RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 49, NUMBER 6 1 FEBRUARY 1994-II

Low-energy excitations of neutral C_{60}

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(Received 2 September 1993)

Low-energy excited states of a neutral C_{60} molecule are studied in detail. The system is described by a Su-Schrieffer-Heeger Hubbard-type Hamiltonian which is solved perturbatively in the electron-electron interactions. The optical-absorption spectrum is computed including both the direct and one-phonon-induced processes. Electronic-correlation effects are qualitatively important and, if and only if the electron-electron interaction is taken to be large enough, good agreement with experiments is achieved. Furthermore, it is shown that, in this model, the lowest-energy spin-triplet state is stable against decay due to a large Coulomb binding. Also, the theory predicts a triplet-triplet band about at 0.45 eV which, to my knowledge, has not yet been observed experimentally.

The mechanism of superconductivity in doped fullerenes is still an open problem although various mechanisms have been suggested: in general, they either emphasize the role of phonons[1] or electronic-correlation effects.[2] A related problem is the identification of the simplest model which incorporates the essential physics of these materials. My aim is to study a simple model for a neutral C_{60} molecule—a generalized version of the Su-Schrieffer-Heeger (SSH) Hubbard Hamiltonian[3]—which includes both the electron-electron and electron-phonon interactions of the shortest possible range.

Recently, the same model was used to study isotope effect in superconducting C_{60} when the attractive interaction is of purely electronic origin[4] and to investigate intramolecular properties of a neutral C_{60} molecule; in particular, the phonon spectrum, infrared absorption, and Raman scattering.[5] It was found that the model captures relevant features of fullerenes reasonably well, despite the fact that it does not contain Coulomb interactions between electrons on different sites. (Although the model Hamiltonian has been described elsewhere[5]—including the appropriate values of parameters—the model is defined and briefly reviewed in the Appendix.) These studies yielded reliable estimates of the electron-phonon coupling constants, which are crucial to the present study. However, reliable estimates of the strength of the electron-electron interaction could not be obtained since it was found that the phonon spectrum and related properties are rather insensitive to these interactions. From this standpoint, it is interesting to ask how the generalized SSH-Hubbard model can explain the excited states of a neutral C_{60} molecule and what effective value we should assign to the electron-electron interaction.

Since, as we shall see, the excited states are sensitive to the strength of the electron-electron interaction they *can* therefore be used to determine the interaction strength quite accurately. My main results are summarized in Table I which, for example, lists the calculated energies of the most interesting excited states for various values of the on-site Hubbard interaction U/t and the corresponding experimental values for solid C_{60}. I find the Hubbard U/t to be somewhere between 4 and 5. Indeed, good agreement with experiments is achieved even though the theory contains *only one* adjustable parameter, U/t.

There are at least two other theoretical studies[6,7] which consider the effect of the electron-electron interaction on the lowest-energy dipole-allowed optical transitions in a neutral C_{60} molecule. They also find that the electron-electron interaction is important in understanding experimental findings. However, considerable confusion has arisen in interpreting optical absorption spectra; for example, Friedman and Kim[7] interpret the first dipole-allowed transition to be around 3.7 eV. This is not surprising because it is the lowest-energy peak to have large enough intensity to be clearly observable in every experiment. Nevertheless, many experimental works[8–11] confirm the existence of a very weak peak at a lower energy, 3.0–3.2 eV. As can be seen from Table I, I find that for moderate to large U/t, there should exist a lowest en-

TABLE I. Theoretical values of excitation energies of the neutral C_{60} molecule as a function of U/t with $t=2.5$ eV and $t'/t=1.1$. The energies of the states are given relative to the ground state, while where a transition is indicated, the energy is the difference between the final and the initial spin-triplet states. $\mathcal{R}$ is the ratio of the transition intensities for the ground state to the state ${}^1T_{1u}(1)$ and the ground state to the state ${}^1T_{1u}(2)$ transitions. All theoretical values are computed by perturbation theory up to second order in U/t. Also shown are the corresponding experimental values (references are in square brackets).

		U/t		
Observable	0.0 (eV)	2.0 (eV)	4.5 (eV)	Expt. (eV)
${}^1T_{1u}(1)$ state	2.87	3.00	3.21	3.21 [8]
${}^1T_{1u}(2)$ state	3.16	3.32	3.51	3.65 [14]
${}^3T_{3g}(1)$ state	2.24	2.06	1.59	1.55 [18]
${}^3T_{3g}(1)\rightarrow{}^3G_u(1)$	0.63	0.60	0.45	not observed
${}^3T_{3g}(1)\rightarrow{}^3H_u(1)$	0.63	0.82	1.29	1.2 [19]
${}^3T_{3g}(1)\rightarrow{}^3H_u(2),{}^3G_u(2)$	0.92	$\begin{cases}1.08\\1.03\end{cases}$	$\begin{cases}1.63\\1.72\end{cases}$	1.65 [19]
${}^3T_{3g}(1)\rightarrow{}^3H_u(3),{}^3G_u(3)$	1.01	$\begin{cases}1.19\\1.23\end{cases}$	$\begin{cases}1.87\\1.99\end{cases}$	1.8 [19]
Intensity ratio $\mathcal{R}$	0.74	0.14	0.03	~0.06 [17]

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ergy peak with very small intensity (oscillator strength). Therefore, in comparing theory and experiment, I have made different assignments of the experimental peaks than Friedman and Kim.

In this paper, I focus on low-energy excitations below 4 eV. I therefore consider excited states which, in the single-particle picture, are composed from the electronic states of t_{1u} and t_{1g} symmetry and hole states of h_u, h_g, and g_g symmetry. Here t_{1u} and t_{1g} are the symmetries of the lowest and second-lowest unoccupied single-electron states of a neutral C_{60} molecule. Similarly, h_u, h_g, and g_g are the symmetries of the highest, second-highest, and third-highest occupied single-electron states. As a result of the electron-electron interaction, the excited states are further split into spin-singlet and -triplet states of T_1, T_3, G, and H symmetry.[12] Energies and transition amplitudes are calculated using nearly degenerate many-particle perturbation theory in powers of U/t.[13] First, the lattice fluctuations are ignored (a rigid-molecule approximation). As a consequence of icosahedral symmetry, a large number of topologically distinct diagrams in the perturbation expansion are identically zero which allows the calculations to be carried out *exactly* up to second order in U/t for both the energies and the transition amplitudes. Second, I study one-phonon-induced transitions. Unfortunately, the reduced symmetry now makes the calculations much more tedious and time consuming. Therefore, I truncate perturbation expansions at linear term in U/t. Below, all numerical examples are computed with $t=2.5$ eV and $t'/t=1.1$ where the hopping matrix element t is assigned to the bonds on the pentagons and t' to the bonds connecting two pentagons. A calculation with nearest-neighbor Coulomb interactions will be presented elsewhere.

SPIN-SINGLET STATES

Below 4 eV, there are only two states of ${}^1T_{1u}$ symmetry which can be excited directly by light from the ground state of a neutral C_{60} molecule. I label them as ${}^1T_{1u}(1)$ and ${}^1T_{1u}(2)$ with increasing energy. As an illustration, consider $U/t=4.5$ for which these two states have excitation energies 3.21 and 3.51 eV, respectively. The corresponding experimental values are 3.21 (Ref. 8) and 3.65 eV;[14] other values have been reported, too.[9–11] The agreement is good in comparison to any effective single-particle theory—such as the current model with $U/t=0$ (see Table I)—which demonstrates the importance of correlation effects beyond the mean-field level. (Notice that the complete neglect differential overlap for spectroscopy method,[6] which predicts the energies 3.4 and 4.1 eV, is quite satisfactory.)

Another interesting quantity is the electron-hole pair-binding energy which determines whether a state is stable against decaying into a $C_{60}^{\pm}$ pair. For the lowest-energy spin-singlet state (which has ${}^1G_g$ symmetry), its lower bound can be estimated from the observed energy difference between the photoconductive threshold and the optical band edge. For $U/t=4.5$, I find the binding energy to be 0.39 eV which is smaller than the experimental estimate.[15] The difference may be an experimental artifact or may indicate the importance of the longer range (intermolecular) Coulomb interactions in neutral C_{60} solid.

Next, consider the transition intensities I_1 and I_2 to the states ${}^1T_{1u}(1)$ and ${}^1T_{1u}(2)$. The ratio of transition intensities $\mathcal{R}$, defined as $\mathcal{R}=I_1/I_2$ and listed in Table I, drops sharply as a function of U/t. The rapid decrease of $\mathcal{R}$, which is almost exponential, comes from I_1 whereas I_2 is rather insensitive to the actual value of U/t. Third-order perturbation theory, which is necessary to compute the transition amplitudes to second order in U/t, has only a minor effect on $\mathcal{R}$. For instance, the difference between it and the second-order perturbation result is less than 5% up to $U/t=5$.[16] Again, for $U/t=4.5$, I find that $\mathcal{R}\simeq 0.03$ which is of the same order of magnitude as the measured value (~ 0.06).[17]

SPIN-TRIPLET STATES

The lowest-energy excited state of a neutral C_{60} molecule is the spin-triplet state of ${}^3T_{3g}$ symmetry which is labeled as ${}^3T_{3g}(1)$. For $U/t=4.5$, its energy is 1.59 eV. there is clear evidence that the onset of the excitation spectrum of a neutral C_{60} molecule is approximately at 1.55 eV,[18] which is close to my theoretical value. One can also test the stability of the state by computing the electron-hole pair-binding energy. I find the binding energy to behave as $E_b/t=0.034\,586(U/t)+0.009\,093(U/t)^2$. Already for $U/t=2$, one gets $E_b=0.26$ eV. This implies that, if $U/t>2$, the ${}^3T_{3g}(1)$ state cannot decay thermally into charged molecules at room temperature.

Due to the spin-orbit coupling, some of the excited spin-singlet states are transformed into spin-triplet states. Once the system gets into the spin-triplet manifold it cannot "leak out" radiatively due to the spin-selection rules. For example, the spin-triplet ground state—the ${}^3T_{3g}(1)$ state—has measured to have rather long lifetime, about 5 ms,[19] which allows studies of spin-triplet states at higher energies. Thus, one can perform spectroscopy on those states which can be excited from the spin-triplet ground state by light. According to group theory, they are states of ${}^3G_u$ and ${}^3H_u$ symmetries. As an example, consider $U/t=4.5$. I find that (i) the states ${}^3G_u(1)$ and ${}^3H_u(1)$, belonging to the $t_{1g}\otimes h_u$ manifold, have energies 0.45 and 1.29 eV above the ${}^3T_{3g}(1)$ state. (ii) Similarly, the states ${}^3H_u(2)$ and ${}^3G_u(2)$, belonging to the $t_{1u}\otimes h_g$ manifold, are located at 1.63 and 1.72 eV above the ${}^3T_{3g}(1)$ state. (iii) Finally, the states ${}^3H_u(3)$ and ${}^3G_u(3)$, belonging to the $t_{1u}\otimes g_g$ manifold, are located at 1.87 and 1.99 eV. Wei *et al.*[19] have observed photoinduced absorption bands at 1.65 and 1.8 eV while an additional band is seen at 1.2 eV in the C_{60} film. It is then plausible that the 1.2-eV band is formed by the ${}^3H_u(1)$ state, the 1.65-eV band by the ${}^3G_u(2)$ and ${}^3H_u(2)$ states, and the 1.8-eV band by the ${}^3G_u(3)$ and ${}^3H_u(3)$ states; see Table I. It may be difficult to resolve the doublet structure of the 1.65 and 1.8-eV bands due to solid-state effects. However, the above scheme makes it reasonable to expect asymmetric line shapes for the measured bands. Interestingly enough, there should exist another band approximately at 0.45 eV due to the ${}^3T_{3g}(1)\rightarrow{}^3G_u(1)$ transition; this so far lacks an experimental verification. Note that a quantum-chemical calculation gives consistently too large energies for these transitions.[20]

ONE-PHONON-INDUCED TRANSITIONS

It is evident from experiments[9,11,14] that there exists a large number of phonon-induced transitions which show up in the optical absorption spectrum as broad bands and shoulders. The most interesting ones are transitions to the $t_{1u}\otimes h_u$ manifold because they are forbidden in dipole approximation by parity and appear well below any dipole-allowed absorption lines; this makes them easy to observe. Figure 1 shows the results of a calculation which uses the adiabatic approximation and computes the fluctuating dipole moment to first order in U/t. Here $U/t=4.5$ and the rest of the parameters are as usual.[21] Indeed, I find structures which will appear in experiments as broad bands and shoulders. The one-phonon-induced transitions below 3.25 eV have about three times more oscillator strength than the direct ${}^1A_g\rightarrow{}^1T_{1u}(1)$ transition at 3.2 eV, whereas all one-phonon-induced transitions (below 4 eV) produce approximately as much oscillator strength as the direct dipole transitions to the ${}^1T_{1u}(1)$ and ${}^1T_{1u}(2)$ states together. In addition, the one-phonon peaks at 3.2 eV are almost as strong as the direct transition to the ${}^1T_{1u}(1)$ state. Also, notice the resemblance between the calculated and experimental phonon structure in the region at 2.8–3.5 eV.[22] Due to the strong phonon-induced transitions in this region, it is difficult to identify the direct dipole-allowed transition in the experimental data. There seems to be no apparent disagreement between above and recent quantum-chemical results.[23]

CONCLUSIONS

I have computed energies and intensities of the low-energy excitations in C_{60} using nearly degenerate perturbation theory up to second order in the electron-electron interaction. The results are summarized in Table I. Good agreement with experiments is found if the Hubbard interaction is large enough. Conversely, U/t can be determined to be about 4 and 5 for a neutral C_{60} molecule by requiring that (i) the energies of the ${}^1T_{1u}(1)$ and ${}^1T_{1u}(2)$ states are large enough, (ii) the transition intensity ratio into these states is small enough, (iii) and the lowest-energy state, namely the ${}^3T_{3g}(1)$ state, has low enough energy.

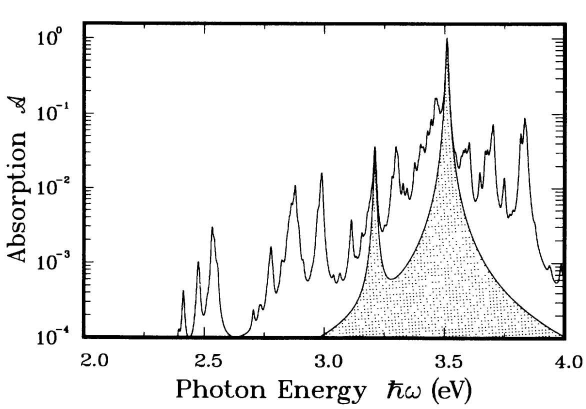

FIG. 1. Absorption spectrum of a neutral C_{60} molecule including the direct and one-phonon-induced transitions at $U/t=4.5$ (Ref. 21). The shaded region highlights the contribution due to the direct dipole transitions. A Lorentzian broadening of resonances with full width at half maximum of 10 meV has been included.

Indeed, the generalized SSH-Hubbard model is able to describe the physics of undoped fullerenes with good accuracy. Even the theoretical triplet-triplet excitation energies are close to their experimental values. Moreover, the theory predicts a new triplet-triplet band at about 0.45 eV.

ACKNOWLEDGMENTS

It is my great pleasure to thank Steven Kivelson and Sudip Chakravarty for fruitful discussions, their critical reading of the manuscript, and an enjoyable stay at UCLA. I would like to thank Z. Vardeny for interpreting his data and A. Hebard for pointing out the usefulness of the photoconductive response in determining the lower bound for the spin-singlet binding energy. This work was supported in part by National Science Foundation Grant No. DMR-90-11803 and by U.S. Office of Naval Research Grant No. N 00014-92-J-1101.

APPENDIX

In general, a weak intermolecular coupling is not relevant when intramolecular properties of fullerenes are to be studied. As a specific model, consider the previously[5] introduced version of the SSH-Hubbard Hamiltonian. The Hamiltonian is naturally divided into three parts: $H=H_{\text{el}}+H_{\text{el-ph}}+H_{\text{ph}}$.

First, the electronic part is given by the Hubbard model on a truncated icosahedron lattice. The single-particle part of H_{el} is represented by a nearest-neighbor tight-binding model with the hopping matrix elements t_{ij}. There are two types of nearest-neighbor bonds on this lattice to which $t_{ij}=t$ is assigned for the hopping matrix elements along the bonds $\langle ij\rangle$ of the pentagons and $t_{ij}=t'$ along the bonds $\langle ij\rangle$ connecting two pentagons. The electron-electron interaction is modeled by the on-site Hubbard interaction of magnitude U. Thus,

$$H_{\text{el}}=-\sum_{\langle ij\rangle,\sigma} t_{ij}(c^\dagger_{i\sigma}c_{j\sigma}+\text{H.c.})+\tfrac{1}{2}U\sum_{i,\sigma} n_{i\sigma}n_{i\bar{\sigma}}\ ,$$

where $c^\dagger_{i\sigma}$ creates an electron of spin σ on the carbon site i, $n_{i\sigma}=c^\dagger_{i\sigma}c_{i\sigma}$. The notation $\langle ij\rangle$ refers to the bonds between nearest-neighbor sites.

Second, it is assumed that there are only two types of elastic terms that enter the lattice potential energy: a bond-stretching energy with spring constant K and a bond-bending energy with spring constant Q. Thus, the lattice Hamiltonian is

$$H_{\text{ph}}=\frac{1}{2M}\sum_i \mathbf{P}_i^2+\tfrac{1}{2}K\sum_{\langle ij\rangle}(\delta l_{ij})^2+\tfrac{1}{2}Q\sum_{\langle ijk\rangle}(\delta\theta_{ijk})^2\ ,$$

where $\mathbf{P}_i$ is the momentum of the ith carbon atom of mass M and δl_{ij} is the change in the distance from its classical ground-state value between sites i and j. The notation $\langle ijk \rangle$ refers to triplets of sites such that i and k are two distinct nearest-neighbor sites of j. Thus, θ_{ijk} is an angle defined by bonds $\langle ij \rangle$ and $\langle kj \rangle$, and $\delta\theta_{ijk}$ is the difference between this angle and its value in the classical ground state of the undistorted molecule. Finally, since the fluctuations about the equilibrium configuration are considered to be small, the harmonic approximation is applied.

Third, consider the electron-phonon interaction, involving only electronic interactions of the shortest possible range:

$$H_{\text{el-ph}} = \alpha \sum_{\langle ij \rangle,\sigma} \delta l_{ij}(c_{i\sigma}^{\dagger}c_{j\sigma} + \text{H.c.}) + \beta \sum_{\langle ijk \rangle,\sigma} \delta[\cos(\theta_{ijk})] n_{j\sigma} \, .$$

The first term, proportional to α, is the coupling between the bond-stretching modes and the electronic structure. The second term, proportional to β, is the coupling between the bond-bending modes and the electronic structure.

The values of the parameters are found by the experience of other organic compounds and by fitting the infrared oscillator strength with experiments.[5,21] Only the value of U/t remains uncertain.

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[1] M. Schlüter *et al.*, Phys. Rev. Lett. **68**, 526 (1992); C. Varma *et al.*, Science **254**, 989 (1991); I. Mazin *et al.*, Phys. Rev. B **45**, 5114 (1992).

[2] S. Chakravarty and S. Kivelson, Europhys. Lett. **16**, 751 (1991).

[3] A. Heeger *et al.*, Rev. Mod. Phys. **60**, 781 (1988).

[4] S. Chakravarty *et al.*, Science **256**, 1306 (1992).

[5] M. Salkola, S. Chakravarty, and S. Kivelson, Int. J. Mod. Phys. B **7**, 2859 (1993).

[6] M. Braga *et al.*, Astron. Astrophys. **245**, 232 (1991); see also S. Larsson, A. Volosov, and A. Rosen, Chem. Phys. Lett. **137**, 501 (1987).

[7] B. Friedman and J. Kim, Phys. Rev. B **46**, 8638 (1992).

[8] J. Heath, R. Curl, and R. Smalley, J. Chem. Phys. **87**, 4236 (1987).

[9] H. Ajie *et al.*, J. Phys. Chem. **94**, 8630 (1990), for instance, measure values 3.06 and 3.77 eV.

[10] S. Ren *et al.*, Appl. Phys. Lett. **59**, 2678 (1991). Their data show two peaks at ~3 and 3.73 eV.

[11] R. Whetten *et al.*, in *Clusters and Cluster-Assembled Materials*, edited by R. Averback, J. Bernholc, and D. Nelson, MRS Symposium Proceedings No. 206 (Materials Research Society, Pittsburgh, 1991), p. 639.

[12] I follow the Mulliken notation which assigns a symbol ${}^{2S+1}X_a$ for many-electron states: X and a give the symmetry and the parity (under inversion) of the orbital part of the state, and S is the spin. According to the irreducible representations of the icosahedral group, X can be either A, T_1, T_3, G, or H, with degeneracies (dimensions) 1, 3, 3, 4, and 5, respectively. A transforms as a scalar, T_1 as a vector, and H as a tensor of rank two; finally, T_3 and G transform as octupoles.

[13] Nearly degenerate perturbation theory is based on second-order Brillouin-Wigner perturbation treatment where the self-consistency condition is removed by replacing $V_{\alpha\beta}V_{\beta\alpha'}/(E-\epsilon_\beta) \rightarrow \frac{1}{2}[(\epsilon_\alpha-\epsilon_\beta)^{-1}+(\epsilon_{\alpha'}-\epsilon_\beta)^{-1}]V_{\alpha\beta}V_{\beta\alpha'}$.

[14] W. Krätschmer *et al.*, Nature (London) **347**, 354 (1990).

[15] M. Kaiser *et al.*, Solid State Commun. **81**, 261 (1992). They find that the photoconductive threshold is located approximately 0.4 eV above the optical band edge. However, due to the band-structure effects, this is the lower bound for the binding energy.

[16] This is a nontrivial result: for instance, consider the perturbed and unperturbed states $|\psi_0\rangle$ and $|0\rangle$ of a neutral molecule. The normalization $\langle 0|\psi_0\rangle = 1$ leads to an expansion $\langle \psi_0|\psi_0\rangle = 1 + 0.138(U/t)^2$ which shows that the second-order correction is important for $U/t > 2$.

[17] R. Whetten (private communication).

[18] G. Gensterblum *et al.*, Phys. Rev. Lett. **67**, 2171 (1991).

[19] X. Wei *et al.* (unpublished).

[20] F. Negri, G. Orlandi, and F. Zerbetto, Chem. Phys. Lett. **144**, 31 (1988).

[21] Here, too, I choose the same values for the parameters as was done in Ref. 5. They are $t = 2.5$ eV, $\alpha = 5$ eV/Å, $\beta = 3.3$ eV, $K = 40$ eV/Å^2, $Q = 0$, and $t'/t = 1.1$.

[22] In particular, see Fig. 6 in Ref. 11.

[23] F. Negri, G. Orlandi, and F. Zerbetto, J. Chem. Phys. **97**, 6496 (1992).

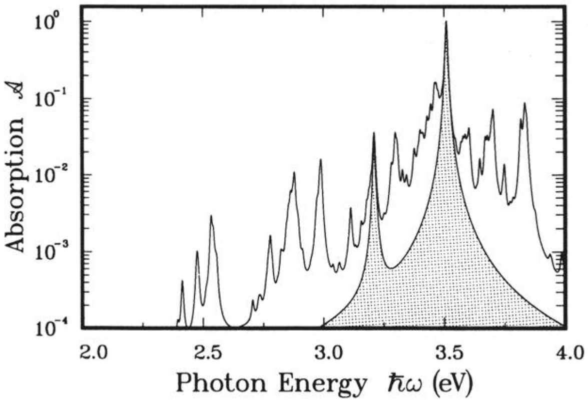

FIG. 1. Absorption spectrum of a neutral C_{60} molecule including the direct and one-phonon-induced transitions at $U/t = 4.5$ (Ref. 21). The shaded region highlights the contribution due to the direct dipole transitions. A Lorentzian broadening of resonances with full width at half maximum of 10 meV has been included.