PHYSICAL REVIEW B VOLUME 45, NUMBER 3 15 JANUARY 1992-I

Polarons in C_{60}

Barry Friedman

*Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5504**
and Department of Physics, Sam Houston State University, Huntsville, Texas 77341†

(Received 13 June 1991; revised manuscript received 8 August 1991)

A simple Su-Schrieffer-Heeger-type model of C_{60} and doped C_{60} is presented. The model is solved numerically in the adiabatic approximation. In the half-filled case the cluster dimerizes, in agreement with experiment and more complicated calculations. When an electron is added to half-filling, a polaron is present in the ground state. This polaron possesses an unusual geometry; it is a loop circling the C_{60} cluster. For two added electrons a bipolaron forms with a similar geometry. It is suggested that this bipolaron may be observable in optical experiments.

There has been much recent interest in the molecule C_{60} and slightly doped C_{60}.[1,2] Adding to this interest is the discovery that by doping C_{60} with electrons it becomes a high-temperature superconductor.[3,4] This discovery poses a number of questions: How is doped C_{60} different and similar to other high-T_c materials? Is the superconductivity in C_{60} surprising and to what extent is it to be expected? Unfortunately, at present, to address these questions theoretically is very difficult. Instead, I will present a simple model that describes some of the normal-state properties of C_{60} and doped C_{60}. Simple consequences of this model will be presented and finally I will discuss the rather speculative relation of this model to high-T_c materials. The most important point of this work is that C_{60} should have very interesting properties when "doped" with light. In the model, doping with light will cause the formation of an unusual elementary excitation, the string bipolaron. Hopefully, this bipolaron will be accessible to experiment.

The model I propose is a simple variant of the Su-Schrieffer-Heeger (SSH) model of conducting polymers (for a review see Ref. 5). From our experience with conducting polymers I expect electron-phonon coupling to be the dominant interaction (that is, I neglect electron-electron interaction). Furthermore, I expect that for a good part of the physics of solid C_{60} I can neglect intermolecular hopping (again by analogy to conducting polymers where a good part of the physics can be described neglecting the interchain coupling). We are then led to the Hamiltonian

$$H=\tfrac{1}{2}k\sum_{\langle ij\rangle}(l_{ij}-a)^2 + \sum_{\langle ij\rangle}[-t+\alpha(l_{ij}-a)](c_{is}^{\dagger}c_{js}+c_{js}^{\dagger}c_{is}) + \text{kinetic energy of the lattice}\,. \qquad (1)$$

Here, l_{ij} is the length of the bond connecting the ith and jth sites (see Fig. 1), k is the "spring" constant, t is the hopping matrix element, a is the unrenormalized carbon-carbon bond length, the c's and $c^{\dagger}$'s are fermion annihilation and creation operators, and α is the electron-phonon coupling constant.

As is well known, to treat this Hamiltonian without approximation is difficult; for the purposes of this study I use the adiabatic approximation and treat the lattice (the l_{ij}'s) as classical degrees of freedom. Again by analogy with conducting polymers I expect this to be reasonable at least for some properties. Under this approximation I look for values of the X_k's $\equiv l_{ij}-a$ satisfying

$$\frac{\partial}{\partial X_k}\langle\Psi|H|\Psi\rangle=0 \qquad (2)$$

such that the energy is a minimum. (Ψ is the wave function for the electronic degrees of freedom, which, under the adiabatic approximation, consists of a single Slater determinant.) There are 90 distinct bonds so (2) is a system of 90 equations. Under this approximation the kinetic energy of the lattice does not enter and thus we leave it unspecified. Since we are using bond variables (and the adiabatic approximation) the geometry of the molecule enters only insofar as it tells us which sites are connected by bonds to other sites. We do not have to deal with the positions of carbon atoms in three-dimensional space.

I do not expect the above approximation to tell us

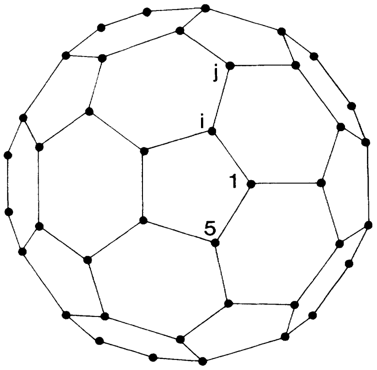

FIG. 1. One side of the C_{60} molecule. The length of the bond connecting sites i and j is denoted by l_{ij}. This figure is essentially taken from Ref. 6. Note i,j is a h-h bond (it separates a hexagon from a hexagon) while 1,5 is a p-h bond (it separates a pentagon from a hexagon).

much about superconductivity (see, however, the comments below). When we move beyond treating the lattice classically it is necessary to specify the lattice kinetic energy. At least for model calculations it may be possible to use the simple (albeit unrealistic form) $\frac{1}{2}M\sum_i(dX_i/dt)^2$ where M is a phenomenological mass parameter. Such a model may be amenable to treatment using fermion Monte Carlo calculations (see, for example, recent[7,8] calculations on the Holstein model). To treat electron-electron interactions it may be reasonable to add an on-site Hubbard repulsion.[9] In the adiabatic approximation, such a term can be handled perturbatively for Hubbard U sufficiently small. In the case of hole doping,[10] such a term appears to be important. Since this paper is my first study of the Hamiltonian (1) for C_{60} (and I study electron doping) I neglect the Hubbard repulsion leaving this term for a later investigation.

I now turn to the results of my calculation. In these calculations the parameter values $t=1$ (energy is measured in units of the hopping parameter), $\alpha=2$, and $k=25$. These parameter values are of the same order of magnitude as the analogous parameters in polyacetylene. In describing hopping between pentagons and hopping within pentagons the same parameter t is used. Any difference in the length of the bonds arises from the coupling of the electrons to the "lattice" by α.

We consider first the undoped C_{60} molecule. Since carbon has four valence electrons it is believed one should assign one electron to each site of the C_{60} cluster, that is, C_{60} is half-filled. (For all known high-T_c materials there is a parent insulating compound which is half-filled.) In the tight-binding model ($\alpha=0$) there is a gap of $0.76t$ separating the valence band (the 30 filled orbitals in the unique ground state) from the conduction band. (For a picture of the complete spectrum see Ref. 6.) When $\alpha=2$ the gap increases to $0.93t$ and the lattice "dimerizes." (That is, two distinct bond lengths arise.) More precisely, bonds separating a pentagon from a hexagon (*p*-*h* bond) become longer relative to the bonds separating hexagons (*h*-*h* bond). From the unrenormalized carbon-carbon bond a the *p*-*h* bond is shortened $\approx 0.075a$ while the *h*-*h* bond is shortened $\approx 0.099a$. Thus for the parameter values I have chosen the differences in bond lengths is ≈ 0.034 Å (assuming an unrenormalized carbon-carbon bond length of 1.4 Å). This is in fair agreement with the experimental measurement[11] (≈ 0.04 Å). I performed these calculations by numerically iterating Eq. (2). (By tuning the parameter values one should be able to get better agreement with experiment.) This calculation is consistent with more microscopic (and more complicated) molecular-dynamics calculations.[12] We thus see at half-filling the ground state is ordered due to bond dimerization. This is analogous to the antiferromagnetism in the cuprates and the charge-density wave ordering in the bismuthates. In graphite no such ordering is present in the undoped case, thus it is not surprising that doped graphite has a much lower T_c relative to doped C_{60}. To clarify this point I have examined a simple model of graphite, namely, I have considered a single graphite plane and used a SSH-type Hamiltonian Eq. (1) (here the tight-binding model corresponds to a two-dimensional honeycomb). To make this model amenable to solution and for purposes of comparison to C_{60} I have made the adiabatic approximation and have considered a 5×5 cluster (25 hexagons) with periodic boundary conditions and the same parameter values as I used for C_{60}. For this model I find, for half-filling, there is no type of bond alternation; each bond is uniformly shrunk approximately $0.084a$.

Another important point to note is that the ground state of C_{60} is unique. Thus C_{60} is more similar to *cis*- rather than *trans*- polyacetylene.

What happens when we add electrons to the C_{60} molecule? First consider the case of one added electron. By iterating numerically I find the lowest energy state is no longer completely dimerized. There is instead a polaronic excitation. This polaronic excitation has an energy of $\approx 0.01t$ lower than adding one electron to the rigid dimerized state and thus should be observable at moderately low temperature (since an order-of-magnitude estimate of t is 2 eV this means temperatures of approximately 100 K). From our experience with *cis*- polyacetylene and the molecular crystal mode[13] it is not surprising that a polaron forms when C_{60} is doped with an electron. The interesting feature of this polaron is its geometry. Namely, the order parameter (the degree of bond stretching) is depressed mainly in a loop circling the C_{60} cluster (see Fig. 2). It is therefore not inappropriate to call this polaron a string polaron. Precisely what I mean by order-parameter depression is the following: Form the order parameter Y_i by subtracting the average bond contraction at half-filling ($\approx 0.087a$) from each of the X_i's and then normalizing (divide by $0.012a$). In the half-filled case the Y_i corresponding to *h*-*p* bonds will have value 1 while the Y_i corresponding to *h*-*h* bonds will have value -1. For the string polaron, the Y_i's are between 0.47 and 0.41 in absolute value with the *h*-*p* bonds on the polaron being positive and the *h*-*h* bonds being negative. All other bonds on the cluster have $|Y_i|>0.75$. The single-particle energy spectrum is affected in the way one would expect for a polaron: one state is pulled up into the gap by $\approx 0.02t$ while another state is pulled down into the gap by roughly the same amount.

It would be interesting to construct an analytic argument for the existence of such a polaron; unfortunately, the evidence at present is solely numerical. (All calculations were performed in double precision ≈ 14 digits of accuracy and thus I believe the calculations are quite reliable.)

When I add a second electron, the lowest energy state is a string bipolaron (see Fig. 2). That is, the order parameter is most drastically changed in a ring around the C_{60} molecule. The bipolaron resembles the polaron with the difference being that the "ditch" in the order parameter is deeper for the bipolaron. That is, the order parameter for the bonds on the bipolaron (the Y_i's for the bipolaron) has values between 0.07 and 0.11 while the bonds on the rest of the cluster have the absolute value of the order parameter in excess of 0.6. On the bipolaron the value of the Y_i's alternates in sign as one goes from one bond to another, for *h*-*h* bonds the Y_i's are positive while

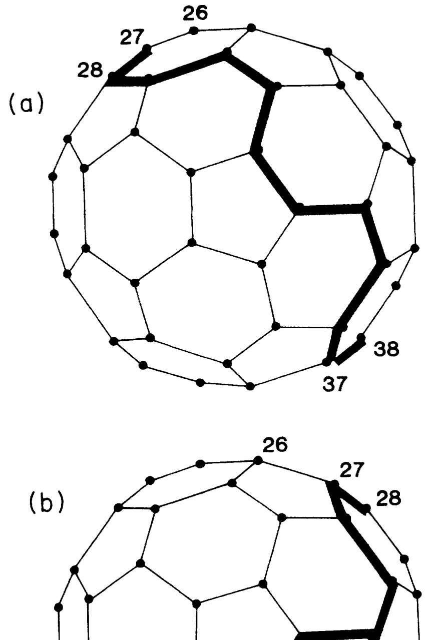

FIG. 2. The string polaron and bipolaron. The heavy curve indicates the path in which dimerization is suppressed for the string polaron and bipolaron (the path is the same in both cases). (a) is the front of the molecule while (b) is the back. The numbers indicate how the front and back are glued together. Note that the position of the string depends on the initial choice of the X_i's in the iterative scheme.

for *h-p* bonds the Y_i's are negative. I have tried several initial conditions and the self-consistent solution with the lowest energy is the string bipolaron. It has an energy of $\approx 0.04t$ lower than adding two electrons to a dimerized rigid band. There are also self-consistent solutions of a different geometry $\approx 0.0002t$ higher in energy than the string bipolaron.

Recall[6] that for the tight-binding model for C_{60} six added electrons fill the lowest "band" above the half-filled Fermi sea. It is thus not without interest to consider what happens when we add six electrons to half-filling. In this case I find perfect dimerization has been restored with the *h-p* bonds being shrunk $0.0823a$ and the *h-h* bonds being shrunk $0.0816a$. The difference in bond lengths is much less than in the half-filled case (about 3%) and here *h-h* is the longer bond. I expect since this bond difference is so slight it will prove to be unobservable. Thus effectively the picture is that starting from a dimerized situation at half-filling the addition of six electrons destroys the dimerization.

Finally we consider the case relevant to "doping" by light, i.e., we keep 60 electrons (half-filled) but we now make a particle-hole excitation from the highest occupied to the lowest unoccupied single-particle energy level. Iterating Eq. (2) from the initially dimerized solution we again go to the string bipolaron solution. In this case the string bipolaron solution $\approx 0.04t$ lower in energy than the energy of the particle-hole excitation in the rigid band. [Starting from other initial conditions we can find other self-consistent solutions slightly higher ($0.01t$) than the string bipolaron. I have also done dynamical calculations using the simple form proposed earlier for the kinetic energy and overdamped classical dynamics. Starting from the initially dimerized state the lattice relaxes rapidly to the string bipolaron. Note that in an optical experiment the dimerized initial state is the physically correct initial state.] I expect if one excites a C_{60} molecule with a pulse from a laser[14] it may be possible to observe the string bipolaron.

What do these calculations tell us about superconductivity? Given the existence of the polaron and bipolaron it is not surprising that electrons have a negative binding energy (i.e., $\Delta = 2E_1 - E_2 - E_0 \approx 0.02t$, there is a tendency for particles to form bound states). The interpretation of this negative binding energy is not unambiguous. Very loosely speaking it is an indication of a tendency toward superconductivity. In the adiabatic approximation, the Holstein model possesses a polaron and bipolaron solution as well a negative binding energy near half-filling.[13] Recent fermion Monte Carlo calculations have indicated an elevated critical temperature near half-filling[7] (recall a half-filling there is a charge-density wave). I expect a similar scenario for doped C_{60} where one replaces "charge density" by the bond ordering present in undoped C_{60}. In this scenario high T_c is due basically to effects within a single C_{60} molecule. Here I am viewing a single C_{60} molecule as being analogous to the 8×8 cluster studied in Ref. 8. This is perhaps not unreasonable since one expects a small coherence length due to the fairly high T_c and low carrier density.

I thank Dr. Greg Levine and Dr. W. P. Su for stimulating discussions. This work was partially supported by the Robert A. Welch Foundation and by the Texas Center for Superconductivity at the University of Houston under Prime Grant No. MDA 972-88-G-0002 to the University of Houston from the Defense Advanced Research Projects Agency and the State of Texas.

---

[*] Present address.

[†] Permanent address.

[1] H. W. Kroto *et al.*, Nature (London) **318**, 162 (1985).

[2] W. Kratschmer *et al.*, Nature (London) **347**, 354 (1990).

[3] A. F. Hebard *et al.*, Nature (London) **350**, 600 (1991).

[4] M. J. Rosseinsky *et al.*, Phys. Rev. Lett. **66**, 2830 (1991).

[5] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W. P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[6] V. Elser and R. C. Haddon, Phys. Rev. A **36**, 4579 (1987).
[7] G. Levine and W. P. Su, Phys. Rev. B **43**, 10413 (1991).
[8] R. M. Noack, D. J. Scalapino, and R. T. Scalettar, Phys. Rev. Lett. **66**, 778 (1991).
[9] S. Chakravarty and S. Kivelson (unpublished).
[10] P. M. Allemand *et al.*, Science **253**, 301 (1991).
[11] J. M. Hawkins *et al.*, Science **252**, 312 (1991).
[12] Q. M. Zhang, J. Y. Yi, and J. Bernhole, Phys. Rev. Lett. **66**, 2633 (1991).
[13] G. Levine and W. P. Su, Phys. Rev. B **42**, 4143 (1990).
[14] L. Rothberg *et al.*, Phys. Rev. Lett. **57**, 3229 (1986).