Quasiparticle Excitations and Photoemission Spectra in Solid C_{60}*

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We report calculations of the electron excitation energies and photoemission spectra in undoped, solid C_{60} using a. quasiparticle self-energy approach. The effects of electron correlatioiis and molecular orientatioiial disorders are included. We find a. quasiparticle band gap of 2.15 eV in agreement with recent experimental data and sizable band dispersions of ~ 1 eV for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) band complexes. The calculated angle-resolved inverse photoemission spectra for the LUMO bands exhibit minimal angular dependence, explaining the observed lack of dispersion in the spectral peak positions in recent experimental work on epitaxial thin films. The present results show that, although many-electron corrections to the band gap and dispersion are sizable, tlie electron excitation energies in undoped fullerites rnay be described in a standard quasiparticle band picture with molecular orientational disorder.

I. Introduction

The study of carbon-based materials has become an extraordinarily active field in the past few years. In xddition to the fullerenes [1], which are carbon clusters in cage-like structures, many other novel structures of pure carbon have recently been synthesized including the fullerites [2] (crystals of fullerenes), the buckytubes [3] (graphitic tubules of nanometer-size diameters), and the fullerene onions [4] (concentric fullerenes of different s zes). These systems all have fascinating new properties which are being actively explored. Of the fullerenes, tlie C_{60} buckyball [1] is the most symmetric and abundant structure with 60 carbon atoms forming an icosahedral cage of 20 hexagons and 12 pentagons. The discovery of superconductivity [5] in doped solid C_{60} has led to further rigorous research activity in this fie d. In particular, the electronic structure of the fullerites has been the subject of numerous experimental and theoretical investigations. Nonetheless, some of the niost fundamental issues still remain unresolved. These include the size of the energy gap, the degree of band dispersion, tlie nature of electron correlation effects, and the effects of electron correlation and/or molecular orientation on optical and photoemission properties of this molecular solid.

To address some of these issues, we have carried out calculations on the electron excitation energies in undoped solid C_{60} using an ab *initio* quasiparticle approach [6]. Tlie 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 [7]. We investigated the electronic structure of solid C_{60} in three different geometric structures: a hypothetical Fm3 structure which has all the molecules identically oriented in an fcc lattice, the lower temperature $Pa3$ structure [8], and the room temperature randomly oriented structure. Our quasiparticle calculation for the ordered $Fm3$ structure yielded a direct energy gap of 2.15 eV as opposed to the 1.04 eV band gap obtained in the standard local density functional approximation (LDA) [9]. This is to be cornpared to a gap of 1.85 ± 0.1 eV from microwave conductivity experiments [10] and 2.3-2.6 eV inferred frorn direct and inverse photoemission data [11–14]. Moreover, the computed results for the HOMO and LUMO band complexes exhibit a 30% enhancernent in band width as compared to those from tlie LDA.

*Invited talk.

Since tlie molecules are orientationally disordered at room temperature, we use a Slater-Koster I-Iamiltoiiian [15] fit to the $Fm3$ quasiparticle band structure to examine tlie effects of molecular orientation. Complete orientational disorder removes sharp features in tlie density of states (DOS) hut yielcls little change in the band edges and widths. Moreover, tlie Slater-Koster Hamiltonian has enabled computation of angle-resolved photoeniission spectra (ARIPES). In good agreement with experiment [16,17], tlie calculated spectra reveal little dispersion of the spectral peak positions with angle for severa1 reasons (see below). The issue of the observed apparent lack of dispersion is a subject of current interest and debate. It has been used by some as evidence for nondispersive bands in this material and hence strong electron correlation effects.

The remainder of the paper is organized as follows. In Sec. II, the theoretical methods and some of the computational details are discussed. In Sec. III, we present tlie calculatecl results and compare them with experimental data, in particular those from photoemission measurements. Finally, in Sec. IV, a summary aiid some conclusions are presented.

II. Theoretical Methods and Computational Details

The present study was carried out in four stages to investigate various effects on tlie electron excitation spectrum of solid C_{60}. First, we performed an ab initio pseudopotential LDA calculation to determine the self-consistent valence charge density in the $Fm3$ structure. This also gave tlie Kohn-Sham one-electron energies and wavefunctions. Next, we carried out a first-principles quasiparticle calculation to obtain the electron excitation energies including many-electron self-energy effects. Subsequently, a Slater-Koster tight-binding Hamiltonian was obtained by fitting to the calculated quasiparticle energies. Using the Slater-Koster Haniiltonian, calculations of the quasiparticle density of states and simulated angle-resolved photoemission spectra rvere performed. *Effects* of *molecular* orientation were included tlirough rotating the rnolecules in a supercell geoinetry.

For tlie LDA calculation, we employed a planewave ab iiiitio pseudopotential formalism [18] and the Ceperley-Alder exchange-correlation potential [19]. The carbon norm-conserving pseudopotential was generated using the scheme of Hamann, Schluter and Chiang [20]. Convergent results were ohtained with a 48-Ry planewave cutoff for the one-electron wavefunctions. In tlie case of the $Fm3$ structure which contains one molecule (60 carbon atoms) per unit cell, this corresponds to 27.000 x 27,000 Hamiltonian matrices to be diagonalized. To make the calculations feasible while still obtaining 2,400 conduction band states required in tlie evaluation of the electron self energy in the quasiparticle calculation, we adopted a symmetrized-planewave basis to block-diagonalize these matrices. Our LDA results are in excellent agreement with previous planewave pseudopotential LDA calculations [21].

The quasiparticle calculations were done using the Hybertsen-Louie approach [6]. Because of exchange and correlation effects, the electron excitation energies in a solid can be significantly different from those of one-electron theories. The energies and wavefunctions appropriate for the particle-like excitations in an interacting many electron system are given by the quasiparticle equation [7]:

$$[T + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r})]\psi(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E^{qp})\psi(\mathbf{r}') = E^{qp}\psi(\mathbf{r}) \qquad (1)$$

where T i s tlie kinetic energy operator, V_{ext} the externa1 potential due to the ions, V_H the average electrostatic Hartree potential, and C the electron self-energy operator respectively. The self-energy operator C contains tlie effects of exchange and dynamical correlations. In general, it is nonlocal, energy-dependent and nonhermitian with the imaginary part giving the lifetime of tlie quasiparticles.

In the GW approximation, the self-energy operator is cxpanded to first order in the screened Coulomb interaction:

$$\Sigma(\mathbf{r},\mathbf{r}';E) = \frac{i}{2\pi}\int d\omega e^{-i\delta\omega}G(\mathbf{r},\mathbf{r}';E-\omega)W(\mathbf{r},\mathbf{r}';\omega)\ . \qquad (2)$$

Here, G is the crystalline electron Green's function and W the dynaniically screened Coulomb interaction. In

the calculations, the electron Green's function was constructed initially using tlie LDA Kohn-Sham eigenfunctions and eigenvalues, and subsequently updated with tlie quasipsrticle spectrum from Eq. (1). The dielectric response matrix used to construct the screened Coulomb interaction W was obtained by first calculating the static dielectric matrix using the Levine-Louie-Hybertsen approach. [22]. This dielectric matrix, which includes tlie local field screening effects, was extencled to finite frequencies within a generalized plasmon pole model employing exact dispersion and sum rule relations [6]. There were no adjustable parameter in tlie calculations, and tlie approach lias been found to be highly reliable for a wide variety of systems, including diamond and graphite [6,23]. We estimate tlie convergente in tlie calculated values with respect to numerical cutoffs to be a few hundredths of an eV.

Using the calculated quasiparticle results, a Slater-Koster Haniltonian was constructed with a molecular orbital basis employing tlie angular character [21] of the $\ell = 5$, 6 molecular orbitals in tlie HOMO (H,,), LUMO (T_{1u}) and next higher (T_{1g}) band complexes. This tight-binding Hamiltonian allowed us to study the effects of molecular orientational disorder on tlie electronic states near tlie band gap. We found that the important banding effects were restricted to next-neighbor (i.e. next molecule) H, $-$ H,, $T_{1u} - T_{1u}$ and $T_{1g} - T_{1g}$ hopping, in agreement with the work by Satpathy et *al.* [24] Within each band complex, we included a term energy and parameters for the $\sigma-$, $\pi-$ and δ-hybridization between neighboring molecular orbitals of the same type (e.g., H,.). This Hamiltonian was then used to study the electronic structure of the $Fm3$ structure, tlie low temperature $Pa3$ structure, and tlie rooin temperature random structure. The room temperature solid was simulated using an ensemble of supercells with periodic Born-von Karman boundary conditions containing up to several thousand randomly oriented C_{60} molecules. The Haydock recursion method [25] was used to evaluate tlie density of states (DOS).

For siniulating an angle-resolved direct or inverse photoemission spectrum, a "**k**- resolved" DOS is computed as follows. Here, although orientational disorder formally destroys all translational symmetry, energy-momentum dispersion is still a meaningful concept if tlie disorder is a relatively weak perturbation to the total Hamiltonian. We use the following spectral function to approximate the k-resolved DOS:

$$A_{\mathbf{k},\mathbf{k}}(E) \sim \sum_n \sum_\mu | < nk|\psi_\mu >_S |^2 \delta(E - \epsilon_\mu). \quad (3)$$

Here $|n - k >$ are Bloch states for an ordered system, while $|\psi_\mu >$ and ϵ_μ are associated with a quasiparticle state μ in the presence of disorder. S denotes integration only over one supercell. For a given k, such an expression for the unoccupied states should approximately mimic an angle-resolved inverse-photoemission spectrum for a randomly oriented crystal if initial-state DOS effects may be neglected. Also, the short mean-free-path and the presence of a crystal surface in photoemission requires Brillouin-zone integration over the component of k normal to the surface. We have made these assumptions below in our comparison of the theoretical spectra with photoemission data.

III. Results and Discussions

At room temperature, the C_{60} molecules condense to form a crystal in a fcc arrangement but with the molecules dynamically randomly oriented. Each molecule is spinning rapidly at a rate of about 10^9 rotations/second. Fig. 1 shows a model of solid C_{60} il1 whicli all the molecules are oriented the same way. This is tlie hypothetical $Fm3$ structure which has been used extensively as a reference structure in various studies because it contains only one C_{60} molecule per unit cell. At temperatures below 249 K, the free rotation of the molecules ceases and the solid transforms to a $Pa3$ structure which has a simple-cubic unit cell with four molecules in the basis [8]. The $Pa3$ structure may be obtained by taking the $Fm3$ structure in Fig. 1 and rotating each of the four molecules in the fcc cubic cell by $\sim 22^o$ about a different $< 111 >$ axis in a prescribed fashion [8].

The electronic structure of solid C_{60} is basically one of a molecular crystal. For an isolated C_{60} molecule, there are 240 valence electrons or 120 occupied molecular orbitals. The highest occupied molecular orbitals and the lowest unoccupied molecular orbitals are both angular momentum $\ell = 5$ states made up of the π orbitals of the carbon layer. The HOMO is five-fold degenerate aiid the LUMO is 3-fold degenerate. In the

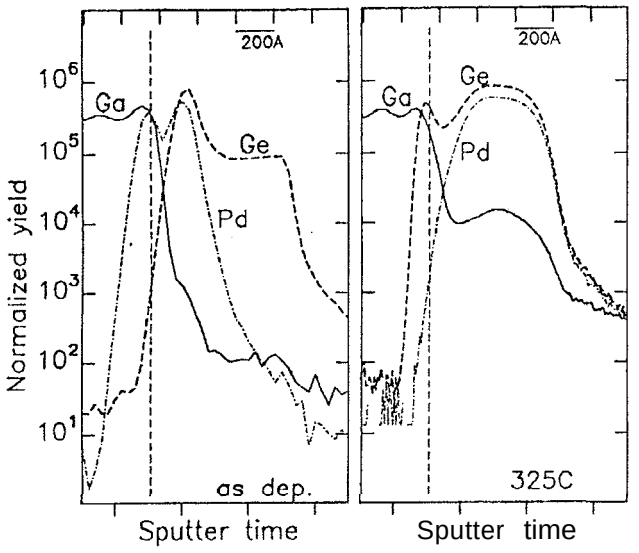

Figure 1: Scheinatic picture of solid C_{60} in the $Fm3$ structure.

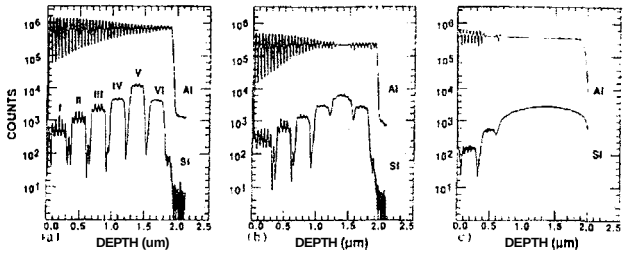

Figure 2: Calculated IIOMO (H,), LUMO (T_{1u}), aiid next higher (T_{1g}) bands for undoped, solid C_{60} in the $Fm3$ structure: (a) LDA and (b) yuasiparticle results.

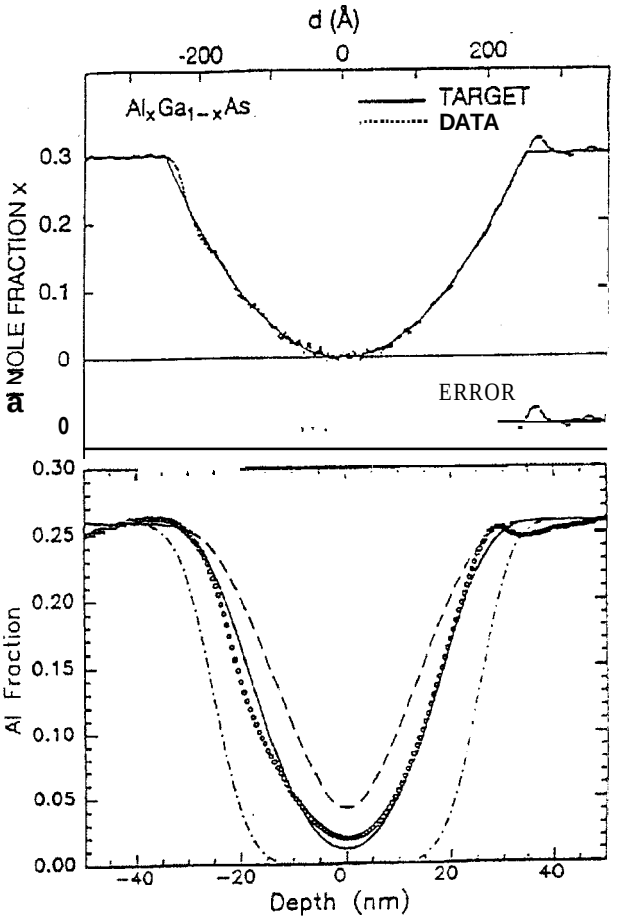

Figure 3: Quasiparticle density of states for solid C_{60} in different orientational configurations.

$Fm3$ structure, the HOMO's aiid LUMO's interact to form the HOMO-derived complex of the 5 highest valence bands aiid the LUMO-derived complex of the 3 lowest conduction bands. LDA calculations give a. direct gap material for this structure with a. band gap of 1 eV and band dispersion of about 0.5 eV for the HOMO aiid LUMO complexes.

Figure 2 depicts our calculated quasiparticle HOMO and LUMO bands in the $Fm3$ structure together 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 tmo from 1.04 eV to 2.15 eV. This enhancement of the gap brings the theoretical result into good agreement with tlie experimental data (see Table 1) aiid 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 tlie 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 that the band widths of both the HOMO and LUMO complexes are increased by approximately *30%*. As discussed below, this latter correction also has important consequences in interpreting photoeinission data.

Ill Fig. **3,** tlie effects of molecular orientation are demonstrated by contrasting the quasiparticle DOS for the $Fm3$, $Pa3$, and the room temperature randomly oriented structure. The results for the random structure in Fig. *3* were simulated using an ensemble of supercells containing 512 C_{60} molecules. The H,,, T_{1u} and T_{1g} densities of states have been broadened by *0.05, 0.15,* aiid *0.15* eV half-widths respectively to mimic reported experimental resolution. Orientation randomness removes tlie sharp structures in the HOMO complex which exist in the two ordered crystal structures. However, the orientational disorder does not significantly cliange the widths of tlie DOS from those of tlie

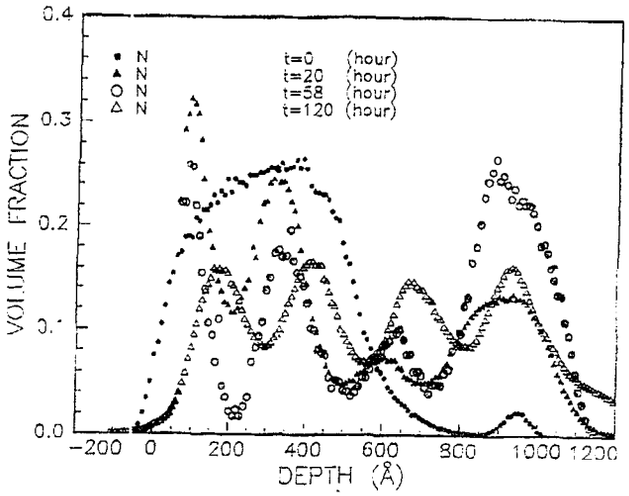

Figure 4: Density of states for solid C_{60} for a crystal with random molecular orientations, as given by LDA calculations, quasiparticle calculations, and as inferred from direct and inverse photoemission spectroscopy (PES and IPES). Experimental data are from Rcf. 13.

$Fm3$ structure. In fact, the DOS for the T_{1u} and the T_{1g} complexes are sharpened for the $Pa3$ structure and the random structure. These trends are qualitative similar to those from a previous study [26].

The quasiparticle and LDA density of states are presented i ı Fig. 4 along with typical photoemission (PES) and inverse photoemission (IPES) data [13]. 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 tlie excitation energies as the encrgies needed to add a. quasiparticle or quasihole to tlie interacting many-electron system. Table I summarizes our results and data from various experiments. The calculated quasiparticle minimum gap is sliglitly small compared to values from PES/IPES [11–14], but too large compared to the result from microwave conductivity measurements [10]. Tlie microwave conductivity results would in fact suggest a. smaller $H_u - T_{1u}$ peak-to-peak distance leading to a. better agreement between theory and experiment. There are also issues of tlie surface sensitivity of PES/IPES, sample characterization, or difficulty in aligning tlie electron chemical potentials in tlie separate PES and IPES experiments due to charging effects or sample damage in the latter case. Thus. the origin of the remaining discrepancy of 0.5 eV in tl e peak-to-peak distance remains uncertain.

We now examine the angle-resolved photoemission data and the issue of tlie band widtlis in solid C_{60}. Angle-resolved photoemission spectra were simulated, using the **k**-dependent DOS method described in Sec. II, for an ensemble of ten, ranciomly orieiited 12×12 surface primitive cells mhicli were 6 layer thick, oriented in the (1 11) direction. Such spectra could be compared to recently published ARIPES results hy Themlin *et al.* [17] which were obtaiiied on expitaxially grown C_{60} films oii a. GeS(100) substrate. Tlie simulatecl spectra in the $\bar{\Gamma} - \bar{K} - \bar{M}$ direction of the fcc (111) surface Brillouin zone are presented in Fig. 5a. We note that, even though there are 3 dispersing bands in the T_{1u} and the T_{1g} complexes, the calculated spectral peaks show negligible $k_{\|}$ dependence. In Fig. 5b, we trace the dispersion of tlie tlieoretical peaks as compared with that reported by Themlin *et al.* Since the experimental energies are referenced to tlie Fermi level which was not known with respect to tlie valence band maximum, we have aligned in Fig. 5b the theoretical and experimental peak positions of tlie T_{1u} complex at $\bar{\Gamma}$.

Tlie absence of strong, visible dispersion effects is seen in both theory and experiment, while the small visible dispersion is qualitatively similar in both sets. As finite energy or angular resolution in experiment or theory (due to tlie finite size of tlie supercell used), details of lifetime broadening, and small changes in our Slater-Koster fit would affect the results somewhat, more detailed comparison is difficult at present. Our quasiparticle results however clearly estahlish that the dispersive T_{1u} and T_{1g} states can lead to apparently non-dispersive ARIPES spectra. We find that the abscnce of dispersion in the spectra is caused by several factors: orientational disorder, the required Brillouin-zone integration normal to the surface, finite-resolution effects, and tlie multi-band nature of the complexes studied. Thus, it would be incorrect to deduce that tliis is an extremely narrow-band system based solely ori non-dispersive ARIPES data. This subtlety has been discussed by others [16].

In addition to shedding light on the issue of dispersion, tlie quasiparticle results are in excellent 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

Table I. Tabulated are the bandgap (E_g) and tlie $H_u - T_{1u}$ peak-to-peak interval, as given by direct and/or inverse photoemission (PES/IPES), microwave conductivity, LDA, and our quasiparticle (GW) calculation. All energies are in eV.

	PES/IPES	Microwave conductivity	LDA	Quasiparticle (GW)
E_g	2.3[a], 2.5[b], 2.6"	1.85[d]	1.04	2.15
H_u - T_{1u} peak-to-peak	3.5[a,b], 3.7"		1.6	3.0

a Ref. 13, *b* Ref. 12, *c* Ref. 14, *d* Ref. 10

included in the quasiparticle energies. As mentioned above, tlie corrections lead to an approximately 30% increase ill the band widths and in tlie separation between the T_{1u} and T_{1g} coinplexes.

The effects of merohedral orientational randomness [26] on tlie k-dependent. density of states are illustrated in Fig. 6 for tlie T_{1u} states. We see that tlie delta-function spectrum at a given k-poiiit for a perfect crystal is now significantly broadened. The large widths of the spectral peaks of tlie individual electronic states indicate a short mean-free-path of tlie electrons arising from scattering due to tlie molecular orientational disorders. It is tlie combined effects of tliis type of broadening with the multi-band nature of tlie complexes and $k_\perp$ integration which give rise to the non-dispersive ARIPES peaks.

Our calculations also show that, for the HOMO complex, the band nature of the electronic states may be seen in high-resolution angle-resolved photoemission experiments. Figure 7 depicts tlie calculated quasiparticle ARPES along $\bar{\Gamma}$ to $\bar{M}$ in tlie fcc (111) surface Brillouin zone simulated using an ensemble of supercells containing 1536 niolecules. The spectra were convoluted with a halfwidtli of 0.05 eV to mimic typical experimental resolution. The width of the overall spectral distribution is in good agreement with experimental PES data. More importantly, the curves clearly demonstrate that there is a dispersion of a few tenths of an eV as one goes from $\bar{\Gamma}$ to $\bar{M}$. It should be noted that the theoretical results have neglected matrix elements and final state effects. These effects would alter the exact shapes of the observed spectra froin those given by the simulation here. Recent high resolution ARPES experiments by Gensterblum *et al* [27] have indeed observed dispersive features similar to those given in Fig. S.

IV. Suininary and Conclusions

We have carried out a study of the electron excitation energies in undoped, solid C_{60} within the theoretical framework of quasiparticles. For the Fm3 structure, an *ab initio* quasiparticle calculation was done using tlie method of Hybertsen and Louie within the GW approximation. A quantitative, tight-binding paranieterization of our results has facilitated comparison of computed densities of states for crystals with a variety of orientational order or disorder, as well as comparison with angle-integrated and angle-resolved PES and IPES data. Using a quasiparticle picture in place of a. LDA eigenvalue picture, we obtained substantial iinprovement in the agreement between theory and experiment for the band gap and the interval between the PES and IPES peaks closest to the gap. There is also a 30% increase in bandwidths compared to LDA results due to self-energy corrections. The theoretical results provide an explanation for the apparent lack of dispersion in tlie spectra peak positions observed in recent ARIPES experimental on the unoccupied states. Moreover we show that the band nature of the HOMO complex should be observable in high-resolution ARPES. The present theory thus provides a quantitative description of many of the salient features in the experimental excitation spectra of solid C_{60}. Our results suggest that, although many-body corrections to the band gap and dispersion are sizable, the general electronic structure of this system is well described in a quasiparticle

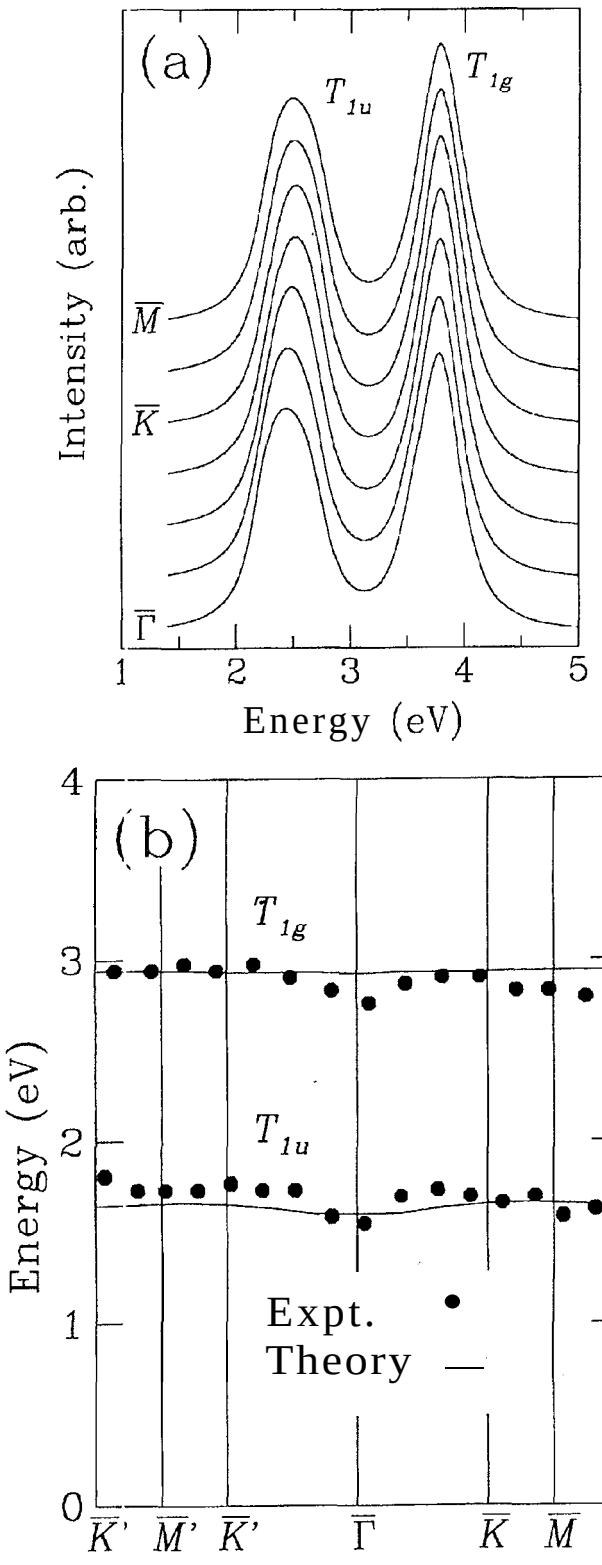

Figure 5: (a) Simulated ARIPES spectra for solid C_{60} with random molecular orientations for tlie T_{1u} and T_{1g} complexes for various wavevectors $k_{\|}$ in tlie (111) surface Brillouin zone; (b) dependence of spectral peak position on $k_{\|}$ as given by our results (theory) and the experimental results of Ref. 17. The origin of the experimental energy scale is arbitrary, Eut this does not affect the $T_{1u} - T_{1g}$ splitting.

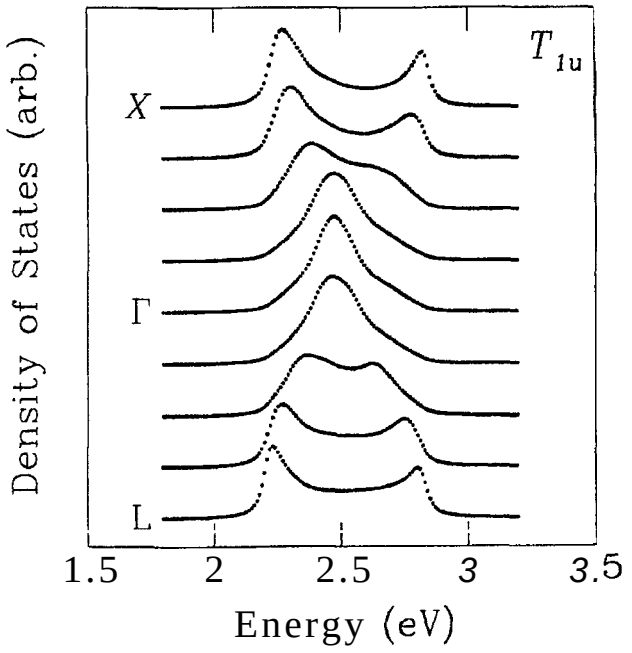

Figure 6: Calculated k-resolved density of states with meroliedral orientational randomness for the T_{1u} complex for various k-vectors along tlie $L - \Gamma - X$ direction in the bulk fcc Brillouin zone.

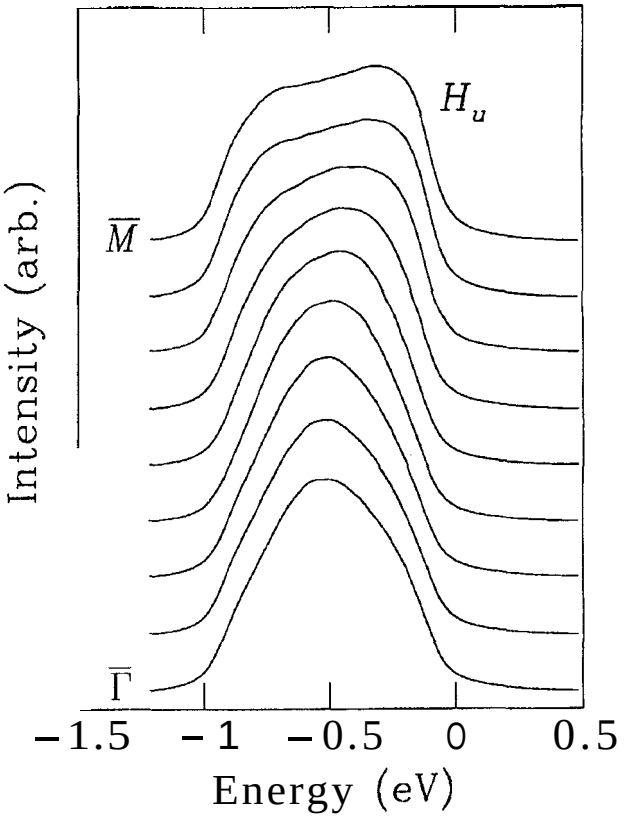

Figure 7: Simulated ARPES spectra for solid C_{60} with random molecular orientations for the HOMO complex along the $\bar{\Gamma} - \bar{M}$ direction in the (111) surface Brillouin zone.

band picture with molecular orientational disorder

Acknowledgments

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