Comment on "C 1s Autoionization Study of Electron Hopping Rates in Solid C_{60}"

Brühwiler *et al.* [1] reported that nearest-neighbor hopping of valence band electrons in the presence of the C 1*s* core hole in solid C_{60} is facilitated by a nearest-neighbor Coulomb repulsion V of the order of 0.7 eV. They assert, with reference to the paper by Antropov, Gunnarsson, and Jepsen [2], that the on-site Coulomb repulsion $U \approx 1.5$ eV [3] is effectively reduced by V, such that the conductivity gap E_{gap} is not opened, in spite of the relatively small one-electron bandwidth $W \approx 0.5$ eV, and conclude that stoichiometric K_3C_{60} is not a Mott-Hubbard insulator. These assertions, however, are invalid, and we will show below that E_{gap} is determined by U and W only, independent of V, except for large V, for which the system undergoes a phase transition to form charge density waves (CDW) [4], in which case E_{gap} even increases with V.

The conductivity gap is determined by $E_{\text{gap}} = E_I - E_A = E_{\text{GS}}^{N+1} + E_{\text{GS}}^{N-1} - 2E_{\text{GS}}^{N}$, where E_I (E_A) refers to the electron ionization (affinity) energy, N the number of electrons in the ground state and E_{GS}^{X} the ground state energy of the system with X electrons. For a one dimensional m-fold degenerate extended Mott-Hubbard model in the atomic limit ($W = 0$), it is easy to show that $E_{\text{GS}}^{N+1} = E_{\text{GS}}^{N} + nU + 2nV$ and $E_{\text{GS}}^{N-1} = E_{\text{GS}}^{N} - (n - 1)U - 2nV$. Therefore we find that $E_{\text{gap}} = U$, independent of V. For $V > U/2$, a CDW forms with $E_{\text{gap}} = U + 4m(V - U/2) > U$ for half filling and $E_{\text{gap}} = U$ otherwise.

These considerations will not change fundamentally when including intersite hybridization, which we verify by exact diagonalization with the resulting electron removal (PES) and addition (IPES) spectra shown in Fig. 1. It can be seen that E_{gap}, shown in the inset, is hardly affected by V, except for $V > U/2$ (CDW) for which E_{gap} *increases* with V.

That the gap cannot be reduced by V is not necessarily inconsistent with the experimental observations of Brühwiler *et al.* [1], because the energy involved for a nearest neighbor hopping is indeed reduced by V. It is, however, important to realize that the corresponding state is a charge neutral exciton at about $U - V$, which may be seen in optical experiments, and that the energy involved to break up this exciton to separate the charges as in a conductivity gap measurement will require an additional V, canceling the influence of V for the size of the gap.

Clearly the same conclusions will hold in two and three dimensions, including stoichiometric K_3C_{60} which crystallizes in a nonbipartite fcc lattice, except that the conditions for forming CDW will be different. Therefore, an intersite Coulomb repulsion V will not reduce the effective on-site Coulomb repulsion U to close the conductivity gap, although it may lead to the formation of excitons inside the gap observable in optical spectra. It is therefore not at all obvious that stoichiometric K_3C_{60} is not a Mott-Hubbard insulator, given the fact that U is much larger than the one-electron bandwidth W.

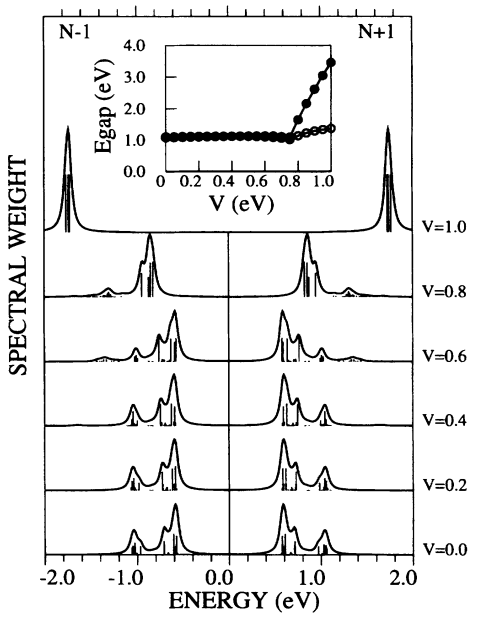

FIG. 1. PES/IPES spectrum, calculated for a twofold degenerate, half filled ($n = 2$) four-site Mott-Hubbard ring with $U = 1.5$ eV and $W = 0.48$ eV for different values of the nearest-neighbor repulsion V. The inset shows the value of E_{gap} at half filling (•, $n = 2$) and away from half filling (○, $n = 1, 3$).

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