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Steven G. Louie

Department of Physics
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ELECTRONIC STRUCTURE OF C₆₀ FULLERITES AND NANOTUBES

Steven G. Louie

Department of Physics, University of California, and
Materials Sciences Division, Lawrence Berkeley Laboratory
Berkeley, California 94720 USA

ABSTRACT

We present results on the electron excitation energies of solid C₆₀ calculated using a first-principles quasiparticle theory. The effects of electron correlations and molecular orientational disorders are included. The single-particle properties of solid C₆₀ are found to be well described in a quasiparticle band picture with orientation disorders. Electron-hole interactions are shown to be very strong in optical processes resulting in Frenkel excitons and sizable difference between the optical and photoemission gaps. The electronic and structural properties of carbon and other nanotubes are also investigated. Total energy results predict that the tubules are stable with respect to the formation of strips down to very small radii. Hybridization of the σ^* and π^* states is shown to be as important as band-folding effects in determining the metallicity of small radius tubules.

1. Introduction

The electronic properties of solid C₆₀ have been a subject of numerous experimental and theoretical investigations¹. Issues of importance include the size of the energy gap, the degree of band dispersion, the nature of electron correlation effects, and the effects of electron interactions and molecular orientation disorder on optical and photoemission properties. Photoemission experiments have given conflicting interpretations on the width of the electron bands, and optical and photoemission experiments yielded different band gap values indicating strong electron-hole interactions²⁻⁸. For the carbon nanotubes, although there are presently few direct experimental data, their electronic structures have been predicted to be highly unusual and sensitive to their geometric structures⁹, varying from metals to semiconductors depending on size and chirality. Furthermore, single-wall tubules with a narrow distribution of diameters have been synthesized recently¹⁰.

In this short review, we discuss some results of electron excitation energies in undoped solid C₆₀ calculated using an *ab initio* quasiparticle approach¹¹. The approach is based on an expansion of the electron self energy (the many-electron correction to an electron excitation energy) to lowest order in the dynamically screened Coulomb interaction, the so-called GW approximation. We also present results on the small-radius single-wall nanotubes. Questions of structural stability and effects of σ - π hybridization are examined.

2. Band Gaps, Photoemission, and Optical Properties of Solid C₆₀

We investigated¹² the electronic structure of solid C₆₀ in three different geometric structures: a hypothetical *Fm3* structure with all the molecules identically oriented in an fcc lattice, the experimental low temperature *Pa3* structure with four molecules per cell, and the

room temperature randomly oriented structure. The calculations of the electron excitation energies were carried out for the $Fm3$ structure using the *ab initio* quasiparticle self-energy method developed in Ref. 11. A Slater-Koster Hamiltonian was obtained by fitting to the $Fm3$ quasiparticle results. This Slater-Koster Hamiltonian was then used to examine the effects of molecular orientation and to compute direct and inverse angle-resolved photoemission spectra.

Photoemission experiments³⁻⁶ have given values of 2.3-2.6 eV for the band gap of solid C_{60} . These values are significantly different from that of a 1.83 eV gap observed in optical experiment⁸ and a theoretical value of ~ 1 eV from local density functional (LDA) band calculations¹³. Another interesting experimental finding is the apparent lack of dispersion in the spectral peaks in angle-resolved photoemission spectra^{3,7}. This observation has been used by some as evidence for nondispersive bands in this material.

Figure 1 compares the calculated quasiparticle HOMO (H_u) and the first two LUMO (T_{1u} and T_{1g}) bands in the $Fm3$ structure with the LDA results. Many-electron effects give rise to two major corrections to the LDA results. The energy gap is enlarged by a factor of two from 1.04 eV to 2.15 eV. This enhancement of the gap brings the theoretical result into good agreement with the photoemission data and is consistent with trends in previous quasiparticle calculations for semiconductors and insulators. The self-energy operator seen by a quasielectron is very different from that of the quasihole. The many-body effects are not reproduced well by the simple LDA exchange-correlation potential which depends only on the local electron density. Another notable many-body correction is

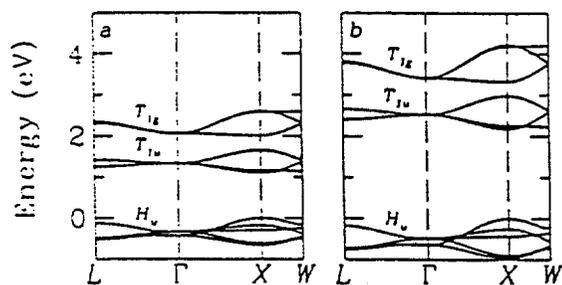


Fig. 1. $Fm3$ band structure of solid C_{60} obtained in LDA (a) and in quasiparticle approach (b).

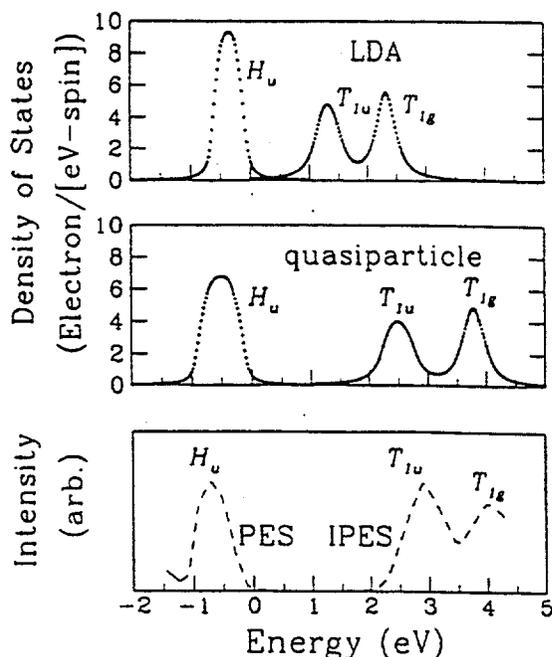


Fig. 2. DOS of solid C_{60} based on LDA results, quasiparticle results, and experimental data⁵.

that the band widths of both the HOMO and LUMO complexes are increased by approximately 30%.

The quasiparticle and LDA density of states are presented in Fig. 2 along with typical room temperature photoemission (PES) and inverse photoemission (IPES) data⁵. The theoretical results are for the random structure and were simulated using an ensemble of supercells containing 512 C₆₀ molecules. Orientation randomness basically removes the sharp features existed in the density of states (DOS) of the ordered *Fm3* structure without significantly altering the band gaps and widths. We note the remarkable improvement in agreement with PES/IPES results for the quasiparticle results as compared to LDA for both the minimum band gap and the H_u - T_{1u} peak-to-peak distance. The present theory correctly calculates the excitation energies as the energies needed to add a quasiparticle or quasihole to the interacting many-electron system.

To obtain the optical gap, one must add in the interaction between the quasidelectron and quasihole. We used a simple model Hamiltonian¹⁴:

$$H = H_e + H_h + H_{e-h} , \quad (1)$$

where H_e and H_h are tight-binding Hamiltonians for the independent H_u quasiparticle and T_{1u} quasihole states given above. The third term is a screened electron-hole Coulomb interaction. For electron and hole at different molecules, H_{e-h} is given by the bare Coulomb interaction screened by the C₆₀ lattice in a self-consistent point-dipole model. The intramolecular interactions are taken to be the Lowdin π - π Coulomb integrals in quantum chemistry, but scaled by a single-parameter to match the known on-buckyball attraction measured in the gas phase¹⁵.

Within this model, electron-hole interactions are found to be very large, resulting in a series of Frenkel exciton bands deep in the quasiparticle gap. For the singlet states in the *Pa3* structure, the lowest exciton level is of T_{2g} symmetry with excitation energy of near 1.6 eV and wavefunction mostly localized on a single molecule¹⁴. This large exciton binding energy explains the observed discrepancy between the quasiparticle gap and optical absorption threshold. Further, we find the onset of the triplet exciton series is at 0.26 eV below that of the singlet series, in good agreement with the observed singlet-triplet splitting of 0.28 eV¹⁶.

Angle-resolved photoemission spectra were simulated by computing the k -dependent quasiparticle DOS for an ensemble of ten, randomly oriented 12x12 surface primitive cells that were 6 layer thick, oriented in the (111) direction. Such spectra may be compared to the angle-resolved inverse photoemission (ARIPES) results in Ref. 7 on epitaxially grown C₆₀ films. The calculated spectra in the $\bar{\Gamma}$ - \bar{K} - \bar{M} direction of the surface Brillouin zone are given in Fig. 3a. We note that even though there are several dispersing bands in the T_{1u} and the T_{1g} complexes, the calculated spectral peaks show negligible k_{\parallel} dependence. In Fig. 3b, the dispersions of the theoretical peaks are compared with those reported in Ref. 7. The absence of strong, visible dispersion effects is seen in both theory and experiment. Thus the dispersive T_{1u} and T_{1g} states can lead to apparently non-dispersive ARIPES spectra. The absence of dispersion in the spectra is caused by several

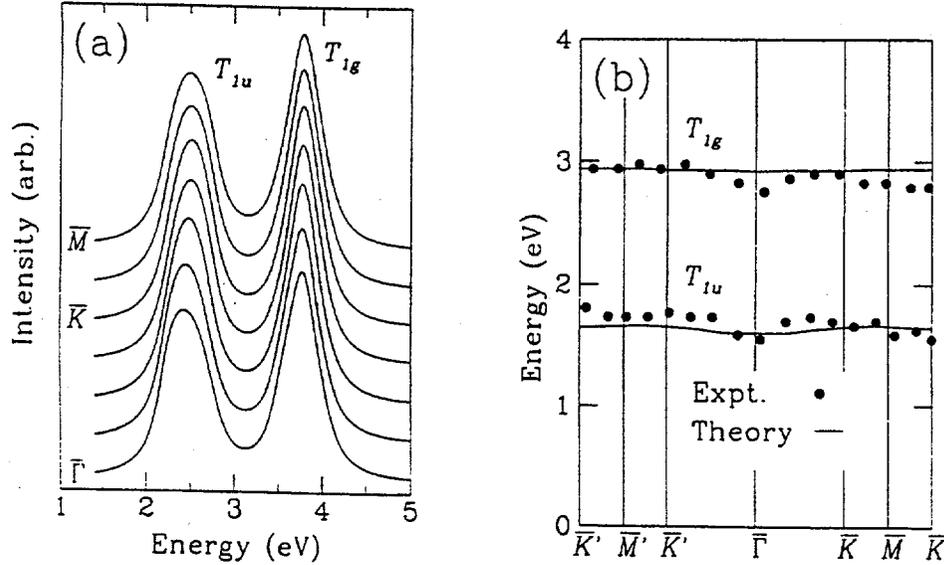


Fig. 3. Simulated angle-resolved inverse photoemission spectra for the T_{1u} and T_{1g} complexes in the $\bar{\Gamma}$ - \bar{K} - \bar{M} direction (a); peak position as function of k_{\parallel} (b). Experimental data are from Ref. 7.

factors: orientational disorder, the required Brillouin-zone integration normal to the surface, finite-resolution effects, and the multi-band nature of the complexes studied. Hence, it would be incorrect to deduce that this is an extremely narrow-band system based solely on non-dispersive ARPES data. Also, the results are in good agreement with experiment both in the peak widths and the peak-to-peak distance between the T_{1u} and T_{1g} complexes. This level of agreement is achieved only when the energy-dependent self-energy corrections are included in the quasiparticle energies. As mentioned above, the corrections lead to an $\sim 30\%$ increase in the band widths and in the separation between the T_{1u} and T_{1g} complexes.

For the HOMO complex, our calculated the k -dependent DOS predicted¹² that the band features should be observable in photoemission experiments with fine angular resolutions. Recent high resolution ARPES experiments¹⁷ have indeed observed dispersive features consistent with a bandwidth given by the quasiparticle calculation.

3. Nanotubes

We focus the discussion here on small diameter single-wall nanotubes which, for carbon, have been synthesized recently using transition metal catalysts¹⁰. Our LDA calculations¹⁸ revealed that carbon tubules are energetically stable with respect to strips down to quite small radii. For example, for a (6,0) tube (in the notation of Saito *et al*⁹) with diameter of $d=4.78$ Å, its calculated energy is lower by more than 0.2 eV/atom compared to that of the corresponding strip. The elastic energy in the tubule (which scales as d^{-2}) is still considerably lower than the dangling bond energy in forming the strips at $d\sim 4$ Å, in agreement with a previous classical force-field calculation¹⁹.

The large curvature of the small diameter tubes results in the hybridization of the σ^* and π^* states¹⁸. The electronic properties of small tubes are significantly altered from

those obtained in previous tight-binding (TB) calculations. Strongly modified low-lying conduction band states are introduced into the band gap of insulating tubes because of strong $\sigma^*-\pi^*$ hybridization. As a result, the LDA gaps of some tubes are lowered by more than 50%, and the (6,0) tube which previously predicted to be semiconducting is shown to be metallic. (See Table 1). The band structure and DOS for the (6,0) are shown in Fig. 4.

Table 1. Band gap (in eV) of selected carbon tubes.

Tubes	TB	LDA
(6,0)	0.05	(-0.83)
(7,0)	1.04	0.09
(8,0)	1.19	0.62
(9,0)	0.07	0.17

The state labeled (a) is especially interesting. It corresponds to a strongly hybridized $\sigma^*-\pi^*$ state (see Fig. 5) whose energy at Γ is 0.83 eV below the doubly degenerate state that forms the top of the valence band in TB calculations.

Similar calculations²⁰ for nanotubes of BN and other combinations of B, N and C have been carried out. We find that, for BN, BC₃, and BC₂N, the relative energy differences between a tubule and a sheet and between a tubule and a strip are very similar to those of the carbon tubules of similar diameters, making the experimental synthesis of these tubules likely. However, in contrast to the carbon tubes, we find that all BN tubes are insulators and have a nearly constant quasiparticle band gap of ~ 5.5 eV independent of diameter and helicity for tubes with $d \geq 9.5$ Å. Furthermore, the bottom of the conduction band of the BN tubes is predicted to be a new type of free-electron-like tubule state with wavefunction concentrated in the interior of the tube.

4. Summary

We have performed *ab initio* calculations on the energy gap and quasiparticle ener-

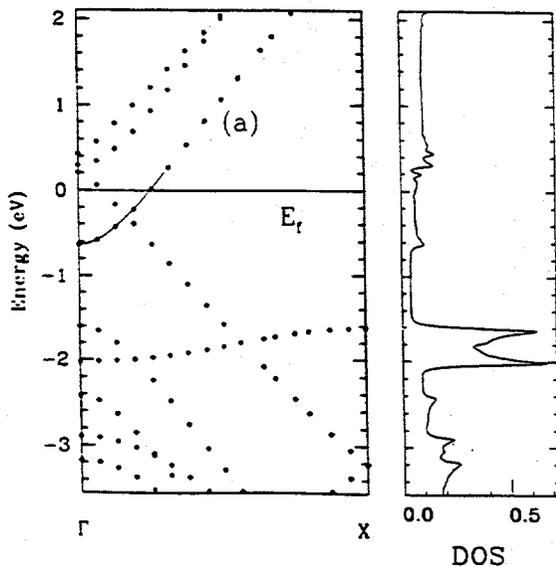


Fig. 4. Band structure and DOS for the carbon nanotube (6,0).

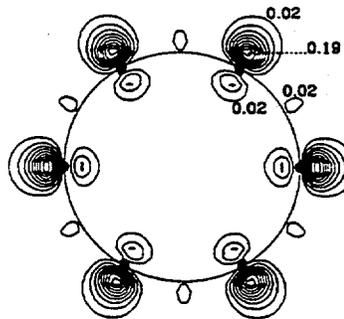


Fig. 5. Charge density of state (a) in Fig. 4.

gies in solid C₆₀ showing that both many-electron and molecular orientation disorder effects are important. The single-electron excitation spectra of this material may be understood in a standard quasiparticle band picture. The description of the optical gap however requires the inclusion of electron-hole interactions (exciton effects). We have also performed studies on the electronic and structural properties of the carbon nanotubes using the LDA and uncovered a large σ - π hybridization effect on the metallicity of small diameter tubes which is as important as band-folding effects considered by earlier theories. Further our total energy calculations show that formation of other nanotubes such as those involving B, C, and N may be possible.

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