Estimate of Hubbard U for C$_{60}$ by use of optical absorption

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We consider the optical absorption of C$_{60}$ within a simple tight-binding model. To obtain a reasonable agreement with experiment a sizable Hubbard U must be included. We estimate U to be in the range from one-half to the full "bandwidth" where the bandwidth is roughly 13 eV. In our picture the two lowest-energy large-absorption peaks are due to single-particle transitions: H_u goes to T_{1g} and H_g goes to T_{1u}, respectively. The weak absorption from 3.0 to 1.9 eV is attributed to the dipole-forbidden transition: H_u goes to T_{1u} "split" by electron-electron repulsion.

Recently, a number of authors have proposed simple tight-binding models to explain the low-energy electronic excitations of C$_{60}$ and doped C$_{60}$.[1-3] The question we wish to address in this paper is, do such models really work? For example, can a tight-binding model explain the low-energy part of the optical absorption of C$_{60}$? Our main conclusion is that such models cannot work without including a sizable Hubbard U. With the inclusion of such a Hubbard interaction term our results indicate the optical absorption can be understood fairly well by a simple model.

The model we consider is the Su-Schrieffer-Heeger (SSH) model of conducting polymers[4] applied to C$_{60}$.[1-3] That is, we consider the Hamiltonian

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

Here l_{ij} is the length of the bond connecting the ith and jth sites, (nearest neighbors only) 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. To model direct electron-electron interaction an on-site Hubbard repulsion has been included.[5] We use the parameter values $\alpha=7.0$ eV/Å, $t=1.35$ eV, $k=53$ eV/Å^2. These parameter values work well for polyacetylene. There is nothing fundamental about these parameter values but we do expect the "true" parameters (which may well be sample dependent) to be in at least an order of magnitude agreement. The parameter U will be fitted in comparison to the optical absorption. For simplicity, we have only considered on-site repulsion. To a certain extent, we believe longer-range interactions will merely "renormalize" t and U.

We will treat the above Hamiltonian in the adiabatic approximation (consequently the kinetic term for the lattice does not enter). Such an approximation[4] appears to be quite good (at least for some properties) for models of conducting polymers and hence we adopt such an approximation here. Our model considers only a single C$_{60}$ molecule (i.e., we neglect intermolecular hopping). For conducting polymers such single-molecule models have been used successfully in calculating the optical absorption in the solid phase. For C$_{60}$, the optical absorption of C$_{60}$ films and C$_{60}$ in solution is rather similar.[6] Therefore, it seems experiment justifies considering only a single C$_{60}$ molecule when we compute the optical absorption even for C$_{60}$ films.

In calculating the optical absorption we invoke the Franck-Condon principle, we determine the bond lengths by minimizing the ground-state energy, and assume these bond lengths stay the same even for the excited states. For an excited state the lattice will eventually relax to form polarons;[1,2,7] we assume here there is insufficient time for this to occur since the electrons are moving much faster than nuclear degrees of freedom.

We initially consider the optical absorption for the case of no direct electron-electron interaction ($U=0$). Minimizing the ground-state energy we find two distinct bond lengths. The bond separating a hexagon and a pentagon is shrunk about 0.12 Å while the bond separating two hexagons shrinks about 0.18 Å. Consequently the bond length difference is about 0.06 Å in reasonable agreement with experiment. Throughout our calculation we neglect the effect of electron-electron interaction on the bond lengths. This neglect causes an error of order higher than U^2 in the ground-state energy.

In the dipole approximation the optical density is given by $CE_{\text{fi}}\langle r_{\text{fn}}\rangle^2$ where C is an energy-independent constant, E_{fi} is the energy between the initial and final states and

$$\langle r_{\text{fn}}\rangle^2 = \langle f|X|i\rangle^2 + \langle f|Y|i\rangle^2 + \langle f|Z|i\rangle^2 ,$$
$$X=\sum_i X_i , \quad Y=\sum_i Y_i , \quad Z=\sum_i Z_i ,$$

where (X_i, Y_i, Z_i) is the coordinate of the ith electron. Since the final states are degenerate we include another summation over the final degenerate states.

The only parity-allowed transitions (less than 5 eV for the noninteracting model with the chosen parameter values) are promoting an electron from one of the degenerate single-particle levels 26–30 (of symmetry H_u) to the T_{1g} levels 34–36, 21–25 (Hg) goes to 31–33 (T_{1u}), 17–20 (G_g) goes to 31–33 (T_{1u}), and 26–30 (H_u) goes to 37–41 (Hg) Ref. (8) (see Fig. 1). The energy of the respective transitions are approximately 2.8, 3.0, 3.2, and 4.4 eV. A straightforward calculation yields the oscillator strengths $(E_{fi}\langle r_{fn}\rangle^2)$ for the various transitions. (See Fig. 2) The strength of the transition at 3.2 is zero although this transition is dipole allowed). Obviously there is a poor agreement between theory and experiment.[6,9–11] For example the theoretical transition lowest in energy (2.8 eV) has a substantial oscillator strength. The strength of the lowest observed transition (at 3.0 eV) is very small (on the scale of Fig. 2, roughly 0.03). Within the context of the SSH model, Harigaya[12] has done a similar calculation and obtained equivalent results. First-principles methods suffer from similar problems (see Fig. 3 of Ref. 13). We have investigated the effect of changing parameter values (t, k, α) on the energy of the excited states and find that this does not really improve matters much. In particular whatever parameter values are chosen it seems difficult to get a nearly 1-eV energy difference between the lowest two dipole active excited states, the experimental peaks with energy 3.7 and 4.7 eV. Noting this disagreement within the context of a more microscopic model Bertsch et al.[14] proposed the source of this disagreement is due to the neglect of Coulomb repulsion (for a quantum-chemical calculation see Ref. 15). Although we believe these authors are essentially correct, we differ somewhat in the interpretation of our calculation (see below).

Although on the surface the noninteracting result looks very different from the experimental result, the difference is not really that great. That is, the experimental peaks at 3.7, 4.7, and 5.7 eV correspond to noninteracting peaks at 2.8, 3.0, and 4.4 eV. The direct electron-electron repulsion causes the noninteracting peaks to shift in energy. That is, we identify the experimental transition at 3.7 eV with the H_u to T_{1g} transition
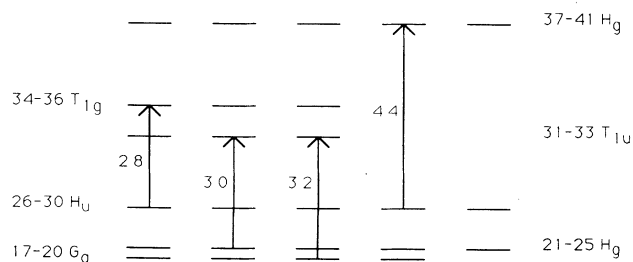

FIG. 1. Single-particle energy levels participating in the low-energy dipole-allowed transitions. The vertical arrows indicate the allowed transitions with the energy of the transition (in eV) written to the left of the arrow.
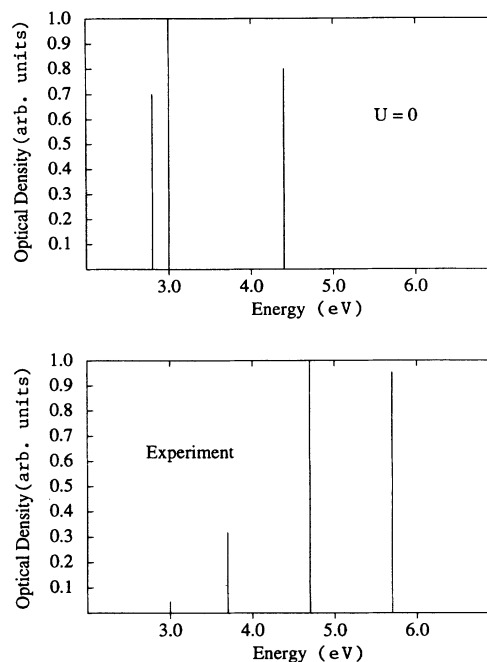

FIG. 2. Optical density vs excitation energy. The top figure is a calculation for $U=0$. The largest absorption has been normalized to unity. The bottom figure is the experimental result taken from the solution data of Ref. 6. We have plotted the maximum of the absorption bump and the largest absorption has been normalized to unity.

and the 4.7-eV transition with H_g goes to T_{1u}. Experimentally the peak at 3.0 eV corresponds most likely to a dipole-forbidden transition in the noninteracting case having energy 2.2 eV. To substantiate these statements we now consider the effects of electron-electron interaction.

We initially consider the conceptually simplest scheme, straightforward second-order perturbation theory in U. This scheme has been successfully applied to the optical properties of conducting polymers.[4] Therefore, we apply perturbation theory to the levels having unperturbed energy 2.8, 3.0, 3.2, and 4.4 eV relative to the ground state. Technically, there is a complication in that each of these levels is "moderately" degenerate, 2.8 is 30-fold degenerate, 3.0 is 30-fold degenerate, 3.2 is 24-fold degenerate,and 4.4 is 50-fold degenerate. It should be possible to find the "good" (stable to perturbation) linear combinations by using group theory.[16] However, we have found it simpler to brute force diagonalize the secular matrix (i.e., do straightforward second-order perturbation theory[17]). Actually, the stable linear combination is resolved by using first-order perturbation theory for all levels other than the level at 4.4 eV.

Since the "good" linear combinations are related to the original states by a unitary transformation the sum of the squared dipole matrix elements for the eigenfunctions of the secular matrix is the same as the sum of the square dipole matrix elements of the original states. The only possible redistribution is among the degenerate states. Consequently, even in the presence of a small U 3.2 eV

remains dipole inactive. In each of the other levels (2.8, 3.0, 4.4) three degenerate spin-0 states are dipole active. Each of these three degenerate states has the same squared dipole matrix element with the ground state ($\frac{1}{3}$ of the total noninteracting weight for that level).

This threefold degeneracy is easy to understand, namely as noted by a number of authors[5] the icosahedral symmetry of the C_{60} molecule is "close" to full rotational symmetry, i.e., there is conservation of angular momentum. We therefore interpret the threefold degeneracy as an $L=1$ state. Since the ground state has $L=0$, $S=0$ this assignment is consistent with the normal selection rules. It is also interesting to note that within each of the formerly degenerate subspaces half the states have spin 0 and the other half have spin 1 with the spin-1 states generally lower in energy.

For small values of U (where our treatment is valid, the difficulty being in knowing what is small) the relevant energy levels are not shifted much relative to the ground state. For example, for $U=1$ eV the three relevant energy levels are shifted less than 0.03 eV. It appears that to have the possibility of agreement with experiment considerably larger values of U are necessary.

We therefore adopt the following perturbative scheme. Let P_1, P_2, P_3, and P_4 be the projection operator into subspaces of states having unperturbed energy $E_1=2.8$, $E_2=3.0$, $E_3=3.2$, and $E_4=4.4$. We choose the unperturbed Hamiltonian $H_0'=H_0-\sum_i(E_i-E_1)P_i$ and the perturbation as $H_I'=H_I+\sum_i(E_i-E_1)P_i$. Under this perturbation the 134 states having energy E_1, E_2, E_3, and E_4 are degenerate and we consequently use second-order degenerate perturbation theory with respect to H_I'. All other states with "H_0" energy less than 5.0 eV have the same parity as the ground state and consequently do not mix with the low-lying dipole-allowed excited states. We expect this perturbation theory to be good for the low-lying excitations if U is of order half the bandwidth[18] (the "bandwidth" being approximately 13 eV with our parameters; by bandwidth we mean the difference in energy of the single-particle state highest in energy from the single-particle state lowest in energy).

We initially consider our results for $U=5$ eV. The states with unperturbed energy 2.8, 3.0, and 4.4 are shifted (relative to the ground state) to 3.0, 3.3, and 5.3. That is, of the 134 states we consider only nine are dipole active. Of these nine, there are three sets of three degenerate states at 3.0, 3.3, and 5.3 (i.e., as for the $U=1$ case this degeneracy is not lifted). This pattern of degeneracy and dipole activity persists even to $U=15$ (which is not surprising since it is essentially the conservation of orbital angular momentum). The general trend here agrees with experiment; the levels are shifted upward in energy with a growing space between the two lowest levels. For the squared dipole matrix element we find 1.0, 4.5, and 2.2 (in arbitrary units, only ratios are meaningful). This is in general agreement with experiment since weight is shifted from the lowest-energy peak to the peak second lowest in energy (of course the experimental results are broadened, we compare the maximum of the experimental "bump" to theory). Even for this value of U we do

not believe the calculation of the highest-energy peak (which is shifted to 5.3 eV, recall our "cutoff" is 5.0) is reliable. Clearly this peak will interact strongly with higher-energy levels not included in the initial diagonalization. Recall that the energies we calculate will be more accurate than properties that depend on wave functions. That is, energies are accurate to second order in H_I' while the wave functions are only the correct zero-order wave function with respect to the perturbation H_I'.

We next consider $U=10$ eV. Here the three lowest levels are shifted to 3.3, 3.9, and 7.3 with squared dipole matrix elements 1.4 and 4.0, and 2.3. Undoubtedly the results for the highest level are unreliable. We still, however, believe the results for the lowest-lying levels to be reasonably trustworthy. The general tendency of these two levels with respect to experiment is correct, an overall shift plus more level splitting. To check the reliability of the calculation we have considered a different perturbative scheme, namely we allow "interaction" of the two lowest levels only. Using this scheme we find again the two lowest levels are shifted to 3.3 and 3.9 with squared dipole matrix element 1.5 and 4.4, respectively, in good agreement with the previous calculational scheme. If we do straightforward degenerate perturbation theory (no "interaction") for $U=10$ we find these levels are shifted to 3.0 and 3.6 eV. We therefore are hesitant to call this splitting level repulsion.

Finally we consider $U=15$ eV. Here the value of U is sufficiently large (of order the bandwidth) that our calculation (even for the two lowest states) is without theoretical justification. We nevertheless report our results for the two lowest levels; the lowest level is shifted 0.92 to 3.7 and the second lowest level is shifted to 4.7. This is in good (perhaps fortuitous) agreement with experiment. In essence, by fitting one parameter U we can predict two bits of experimental information. We find the squared dipole matrix elements to be 2 and 3.3, not ridiculous in comparison to experiment.

The lowest-energy transition in our model (H_u goes to T_{1u}) is of course dipole forbidden. For $U=0$ this transition is 30-fold degenerate with an energy of 2.2 eV. Although it is beyond the scope of this work to calculate transitions into this level, it is nonetheless interesting to examine how this level is effected by electron-electron interaction. Since this level is relatively isolated from other even-parity states (the "closest" being an excited state having energy 3.6 eV) it seems reasonable to merely apply second-order degenerate perturbation to the 30 degenerate states. Doing this, for $U=10$ we find the 30 states "span" the region from 2.0 to 2.9 eV with spin 0 and spin 1 interspersed in this energy region (1–6, 11–15, 27–30 having spin 1 and the rest with spin 0). These results are not in obvious disagreement with the experimental optical absorption.[9,10]

What conclusions can we draw from these calculations? A firm conclusion is that there is a "sizable" Hubbard U very likely greater than half the bandwidth and probably in the range from half to the full bandwidth. We put sizable in quotation marks since in conducting polymers U is of this order relative to the bandwidth yet

still a good deal of the qualitative physics can be extracted from the noninteracting ($U=0$) limit. Using the notation of Ref. 5 the values of U/t we obtain are in the range $3 < U/t < 7$ (note that the t of Ref. 5 "contains" our α multiplied by the bond length).

There are two possibilities for improving these calculations. First of all one could work to higher order and attempt some sort of extrapolation procedure in U. This appears to be difficult since the present second-order calculation took about 40 h on a Digital Equipment Corporation VAX 6420 computer with the computation time being spent mainly on the second-order matrix elements. The other improvement would be to include more states in the diagonalization (increase the energy cutoff). Since our matrices are of order 100 it is possible to increase the size of the diagonalization substantially, say 10000, assuming matrix elements can be rapidly computed. This should be possible with sufficient supercomputer time and

should certainly improve the 4.4-eV state. Since U is fairly large, it is tempting to consider a strong-coupling approach (a Heisenberg model). From our experience such an approach is meaningful only for larger U's (say, much larger than the bandwidth). We still therefore prefer the itinerant approach taken here. In conclusion, our calculations indicate that a simple model can explain the low-energy optical absorption of C_{60}.

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