\sin(\theta)}\partial_\phi+\frac{i(1-l)\cos(\theta)}{2\sin(\theta)}\right]\psi_\downarrow=R\epsilon\psi_\uparrow\,, \tag{1}$$

where the unit of energy is $3ta/2R$, t is the π-π hopping energy, a is the distance between neighboring carbon atoms, and R is the radius of the sphere. The integer l stands for twice the charge of the monopole.

Equation (1) can be solved by means of the operators

$$\begin{aligned} J^+ &= e^{i\phi}\partial_\theta + ie^{i\phi}\frac{\cos(\theta)}{\sin(\theta)}\partial_\phi + e^{i\phi}\frac{l-1}{2\sin(\theta)}\,, \\ J^- &= -e^{i\phi}\partial_\theta + ie^{-i\phi}\frac{\cos(\theta)}{\sin(\theta)}\partial_\phi + e^{-i\phi}\frac{l-1}{2\sin(\theta)}\,, \\ J^z &= -i\partial_\phi\,, \end{aligned} \tag{2}$$

because the square of Eq. (1) can be written as

$$A^+A = \mathbf{J}^2 - (l^2-1)/4\,. \tag{3}$$

Thus, the solutions of (1) can be expressed as eigenvalues of a generalized angular momentum operator [10]. The monopole, however, restricts the possible values of the angular momentum, so that $j \geq ||l|-1|/2$. This result implies that the multiplicity of the states at zero is equal to l.

We now determine the value of l by analyzing the spectrum of graphite spheres of different sizes. The low energy levels of different inflated fullerenes are shown in Fig. 1.

The states closest to zero are two triplets, which tend to become degenerate at zero energy as the molecule becomes larger. The next states converge towards two degenerate quintuplets at positive and at negative energies. This is the spectrum obtained from Eq. (1) when $|l|=3$. A detailed discussion of the reasons for this value of l will be given elsewhere [10]. Here, we will take as a given fact that $|l|=3$ is the best choice to adjust the spectra of the fullerenes.

The observed doubling of the spectrum is due to the fact that, for every solution with $l=+|l|$, there is another one with opposite chirality and $l=-|l|$. In terms of the original graphite planes, each of these solutions arises from one of the two inequivalent Fermi points.

The differences between the continuum and the discrete calculations are due to perturbations associated to the discreteness of the lattice. We consider two such effects to be the most relevant: (i) a spherically symmetric coupling between the two Dirac equations, which splits each multiplet in two, and (ii) deviation from spherical symmetry, which distorts the high j multiplets. Also, even for flat graphite planes, the Dirac equation ceases to be a good approximation at energies of order t, so that only the lowest lying states can be well described in C_{60}. That suffices, however, to study the most relevant electronic features of lightly doped systems, in which the conduction band of the crystal is derived from the lowest triplet. The eigenfunctions for this triplet are

$$\begin{aligned} \psi_\downarrow &= \sqrt{3/4\pi}\cos^2(\theta/2)e^{i\phi}, \quad \psi_\uparrow = 0\,, \\ \psi_\downarrow &= \sqrt{3/2\pi}\sin(\theta/2)\cos(\theta/2), \quad \psi_\uparrow = 0\,, \\ \psi_\downarrow &= \sqrt{3/4\pi}\sin^2(\theta/2)e^{i\phi}, \quad \psi_\uparrow = 0\,, \end{aligned} \tag{4}$$

The elastic energy can be expressed in terms of the strain tensor,

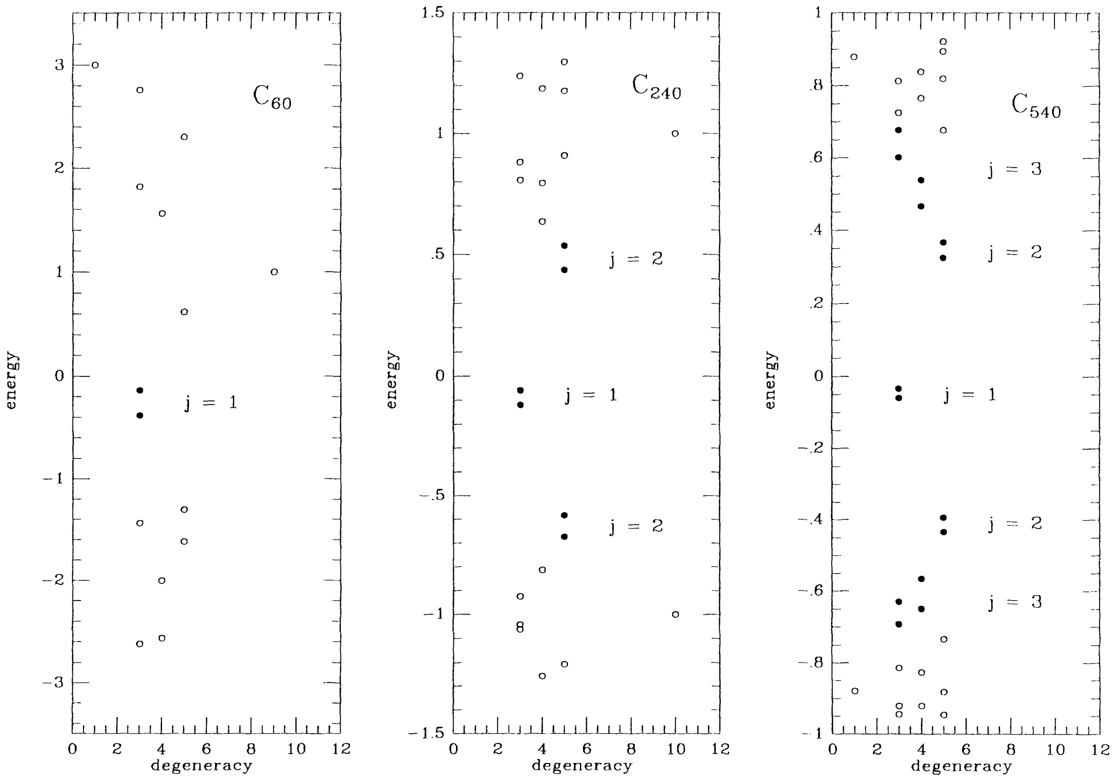

FIG. 1. Low-energy spectrum of different carbon spheres derived from the C_{60} structure. Vertical axis: energies in units of t. Horizontal axis: multiplicity of each state. Full dots are states which can be identified with solutions of the Dirac equation.

$$
\begin{aligned}
u_{\theta\theta} &= u_r + \partial_\theta u_\theta ,\\
u_{\phi\phi} &= u_r + \frac{1}{\sin(\theta)}\partial_\phi u_\phi + \frac{\cos(\theta)}{\sin(\theta)} u_\theta ,\\
u_{\theta\phi} &= \partial_\theta u_\phi + \frac{1}{\sin(\theta)}\partial_\phi u_\theta - \frac{\cos(\theta)}{\sin(\theta)} u_\phi ,
\end{aligned}
\tag{5}
$$

and the Lamé coefficients, λ and μ. Because of the simplified central force model which we use, $\mu = 0$. After some tedious, but straightforward, calculations, we obtain the modes of longest wavelength:

$$
\begin{aligned}
&u_r = b,\quad u_\theta = u_\phi = 0 \ \text{(breathing mode)} ,\\
&u_r = b_x \sin(\theta)\cos(\phi),\quad u_\theta = -b_x \cos(\theta)\cos(\phi),\\
&\qquad\qquad u_\phi = +b_x \sin(\phi) ,\\
&u_r = b_y \sin(\theta)\sin(\phi),\quad u_\theta = -b_y \cos(\theta)\sin(\phi),\\
&\qquad\qquad u_\phi = -b_y \cos(\phi) ,\\
&u_r = b_z \cos(\theta),\quad u_\theta = b_z \sin(\theta),\quad u_\phi = 0 .
\end{aligned}
\tag{6}
$$

Within our model, the frequency of the first mode (of A_g symmetry) is $\omega = \omega_{\text{opt}} a\sqrt{3/2}/R$, and the other three modes are degenerate, building a F_{2u} triplet, with frequency $\omega = \omega_{\text{opt}} a\sqrt{3}/R$, where a is the C-C distance, and R is the radius of the sphere. Taking $a/R \sim 0.3$, we obtain 500 and 700 cm^{-1}, respectively. These modes are the ones of lowest energy which induce a significant change in the local surface element, given by $u_{\theta\theta} + u_{\phi\phi}$. Other low-energy modes have only shear components. As discussed in the next section, coupling to the electrons takes place through modifications in the surface area. Thus, we expect that these modes are the most relevant to the study of the electron-phonon coupling in C_{60}. The frequencies we obtain are in reasonable agreement with more detailed calculations [11–13].

To lowest order in the atomic displacements, two types of coupling to the electrons are allowed by symmetry: a scalar-scalar interaction $(u_{\theta\theta} + u_{\phi\phi})\bar{\psi}\psi$, and a tensorial coupling, $u_{\mu\nu}\bar{\psi}\gamma^\mu \not{\partial}^\nu \psi$. However, doping only changes the occupation of the lowest triplet, for which one of the spinor components vanishes, as discussed before. Hence, the only coupling that we need to analyze is the first one, which describes the change that a local dilatation induces in the electronic wave functions.

In addition to conventional electron-phonon coupling effects, the degeneracy of the electronic states gives rise to nontrivial Berry's phases in the quantum dynamics of the ions. For simplicity, let us consider the quantization of the threefold degenerate vibrations given in Eq. (6). Let us assume that a given deformation is labeled by b_x, b_y, and b_z, in terms of the amplitudes of each of these vibrations. If the C_{60} molecule has an unpaired electron in this triplet, it will tend to be in the combination of the wave functions given in Eq. (4) of lowest energy. The potential induced by the vibration on the electrons, when projected onto the lowest-lying triplet reads

$$
\mathcal{H}_{e\text{-phon}} = \frac{3}{4}\frac{a^2}{R^2}\frac{\partial t}{\partial l}
\begin{pmatrix}
b_z & (b_x + i b_y)/\sqrt{2} & 0\\
(b_x - i b_y)/\sqrt{2} & 0 & (b_x + i b_y)/\sqrt{2}\\
0 & (b_x - i b_y)/\sqrt{2} & -b_z
\end{pmatrix} ,
\tag{7}
$$

where we are using Eq. (3) to represent the electronic states.

The ground state of Eq. (7) is given by

$$
|\Psi\rangle = \tfrac{1}{2}\{[1+\cos(\theta)]e^{i\phi}, \sqrt{2}\sin(\theta), [1-\cos(\theta)]e^{-i\phi}\}
\tag{8}
$$

in an obvious notation. The energy eigenvalue is $\epsilon = -(3a^2/4R^2)\partial t/\partial l (b_x^2 + b_y^2 + b_z^2)^{1/2}$. We can estimate the relevance of this coupling by assuming that $|\mathbf{b}|^2 \sim \hbar/M\omega$, where M is the total mass of the molecule, and ω the frequency of the vibration. Using the values of the parameters discussed in the introduction, we find $\epsilon \sim 0.08$ eV, so that it is a significant effect.

Following Berry [14], the quantum dynamics of the b's include a gauge potential, defined as $A_\phi = \langle\Psi|i\partial_\phi|\Psi\rangle = \cos(\theta)$. This potential defines a monopole of charge 1 at the point $b_x = b_y = b_z = 0$. Its effect is to eliminate the lowest-lying solution with zero angular momentum.

The continuum approximation used here can be extended to a variety of different geometries. We discuss the ones already observed, or proposed.

(i) Elliptical fullerenes.—The above equations can be reformulated in elliptical coordinates. However, it is more intuitive to analyze this shape in terms of its deviation from the spherical symmetry discussed above. An elliptical deformation in which a principal axis differs from the other two splits the triplet which builds up the conduction band of the fullerenes into a doublet and a singlet. If the resulting shape resembles a football, like in C_{76}, the doublet will be lower in energy. When the deformation gives rise to a pancakelike object, the singlet will be occupied first upon doping. In both cases, we expect a reduction in the conduction bandwidth, so that crystals made of these molecules, when doped, should be poorer conductors than the spherical ones.

The existence of chirality, like in C_{76}, does not change the doublet mentioned earlier, but modifies the symmetry of the wave functions. Each orbital in this doublet has a finite angular momentum along the axis of the molecule, $j_z = \pm 1$. In the absence of chiral symmetry, each orbital will accumulate charge at a given pole. Thus, if the molecules, when doped, acquire a finite angular momentum, a charge dipole will also appear. This coupling between the orbital motion and the charge distribution is unique to molecules without chiral symmetry, and may give rise to novel and interesting effects.

(ii) A cylindrical shape reduces to periodic boundary conditions for the Dirac equation.—If the number of atoms around the surface is odd, the two sublattices of the graphite structure are exchanged when going around the cylinder. In this case, a fictitious solenoid needs to be located at the center of the tube, to induce a rotation of the spinors. The graphite bands split into a set of one-dimensional bands, one for each allowed value of $k_\phi = 2\pi n$. The lowest band gives rise to a finite density of states at zero energy, $N(\epsilon_F = 0) \sim a/Rt$, in agreement with detailed calculations [6]. The change in the vibration spectrum can be obtained in a similar way.

(iii) Surfaces with negative curvature.—These systems build a three-dimensional periodic structure. The solutions can be expressed in terms of Bloch functions, once the Dirac equation in the unit cell is solved. It is more intuitive, as in the case of the sphere, to consider the square of the Dirac equation. In the absence of fictitious fields, this equation reduces to Laplace's equation on the curved surface. We expect that the frustration effects induced by the sevenfold rings will give rise to the existence of gauge fields, which will be similar to that of monopoles located at the nodes of the 3D lattice which defines the overall structure. The charge of these monopoles will depend on the type of frustration which generates the curvature.

The solutions with lowest energy correspond to long-wavelength modes of the modified Laplace's equation. These are band edges, embedded in a 3D Brillouin zone. If the structure has cubic symmetry, the dispersion relation must be $\epsilon_{\mathbf{k}}^2 = \mathrm{const} \times t^2 a^2 (k_x^2 + k_y^2 + k_z^2)$, a being the C-C distance. Distortions from cubic symmetry may give rise to anisotropic "masses." Note that the replacement of the Dirac equation by its square is crucial to the argument. In that way, the relevant eigenstates are located at band edges, which can be described by simple symmetry arguments. By taking the square root of the previous expression, we obtain the solutions of the Dirac equations, $\epsilon_{\mathbf{k}} \sim ta|\mathbf{k}|$. An effective *three-dimensional* Dirac equation will describe the low-energy electronic spectrum of the model. We expect that this description will remain valid until wave vectors $|\mathbf{k}| \sim L^{-1}$, where L is the lattice constant of the 3D lattice. At energies greater than ta/L a complicated structure of bands and gaps, determined by the gauge field and the curvature, will appear. Below this scale the density of states per atom near the Fermi level will vary as $N(\epsilon) \sim |\epsilon^2|/t^3$. The system is a semimetal, with vanishing density of states at the Fermi level.

In conclusion, we have shown how the electronic structure and long-wavelength vibrations of fullerene molecules can be analyzed within a simple and unified framework. The method that we have outlined is useful to gain information about the states at the Fermi level, the vibrations to which they are more strongly coupled, and the nature of the coupling itself. The scheme is not specific to a given molecule, and provides an easy way to study trends within fullerene classes, and similarities between molecules of different geometries.

From a theoretical point of view, we show unexpected relations between the properties of the fullerenes and the quantum mechanics of Dirac fermions in a curved geometry. At a more practical level, we predict that carbon sheets with negative curvature will be semimetals, with lower density of states at the Fermi level than graphite, and we show that the size and symmetry of C_{60} give rise to nontrivial Berry's phases.

We are thankful to CICyT (Comisión Interministerial de Ciencia y Tecnología) for financial support.

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