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Photoemission and Optical Properties of C_{60} Fullerites

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Abstract

A theory is presented for excitations in undoped, solid C_{60} involving addition or removal of an electron, as well as creation of an electron-hole pair. Excitation energies are computed using a quasiparticle description of electrons and holes, plus a model for electron-hole interactions. Results are compared with those of direct and inverse photoelectron and optical absorption spectroscopy studies. Reasonable agreement is found in such comparisons, while more complete modeling of experimental spectra might include neglected matrix-element and vibrational effects. These results give values for simple, conceptual parameters, such as a molecular Hubbard U. Some results could also be relevant in doped fullerites.

Introduction

As discussed throughout this Volume, modern electronic structure theory, of which Professor Marvin L. Cohen is a pioneering and central figure, has become an indispensable tool in understanding and predicting properties of real materials. Theory is particularly valuable when studying novel, complex materials. Here, we present theoretical work on undoped, solid C_{60}.

With discovery of the C_{60} molecule [1], and of a process to produce this substance copiously [2], the field of fullerene solids was born. Subsequent discovery of superconductivity in alkali fullerides [3] bolstered interest in fullerene

research tremendously. The metallicity of alkali and alkaline-earth fullerides is achieved by nearly complete transfer of metal valence electrons to available states in unfilled, C_{60} molecular-orbital shells. Consequently, many aspects of the electronic structure in all fullerene solids can be studied by examining undoped, solid C_{60}, especially as such metal ions produce weak scattering effects on electrons [23].

Herein we examine electron excitations in undoped, solid C_{60}. We study excitations involving injection of an electron or a hole, or formation of an electron-hole pair. We compare our results to those given by direct- and inverse-photoemission [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18], and absorption [19, 21] spectroscopic studies. Our work provides direct information on undoped, solid C_{60}, plus indirect insight into features of the electronic structure which persist upon doping.

We first review information relevant to this work on undoped, solid C_{60}, including aspects of both the crystal and electronic structure. Fullerites are complex materials, and their electronic structure is often described in a stepwise fashion. Aspects of the electronic structure included at one step build on a foundation laid in previous steps. Success comes by first treating large-energy contributions to electron levels or electron promotions, and then treating small-energy effects. We therefore discuss a "hierarchy" of various contributions to electron energies.

It is helpful to introduce several, conceptual energy parameters: the molecular Hubbard U, which sets an energy-scale for electron-electron interactions, the typical inter-molecular electron hopping amplitude, t, the typical electron (or hole) band width, W, and the exciton band width, w. Quantitatively describing properties of real materials still requires extensive numerical treatment of the electronic structure, e.g. detailed description of one-electron wave functions. Nonetheless, objects such as a Hubbard U help explain such things as the difference between the apparent energy gaps obtained by joint direct/inverse photoemission versus absorption spectroscopy. This follows because results found in these two approaches are influenced differently by physical effects associated with such a parameter.

To predict electron and hole excitations accurately, one needs to deal with many-electron effects. We outline the quasiparticle approach used here, and present results for the band structure of undoped, solid C_{60}. We compute the insulating band gap and band widths, and analyze effects of molecular orientational disorder. Transfer integrals for inter-molecular electron hopping depend strongly on molecular orientations, so band-structure topologies are affected qualitatively. Also, molecular orientational disorder should strongly influence angle-resolved photoelectron spectra.

The above quasiparticle framework describes a single electron or hole injected into a many-electron system, *viz.* undoped, solid C_{60}. So these results are suitable for comparison to experimental direct- and inverse-photoemission

spectra. To describe optical excitations probed in absorption spectra, such as creation of excitons, one must supplement a quasiparticle picture with electron-hole interactions. We present our description of these interactions and report results for low-lying excitons. In particular, we note the similarity between optical excitations in an isolated C_{60} molecule and in undoped, solid C_{60}.

We intend for this review to provide a cogent, quantitative picture of these elementary excitations in undoped, solid C_{60}: electrons and holes (quasiparticles), and excitons. In forming that picture, one constructs a framework to study related aspects of this material's electronic structure, electron-electron interactions in particular. Details of calculations are given elsewhere [22]; here we review key features of our approach and our salient results. Finally, although we do not study doped fullerides here, our results should guide construction of models used to study such systems, by providing constraints on parameters used.

Crystal and Electronic Structure of C_{60}

The C_{60} molecule—in other ways like graphite and planar, unsaturated organic molecules—has sixty equivalent carbon atoms forming an icosahedrally symmetric, soccer-ball-like cage, with every atom bonded to three others. There are five- and six-fold rings. The twelve five-fold rings contain bonds of length 1.45 Å, and these rings are joined by 1.40 Å bonds. Three of each atom's valence electrons contribute to σ-bonding, and remaining valence electrons form the π-electron complex. The π-electrons occupy "radial" π-orbitals normal to the surface of the "soccer-ball." The π-orbitals on the sixty carbons combine to form molecular orbitals (MO's) with symmetries consistent with the icosahedral group. Coefficients for the sixty, atomic π-orbitals in such MO's are icosahedral harmonics of the polar coordinates of associated carbon atoms. These functions are tabulated in Ref. [23]. The highest occupied and lowest unoccupied MO's (HOMO and LUMO) are such π-states. The HOMO have H_u symmetry; the LUMO have T_{1u} symmetry; the next higher orbitals (LUMO+1) have T_{1g} symmetry.

In undoped, solid C_{60}, the molecules form a face-centered-cubic lattice, but molecular orientations depend on the temperature and history of a crystal [24, 25]. At room temperature, molecules are randomly oriented and tumbling. For electron excitations studied here, the C_{60}'s may be treated as randomly oriented but stationary. We estimate room-temperature quantities by averaging them over an ensemble of random molecular orientational configurations. As the solid is cooled, it undergoes two phase transitions regarding molecular orientational order, with molecules oriented in a $Pa3$ structure (four molecules per simple-cubic unit-cell) at low temperature. Achieving a perfect $Pa3$ lattice is difficult.

In the solid, MO's on one molecule hybridize with those on others, broadening molecular electron levels into bands. The nature of hybridization depends on molecular orientations, which consequently affect topologies of the complexes of H_u, T_{1u} and T_{1g} electron energy bands. However, centroids of these complexes are quite insensitive to orientations. Hybridization is largest between like MO's; hybridization between unlike MO's typically affects band energies by percents of band widths.

The ionization potential and electron affinity of an isolated molecule are respectively around 7.6 eV [26] and 2.7 eV [27]. This gives a vapor-phase value of 4.9 eV for the H_u–T_{1u} separation, if one associates such energies with electron removal or addition. However, the lowest excited (triplet) state in the isolated molecule is only 1.7 eV [28] above the ground state. This implies an intra-molecular attraction of about 3.2 eV between a T_{1u} electron and H_u hole. In the solid, the centroids of the H_u hole and T_{1u} complexes are separated by 3.5 eV-3.7 eV according to joint direct- and inverse-photoemission spectra. This is less than 4.9 eV due to solid-state screening effects. Meanwhile, creating the lowest triplet exciton in the solid requires an excitation of 1.55 eV [29]. Similarity of this to the above 1.7 eV suggests molecular excitons which are insensitive to the crystalline environment, consisting primarily in rearrangement of internal molecular degrees of freedom.

In summary, the H_u–T_{1u} splitting is 4.9 eV for the free molecule, but solid-state screening effects reduce this splitting by about 1.2 eV-1.4 eV. This splitting is the largest part of excitation energies we consider. In the solid, electron and hole band widths are about 1 eV, indicating a Hubbard hopping amplitude, $t \sim 0.1$ eV. Note that the hopping amplitude for an MO on one C_{60} and an MO on another C_{60} depends on the orientations of the molecules. Therefore, the quantity t is non-uniform and variable. Generally, the band width W is still related to typical values of t through the coordination number, $Z = 12$. So when describing single electrons or holes, it is helpful to deal first with the H_u–T_{1u} splitting, and then to consider banding effects related to inter-molecular hopping.

An electron-hole pair by $H_u \rightarrow T_{1u}$ promotion enjoys an attractive, unscreened $U \approx -3.2$ eV in the isolated molecule, but screening effects reduce this U to around -2.1 eV in the solid. It is no accident that screening effects reduce $|U|$ and the H_u–T_{1u} splitting similarly. Solid-state screening effects are favorable for creating an electron or hole, accompanying these charged species with polarization clouds on neighboring molecules. Such effects do not assist forming molecular excitons. The electron-hole U is relevant to optical energies, but not when discussing electron additions or removal. In a one-electron, local-density approximation (LDA) framework, the H_u and T_{1u} band centroids are separated by only 1.6 eV. This is because the LDA neglects many-body corrections to the HOMO-LUMO gap, which for a molecular solid are predominantly a repulsive, electron-electron U of like magnitude to the electron-hole U.

Note that one has a Hubbard U much larger than t. This is why one finds excitons with strongly molecular character: the behavior of low-lying, electron-hole pairs is predominantly influenced by the electron-hole interaction. One expects an exciton band width $w \sim Zt^2/|U|$, if one considers that an exciton can move from one ball to another in two separate steps, in each of which either the electron or the hole moves. This band width is very small ($\sim$ 50 meV). So when describing excitons, it is helpful to deal first with the H_u–T_{1u} splitting, followed by effects related to the electron-hole U, followed by dispersion effects.

Electron and Hole Excitations: Quasiparticle Approach

Direct- and inverse-photoemission techniques probe removals or additions of an electron. Such *quasiparticle* excitations consist of an electron or hole, plus its surrounding polarization cloud. Propagation of quasiparticles is given by the one-electron Green's function, G [30]. For energy E, this may be written as

$$G(\mathbf{r},\mathbf{r}';E) = \sum_{\mu} \frac{\Psi_\mu(\mathbf{r})\,\Psi_\mu^*(\mathbf{r}')}{E-(\epsilon_\mu \pm i\eta)}. \tag{1}$$

There is a pole for each state, μ, created by electron addition or removal, at energy ϵ_μ (that needed to add an electron, or minus that needed to remove an electron). The electron amplitude for such additions or removals depends on Ψ_μ.

For a many-electron system, the Green's function may be found by solution of Dyson's equation, which is written as follows:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_N(\mathbf{r}) + V_H(\mathbf{r})\right]\Psi_\mu(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';\epsilon_\mu)\,\Psi_\mu(\mathbf{r}') = \epsilon_\mu \Psi_\mu(\mathbf{r}). \tag{2}$$

This resembles the one-electron Schrödinger equation. There is a kinetic energy term, as well as terms dealing with the external nuclear potential felt by electrons, and the Hartree potential. The effects of electron-electron interactions are included through the non-local, non-hermitian, energy-dependent self-energy operator, Σ, which accounts for effects of an electron's dynamical polarization cloud.

In local density-functional theory [32], Kohn-Sham eigenvalues may be loosely viewed as excitation energies, and these are found by the replacement of the self-energy operator in Eq. (2) with a local, Kohn-Sham potential, $V_{xc}(\mathbf{r})$. In the LDA [33], this potential is computed from the local density, $n(\mathbf{r})$, with $V_{xc}(\mathbf{r})$ being the self-energy correction to the electron chemical potential in a uniform electron gas of equal density.

In the quasiparticle approach, a version of the Green's Function formalism, one assumes electron additions or removals near the Fermi level possess

a predominantly one-electron-like character, and are amenable to an effective one-electron description. Σ may be thought of as a sort of potential, and ϵ_μ and $\Psi_\mu(\mathbf{r})$ are referred to as a *quasiparticle energy* and *quasiparticle wave function.*

The self-energy operator may be expanded in terms of G and the Coulomb interaction. A better converged expansion involves G and the dynamically screened Coulomb interaction, W. We may write the self-energy operator in the series,

$$\Sigma(\mathbf{r},\mathbf{r}';E) = +i\int \frac{d\omega}{2\pi} e^{i\eta\omega} G(\mathbf{r},\mathbf{r}';E+\omega)\, W(\mathbf{r},\mathbf{r}';-\omega) + \cdots. \tag{3}$$

In the "GW approximation," one includes only the term written[31]. This is permissible when there are large screening effects, as occur in solids: W is then "small," whereas terms being neglected represent effects of higher order in W.

Technical details of our GW, quasiparticle calculations have been given elsewhere[22]. We compute self energies in the Hybertsen-Louie approach [34], with the static W computed using a Levine-Louie-Hybertsen dielectric matrix [35], and with W being extended to finite frequency using a generalized, plasmon-pole model. G is constructed initially using LDA-derived, one-electron wave functions and energies for their quasiparticle counterparts, but quasiparticle energies are then updated self-consistently.

Quasiparticle calculations on a system as complex as undoped, solid C_{60} demanded substantial computational resources. For simplicity, calculations were first carried out for the highly symmetrical, $Fm3$ structure of C_{60}, which has one molecule per unit-cell. Thereafter, we performed an accurate, Slater-Koster [36] parametrization of the results, based on H_u, T_{1u} and T_{1g} term energies and hopping amplitudes. This parametrization used a molecular-orbital basis; we needed only eleven MO's per C_{60} to describe the H_u, T_{1u} and T_{1g} states. Molecular orientational effects could then be included efficiently by using supercells within the Slater-Koster approach.

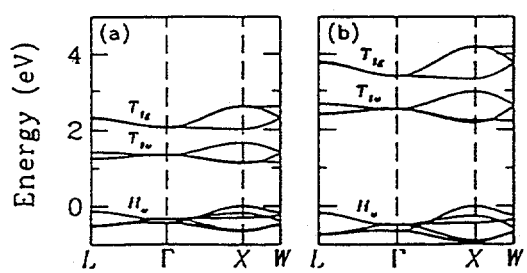

Fig. 1. $Fm3$ band structure of solid C_{60} as obtain in the LDA (a) and in the quasiparticle approach (b).

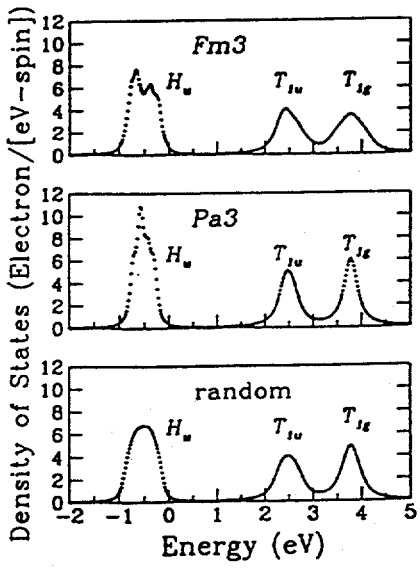

Fig. 2. Quasiparticle, H_u, T_{1u} and T_{1g} densities of states in $Fm3$, $Pa3$ and room-temperature structures of undoped, solid C_{60}.

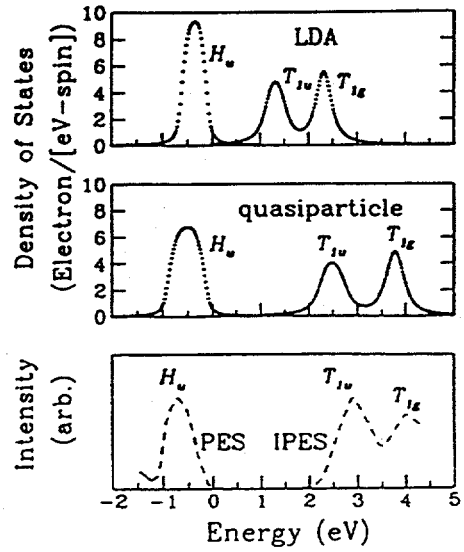

Fig. 3. Total density of states for room-temperature structure of undoped, solid C_{60} as given in the LDA, in the quasiparticle approach, and by experiment (Ref. [9]).

LDA and quasiparticle electron energy bands for the $Fm3$ structure are presented in Fig. 1. The $Fm3$ band gap is about 1.04 eV in the LDA, versus 2.15 eV in the quasiparticle approach, which agrees much better with the experimental value of 2.3 eV-2.5 eV. Compared to LDA results, quasiparticle results show a uniform, 30% enhancement of the widths of the occupied H_u bands, as well as of the unoccupied T_{1u} and T_{1g} bands and T_{1u}–T_{1g} band separation. (By "H_u bands," we mean groups of electron states constructed primarily from the H_u MO's, etc.) In Fig. 2, we give quasiparticle densities of states for the $Fm3$ and $Pa3$ structures, as well as for a room-temperature crystal. Structures visible in the densities of states for ordered phases vanish in the presence of molecular orientational disorder.

In Fig. 3, we present densities of states as found within the LDA and quasiparticle approaches, in addition to angle-integrated direct- and inverse-photoemission spectra. The H_u–T_{1u} peak-to-peak distance is greatly improved in the quasiparticle results as compared to LDA results. We note that results based on joint direct and inverse photoelectron spectroscopy might be influenced by sample-charging or sample-damage effects, as well as surface effects (in particular, a reduced level of screening effects, compared to the bulk, due to lower coordination numbers for molecules at the surface). Throughout this work, we neglect matrix-element effects when comparing theoretical densities of states to experimental spectra.

Angle-resolved photoemission and band-dispersion effects

Whereas angle-integrated photoelectron spectroscopy tends to probe total densities of states, discussed above, much effort has also been devoted to obtaining angle-resolved photoelectron spectra for fullerites. In periodic solids, angle-resolved spectra can be used to ascertain a material's momentum-resolved density of states, i.e. its band structure. In reality, one can sometimes specify only two components of the crystal momentum of electron states probed, because of the surface termination. This is probably true in studies of fullerites, where the mean free path for low-energy photoelectrons is roughly the unit-cell size. Longer mean-free-paths could be obtained at lower photoelectron energies, at the cost of probing states in only a small region of reciprocal space while increasing the susceptibility of spectra to final-state and matrix-element effects, or at higher photoelectron energies, where limited angular resolution means poor momentum-resolution. This limitation is particular severe in fullerites, which have small Brillouin zones.

When interpreting angle-resolved spectra for fullerites, there are other considerations besides the above, kinematical ones. Due to the short mean free path, we assume that angle-resolved spectra represent substantial integration over crystal momentum normal to the surface, $k_\perp$. Further, even when one deals with single-crystal samples, molecular orientational disorder will destroy

periodicity, and molecular orientations may be different at the surface and in the bulk. In the presence of molecular orientational disorder, one may still define a momentum-resolved density of states, i.e.

$$A_{\mathbf{k},\mathbf{k}}(E) \sim \sum_n \sum_\mu |\langle n\mathbf{k}|\Psi_\mu\rangle|_S^2 \, \delta(E - \epsilon_\mu) \,. \tag{4}$$

The $|n\mathbf{k}\rangle$'s form a complete set of Bloch states for a reference periodic system, e.g. the $Fm3$ structure in the case of undoped, solid C_{60}; S denotes sampling over a region of a disordered crystal (a supercell in this work). As written, $A_{\mathbf{k},\mathbf{k}}(E)$ is fully momentum-resolved, whereas integration of this quantity over $k_\perp$ might be more appropriate when modeling angle-resolved photoemission data.

In early angle-resolved work on in undoped, solid C_{60}, where momentum resolution is marginal, Wu *et al.* [10] observe minimal angular dependence in photoelectron spectra. They suggest that the underlying bands are extremely narrow, and that the apparent widths of the H_u, T_{1u} and T_{1g} complexes could be due to vibrational effects. Gensterblum *et al.* [17], using better momentum resolution, found features dispersing up to a few tenths of an eV. Benning *et al.* [18] claimed to find dispersion in high conduction bands due to final-state, joint-densities-of-states effects. However, Themlin *et al.* [14] observed minimal dispersion in the lowest two conduction-band complexes in angle-resolved, inverse-photoemission work.

We suggest there is considerable dispersion in electron energies due to intermolecular hybridization, as shown in Figs. 1 and 2, while orientational disorder and experimental integration over $k_\perp$ suppress traditional signatures of dispersion in angle-resolved spectra. By attempting to establish traditional signatures of dispersion—that spectral features move in energy as the angle of electron emission (entry) or photon energy change—one implicitly assumes a well defined energy-momentum relation for electron states. Merely integrating over $k_\perp$ might obfuscate observing such a relation: integrating over $k_\perp$ would prevent detecting variation of an electron-state energy with $k_\perp$, and the dependencies of a band energy on the remaining two components of crystal momentum might depend on $k_\perp$. Molecular orientational disorder prevents any simple energy-momentum relation, since states lack good momentum. Nonetheless, momentum-resolved densities of states can still be momentum-dependent, and hybridization effects still imply that electron energies within a given complex are dispersive, having a spread of ~ 1 eV even without vibrational broadening.

In Fig. 4, we show fully (three components specified) momentum-resolved densities of states for momenta at three highly symmetric points in the $Fm3$ Brillouin zone. These H_u densities of states are given for the $Fm3$ and room-temperature structures of undoped, solid C_{60}. The $Fm3$ results are δ-functions, broadened for sake of presentation, at the associated $Fm3$ band energies. In the room-temperature case, there are continua in the momentum-resolved densities

of states, and one finds spectra depend weakly on momenta sampled. These results demonstrate the strong effects of molecular orientational disorder.

We next turn to Figs. 5 and 6, which show $k_\perp$-integrated, momentum-resolved (two components specified) densities of states for the H_u, T_{1u}, and T_{1g} complexes in the room-temperature crystal. We present stack-plots that

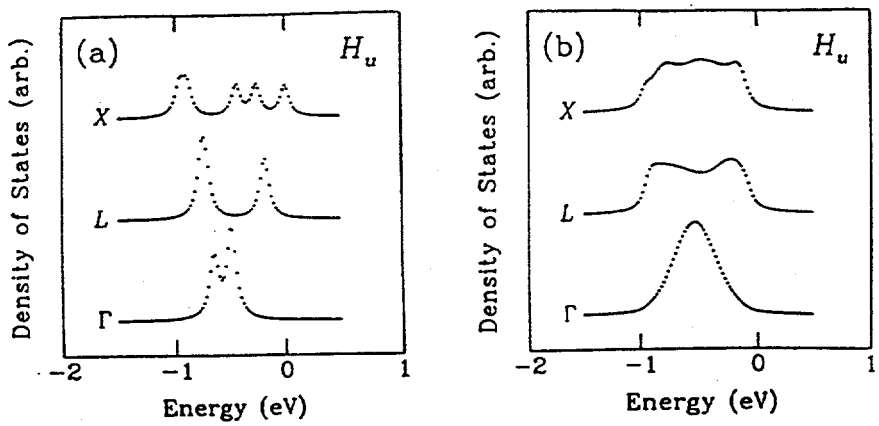

Fig. 4. Fully momentum-resolved densities of states at Γ, X and L for $Fm3$ (a) and room-temperature (b) structures of undoped, solid C_{60}.

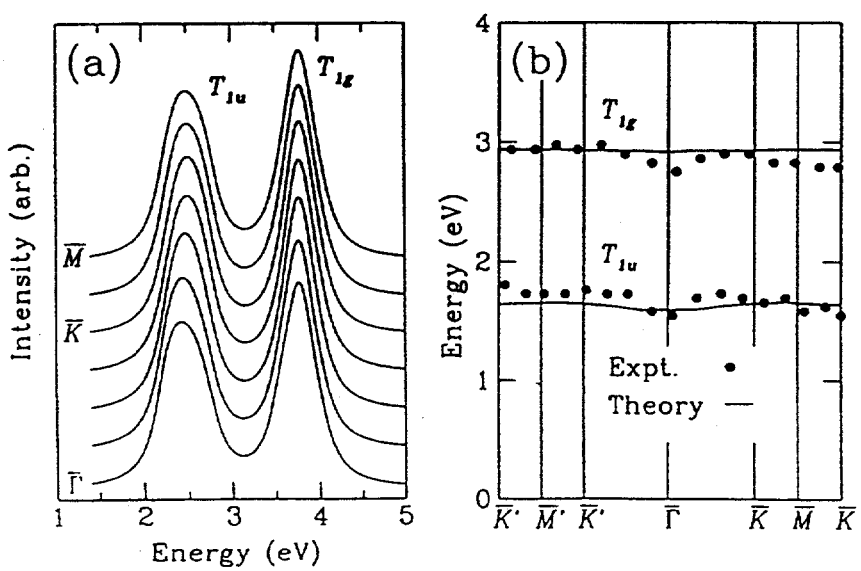

Fig. 5. Momentum-resolved, $k_\perp$-integrated H_u density of states for room-temperature, undoped, solid C_{60} along a path between the center and edge of the surface Brillouin zone.

trace paths in the surface Brillouin zone surveyed by angle-resolved experiments. In Fig. 6(b), we also map energy positions of spectral peaks as one scans the Brillouin zone, which superpose well with experimental results. (The experimental energy zero was arbitrary.) The lowest spectrum in Fig. 5 corresponds to an integration of fully momentum-resolved spectra along the $\Gamma - L$-line. Spectra at the ends of this line are given in Fig. 4. Comparison of spectra shown in Figs. 4 and 5 demonstrates loss of information which can occur under $k_\perp$-integration.

The results presented in Figs. 5 and 6 have the same level of signatures of dispersion as found in experiment, and do not reflect vibrational effects. So a lack of strong angle-dependence in photoemission data does not necessarily rule out energy dispersion in states probed. However, the lack of a strong angle-dependence might suggest the absence of a clear energy-momentum relation. Note that the simulations discussed here selectively include or omit factors potentially influencing angle-resolved spectra. Such controlled manipulation or probing of the physical system is generally inaccessible to experiment.

Low-lying optical excitations: excitons

While the "photoemission band gap" in undoped, solid C_{60} is 2.3 eV-2.5 eV experimentally, with the present quasiparticle results underestimating this gap slightly, optical excitations occur at much lower energies. Creating the lowest, triplet exciton (detected by electron-energy-loss spectroscopy) requires 1.55 eV

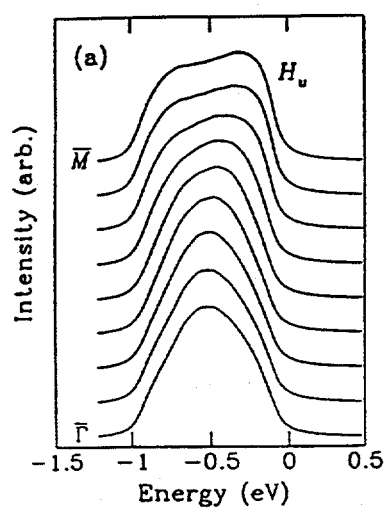

Fig. 6. Momentum-resolved, $k_\perp$-integrated T_{1u} and T_{1g} densities of states for room-temperature, undoped, solid C_{60} along a path between the center and edge of the surface Brillouin zone (a), mapping of energies of the peaks (b). Experimental data are from Ref. [9].

excitation of a crystal. Creating the lowest, singlet (optically accessible) exciton requires 1.83 eV excitation [21]. The magnitudes of these excitons' binding energies, as well as of the singlet-triplet splitting, suggest a tightly-bound, Frenkel (molecular) character. Detailed similarity of n-hexane-solution[20] and solid-state[21] C_{60} absorption spectra indicates that low-lying excitons constitute excitations within single C_{60} molecules. Absence of any detectable diamagnetic shift at 15 Tesla corroborates this hypothesis [21].

We model excitons in solid C_{60} with a Hamiltonian of the form,

$$\hat{H}_{\text{exciton}} = \hat{H}_e + \hat{H}_h + \hat{H}_{e-h}. \tag{5}$$

$\hat{H}_e$ and $\hat{H}_h$ respectively describe a single T_{1u} electron and H_u hole, and these terms are given by the Slater-Koster parametrization discussed earlier. $\hat{H}_{e-h}$ describe the screened electron-hole interaction. The electron and hole interact with each other directly, but they also interact with each other's polarization clouds, which is how their interaction is screened. (Interactions of each particle with its own polarization cloud, i.e. self-energy effects, are already included in $\hat{H}_e$ and $\hat{H}_h$.) The direct interaction between electron and hole on separate molecules is a simple Coulomb interaction (e^2 divided by the separation), whereas we model interactions on the same C_{60} molecule using a Parr-Pariser-Pople [37] treatment of the necessary Coulomb integrals involving π-states. We use Löwdin's parametrized integrals. However, rather than use these integrals directly, we scale them to achieve a 3.2 eV electron-hole attraction for the lowest excited triplet state in vapor-phase C_{60}. (Hence, our work does not constitute a fitting of the solid-state exciton energy, nor even of the vapor-phase excitation energy, but rather of the size of the intra-molecular electron-hole attraction.) Screening of the electron-hole interaction is dealt with using the linear, dipole polarizability of the C_{60} molecule, with intermolecular dipole-dipole interactions included.

In the $Pa3$ phase of undoped, solid C_{60}, we find the lowest triplet and singlet excitons require excitation energies of 1.30 eV and 1.57 eV, respectively, in good agreement with experiment. Symmetry allows for singlet and triplet Frenkel excitons with T_{1g}, T_{2g}, G_g and H_g symmetry. We find the lowest singlet and triplet excitons have T_{2g} symmetry, although the singlet T_{1g} exciton levels are energetically close to the singlet T_{2g} excitons levels. Direct comparison of our exciton densities of states with optical absorption spectra is difficult because of vibrational-replica effects that we omit. We have also studied exciton dispersion effects in the $Fm3$ structure, finding a 50 meV band width for T_{2g} excitons, in accord with the order-of-magnitude estimate presented earlier. In $Pa3$, we find that the lowest sixty excitons are of Frenkel character, with the electron and hole on the same molecule with $> 84\%$ likelihood, usually with as much as 96% likelihood. (In the $Pa3$ structure, there are sixty ways to arrange a T_{1u} electron and H_u hole on the same C_{60} in a given unit-cell.) Meanwhile, the next-lowest excitons have a strong charge-transfer character, there being

roughly an 85% likelihood for the electron and hole to be on adjacent molecules. It has been suggested [38] that the presence of charge-transfer excitons in undoped, solid C_{60}, but not when the molecule is in solution, might explain why films of C_{60} appear yellow, despite the magenta appearance of the solution.

Summary

We have presented quasiparticle results for electronic excitations in undoped, solid C_{60}, discussing electron additions and removals, as well as the formation of excitons. We examined the band gap and band widths, as well as the effects of orientational disorder on electron and hole states. We discussed the apparent lack of traditional signatures of band dispersion as found in angle-resolved direct- and inverse-photoelectron spectroscopy, demonstrating that orientational disorder and the inability to specify one component of the momenta of states probed might obfuscate such signatures. We modeled singlet and triplet excitons, finding excitons of both Frenkel and charge-transfer types. Due to strong, intra-molecular electron-hole attractions, it is reasonable that the absorption edge is at 1.8 eV, albeit considerably lower than the band gap established through joint direct and inverse photoelectron spectroscopy.

We find an electron or hole band width $W \sim 1$ eV, with inter-molecular hopping amplitudes characterized by $t \sim 0.1$ eV. The electron-electron and electron-hole molecular Hubbard U's both have the magnitude 1.4 eV, based on (1) the difference in the average H_u–T_{1u} splittings as found in the local-density approximation and in a quasiparticle approach, and (2) the excitation energy required to form a singlet exciton compared to the average, quasiparticle H_u–T_{1u} splitting. This leads to a 50 meV value for the $Fm3$, T_{2g}-exciton band width w, which seems reasonable.

Over all, there is reasonable agreement between the present theory and experiment. Further extensions of the theory could include matrix-element and vibrational effects on excitation spectra. This would be valuable to fullerite studies by testing models of and understanding in more detail the electronic structure of undoped and superconducting fullerides. For the sake of materials modeling in general, further work would be worthwhile since fullerites provide high-quality samples of complex, molecular solids.

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