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Coulomb integrals and model Hamiltonians for C_{60}

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The effective on-site Coulomb interaction U and the nearest-neighbor interaction V for a C_{60} solid are calculated. We obtain $U = 0.8 - 1.3$ eV and $V = 0.3 - 0.5$ eV. The photoemission spectrum for a finite Hubbard chain is calculated and an appreciable broadening of the spectrum is found for these parameters, due to many-body effects.

C_{60} has attracted much interest after it was found that it can be produced in solid form[1] and that it becomes superconducting.[2] It has been suggested that many-body effects may play an important role for C_{60}.[3,4] The importance of these effects depends on the relative size of the on-site Coulomb interaction U minus the nearest-neighbor interaction V and the hopping energy or bandwidth W, i.e., $(U - V)/W$. An interesting aspect of solid C_{60} is that *both* these quantities are small. By U we mean here the interaction between two electrons in a t_{1u} orbital, which is delocalized over the whole C_{60} molecule. The value of U is therefore correspondingly small. The bandwidth W is determined by the hopping between the C_{60} molecules, which are far apart, leading to a small value of $W \sim \frac{1}{2}$ eV. In this paper we focus on the value of U and V and we obtain $U_0 = 2.7$ eV for a free molecule and $U = 0.8 - 1.3$ eV for a solid. For the nearest-neighbor interaction we find $V = 0.3 - 0.5$ eV. The relevant parameter for the strength of the correlation is then $(U - V)/W \sim 1$, suggesting appreciable correlation effects. We also calculate the photoemission spectrum for a Hubbard chain, using the calculated values of U and V, and find a substantial broadening of the spectrum due to many-body effects, although the width is smaller than the experimental width.

The simplest estimate of U is obtained from the Coulomb integral

$$F^0 = \int d^3r \int d^3r' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{1}$$

where $\rho(\mathbf{r})$ is the charge density corresponding to one occupied t_{1u} orbital. This "unscreened" U has to be renormalized, when used in a model Hamiltonian, to implicitly take into account effects not included explicitly in the model Hamiltonian. Such a renormalization can be performed for "high-energy" ("fast") processes, where the energies involved are much larger than the excitation energies of interest.[5] Here we are interested in a U appropriate for a Hubbard model describing the t_{1u} conduction bands, where the corresponding excitation energies are of the order 1 eV or less. Thus we include renormalizations due to the fact that the occupied orbitals expand when an additional electron is added, leading to a reduced effective U, since these processes involve excitations into high-lying molecular orbitals. We also take into account that in a solid U is further reduced by the polarization of surrounding molecules, since the polarization involves excitations in the range from several eV up to ~ 30 eV. Neither of these effects is included explicitly in a Hubbard model for the t_{1u} bands. We do not, however, include screening due to intraband excitations in the t_{1u} band, which corresponds to low-energy excitations (< 1 eV). This screening, which is very important, must be included explicitly in the Hubbard model.

As a first estimate of the unscreened F^0 we assume that $\rho(\mathbf{r})$ forms a thin shell of charge on a sphere with the radius $R \sim 3.5$ Å. Then $F^0 = e^2/R = 4.1$ eV. If we, somewhat more realistically, assume that $\rho(\mathbf{r})$ forms a shell with the finite thickness δ, we find that $F^0 = e^2(1 - 0.17\delta/R + \cdots)/R$. Assuming that $\delta = 1.42$ Å (approximately the distance between two C atoms), we obtain $F^0 = 3.8$ eV. Alternatively, we can approximate the charges on each C atom with point charges, and calculate the interaction between these,

$$F^0 = (\tfrac{1}{60})^2 \sum_{i \neq j} \frac{e^2}{R_{ij}} + 60(\tfrac{1}{60})^2 F_C^0, \tag{2}$$

where R_{ij} is the separation between two C atoms, and F_C^0 is an atomic on-site interaction. From atomic calculation for a C atom, we estimate $F_C^0 \sim 12$ eV, and obtain $F^0 = 3.7$ eV.

These calculations, apart from using a very simple model of C_{60}, neglect the relaxation of the charge density when an electron is added to the C_{60} molecule. To take this into account, we have performed density-functional calculations for a free C_{60} molecule, using the local-density approximation.[6] To obtain U_0, the U for a free molecule, we perform two calculations for a free C_{60} molecule with a different number of electrons. U_0 is then the increase in the energy of the t_{1u} orbital per electron added to the system.[7]

The calculations are performed using the linear-muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA).[8] In this method each of the 60 C atoms are surrounded by spheres, and there are also interstitial spheres filling up the empty regions. Thus there is a sphere in the center of the molecule, a shell of 32 spheres between the central sphere and the C shell, 32 spheres in a layer outside the C shell, and finally 60 spheres in the outermost layer. The spheres in the two shells next to the C spheres are located above or below the centers of the pentagons and hexagons, and the spheres in the outermost layer are put in the same arrangement as the 60 C atoms. Normally, the choice of interstitial sphere positions and volumes is guided by the principles of having a small overlap between the spheres and of having space filling. To impose these principles for a molecule, we introduce a fictitious Watson sphere surrounding all the other spheres. Space filling then means that the volume outside the Watson sphere plus the volumes of the other spheres fill space. The radii and positions of the other spheres are chosen so that space filling is obtained and the overlaps between these spheres are small (13–20%). After having introduced the Watson sphere to put constraints on the packing and the overlap of the spheres, we took into account that there is little charge outside the Watson sphere, which was therefore not included explicitly in the calculation. The calculations were performed using a program for periodic solids, with the Coulomb interaction between different molecules suppressed and the results extrapolated to infinite lattice parameter.

Using this approach for 240, 241, and 242 electrons, we deduce a value $U = \delta\varepsilon_{t_{1u}}(n_{t_{1u}})/\delta n_{t_{1u}} = 2.7$ eV. This value is almost unchanged if we consider the difference between 241 and 240 electrons or between 242 and 241 electrons. We find that as the number of electrons is increased, charge is shifted to the outer parts of the molecule. Thus when an electron is added to the molecule, about $\frac{1}{2}$ to $\frac{2}{3}$ of an electron is added to the shell of C spheres. The remaining charge is about equally distributed between the first and second shells of interstitial spheres outside the C spheres, and it is much larger than the weight of a t_{1u} orbital in these spheres. This change describes how the Coulomb interaction can be reduced by distorting the already occupied orbitals by shifting weight outwards as an electron is added to the system. Slightly larger values of U_0 (~ 3.0 eV) have been reported by Pederson *et al.*,[9] de Coulon, Martins, and Reuse,[10] and Martin and Ritchie.[11]

These results can be compared with experiment. U_0 can be written as

$$U_0 = I_p(\mathrm{C_{60}}^-) - A(\mathrm{C_{60}}^-). \tag{3}$$

Here the ionization potential $I_p(\mathrm{C_{60}}^-) = 2.7$ eV is known experimentally.[12] If the $\mathrm{C_{60}}^{2-}$ ion exists, it would further follow that the affinity $A(\mathrm{C_{60}}^-) > 0$ and $U_0 < 2.7$. $\mathrm{C_{60}}^{2-}$ has been observed experimentally,[12] but the possibility that it is metastable could not entirely be ruled out.[12] These considerations suggest that U_0 may be close to or slightly smaller than 2.7 eV. Alternatively, we can obtain U_0 from $I_p(\mathrm{C_{60}}) = 7.6$ eV,[13] $A(\mathrm{C_{60}}) = 2.7$ eV,[12] and the band gap $E_g = 1.6$ eV (Ref. 14) as measured by photoabsorption,

$$U_0 = I(\mathrm{C_{60}}) - A(\mathrm{C_{60}}) - E_g = 3.3 \text{ eV}. \tag{4}$$

The U_0 in (4) is larger than in (3), since E_g is reduced because the states of the electron and the hole in the absorption process can adjust so that they have maximum interaction, while in (3) the two electrons in $\mathrm{C_{60}}^{2-}$ adjust to have minimum interaction. Our calculation should therefore be compared with (3), which should also be most appropriate for the doped case.

So far we have considered a *free* molecule. We now turn to a $\mathrm{C_{60}}$ solid. In this case we expect U to be strongly screened by the polarization of the surrounding molecules. To this end we insert the $\mathrm{C_{60}}$ molecules in a fcc lattice and assign a polarizability α to each molecule. We add an electron to the central molecule, and allow the surrounding molecules to be polarized in a self-consistent way, both by the electron on the central molecule and by the polarization of the molecules themselves. This polarization acts back on the electron and reduces the energy increase of the t_{1u} level by an amount δU. The summation over neighboring molecules is extended until it is converged. The U for the solid is then

$$U = U_0 - \delta U, \tag{5}$$

where U_0 is the U for the free molecule. In this calculation we have assumed that the radius of the $\mathrm{C_{60}}$ molecules is small compared with the intermolecular separation, assuming that the molecules have point dipoles. We have estimated the error in this approach by performing the screening, using a model[16] for the dielectric function where the $\mathrm{C_{60}}$ molecules have the appropriate size. We spread out an electron over a molecule and calculate the screening of this charge from another, finite, polarizable molecule. For a given size of α, we find that the finite size of the molecule increases δU by about 12%. We have considered two values for α. A quantum chemical calculation gave the result $\alpha = 65$ Å^3.[15] Alternatively, we can use an experimental value (4.4) (Ref. 17) for the dielectric function together with the Clausius-Mossotti relation. For the lattice parameter $a = 14.04$ Å, this leads to $\alpha = 90$ Å^3. This value also contains contributions from vibrations of the molecule, which should not be included here, since the vibrations are not at high enough energies to be renormalized away. The proper value of α should therefore be between 65 and 90 Å^3. For these values of α we deduce $\delta U = 1.4$ and 1.7 eV, respectively. Taking into account the finite size of the molecules leads to the estimates $\delta U = 1.6$ and 1.9 eV, respectively. Together with $U_0 = 2.7$ we obtain values for U between 0.8 and 1.1 eV, or between 1.0 and 1.3 eV if we do not correct for the finite molecular size. In the following we use the estimate $U = 0.8 - 1.3$ eV. At the surface we expect U to be about 0.3 eV larger, due to the reduced screening. This can be compared with experimental estimates of U based on Auger electron spectroscopy, which gave $U = 1.6 \pm 0.2$ eV (Ref. 4) and 1.4 ± 0.2.[18]

We next consider the nearest-neighbor interaction V, which is obtained by calculating the increase of the energy of a t_{1u} orbital on a molecule 1 when an electron is added to a neighboring molecule 2. This leads to the result $V = e^2/R - \delta V$, where R is the nearest-neighbor separation and $-\delta V$ is the lowering of the t_{1u} orbital on molecule 1 due to the polarization of the surrounding molecules when an electron is added to molecule 2. For

$a = 14.04$ Å, we find δV=0.94 and 1.12 eV, resulting in $V = 0.5$ and 0.3 eV for the polarizabilities α=65 and 90 Å^3, respectively. In this case the effects of the finite size of the molecules on the screening are small.

We now consider the implications of these values of U and V on photoemission spectroscopy (PES). For this purpose we study a Hubbard model

$$H = \sum_{i=1}^{N} \sum_{\nu\sigma} \varepsilon_{t1u} n_{i\nu\sigma} + t \sum_{\langle ij\rangle} \sum_{\nu\sigma} \psi^{\dagger}_{i\nu\sigma}\psi_{j\nu\sigma} + t' \sum_{\langle ij\rangle} \sum_{\nu\neq\mu} \sum_{\sigma} \psi^{\dagger}_{i\nu\sigma}\psi_{j\mu\sigma} + \sum_{ij} \sum_{\nu\mu} \sum_{\sigma\sigma'}{}' U_{ij} n_{i\nu\sigma} n_{j\mu\sigma'} . \quad (6)$$

This model consists of a linear chain with N atoms and periodic boundary conditions. On each atom there is a level with orbital and spin degeneracy. To reduce the size of the problem we consider the orbital degeneracy 2 instead of the more appropriate degeneracy 3. The orbitals are connected by a hopping t for the same orbital quantum number and t' for different quantum numbers, and $\langle ij\rangle$ indicates a summation over nearest neighbors. The electrons on the same atom interact via the Coulomb interaction $U_{ii} \equiv U$ and electrons on different atoms via $U_{ij} \equiv V/|i-j|$. A one-dimensional system leads to certain pathological features, and the spectral features obtained in the present calculations, therefore, cannot be expected to be representative of the true three-dimensional system. The calculations can, nevertheless, give an indication of the magnitude of the many-body effects on the spectrum.

In Fig. 1 we show the spectrum for $N = 5$, $U = 1.2$ eV, $V = 0.5$ eV, and $t = 2t' = -0.08$ eV. For a noninteracting system with N large, this leads to the bandwidth 0.48 eV, which is close to the results of band-structure calculations.[19] For a half-filled band with noninteracting electrons, one then expects to see a PES spectrum which is 0.24 eV broad. In Fig. 1 the width is, however, increased to about 0.6 eV due to the Coulomb interaction. Modest variation of U (e.g., 0.7–2.0 eV) and V (e.g., 0.0–1.5 eV) with $U - V \geq 0.5$ eV give similar spectra with widths of 0.6–0.9 eV and a tendency to shift weight towards higher energies as U is increased. For a one-dimensional model without orbital degeneracy, it is known that in the limit of a large U the PES width is increased to $4t$ for the half-filled case.[20] Thus the PES width is in this case equal to the full noninteracting bandwidth, although the band is only half full. Here we find that with orbital degeneracy, the PES width becomes even larger than the full noninteracting bandwidth for the strongly correlated system. This is related to the fact that after a hole is created in the PES process, there can be either hopping of a hole with the same or with a different orbital quantum number than the hole created in the PES process. The value of U (or $U - V$) in Fig. 1 is not quite large enough to take us into the large-U limit, but the results, nevertheless, show features of this limit.

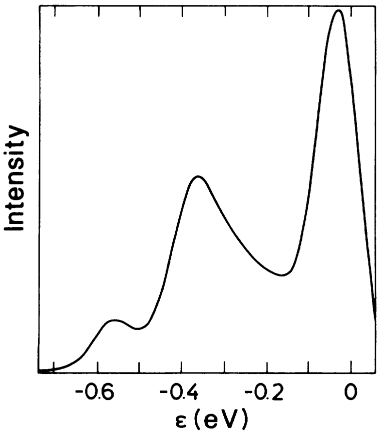

FIG. 1. The PES spectrum for a half-full Hubbard chain with $N = 5$ atoms and orbital degeneracy 2. For a noninteracting system (with a large N) the width of the spectrum is 0.24 eV.

We observe the difference from the case when there is a noninteger number of strongly interacting electrons per atom, as in, e.g., Ni with about 9.6 $3d$ electrons per atom. In such a case there is a satellite split off by $\sim U$ from the main band, and the weight of this satellite remains finite as $U \rightarrow \infty$. The reason is that if there is a noninteger number of electrons per atom, between M and $M - 1$, the atoms in the initial state have different occupancies M and $M - 1$, even for a large U. There is then a finite probability to reach final states where one atom has the occupancy $M - 2$. On the other hand, with an integer number M of electrons per atom, the probability of finding $M - 1$ electrons on an atom in the initial state goes to zero as $U \rightarrow \infty$. Therefore the coupling to final states where an atom has $M - 2$ electrons also goes to zero, and there is no satellite at U below the main band.

Experimentally, the width of the PES spectrum is found to be about 1.2 eV,[21] i.e., larger than our calculated value. This is not surprising, since phonon satellites are expected to contribute to the bandwidth. This is illustrated by the spectrum for a free C_{60} molecule, where a substantial broadening is found for the h_u level.[22] Since there is only one h_u hole in the final state, many-body broadening effects are not expected to be important, and it seems likely that this broadening is due to vibration satellites.[22] The occupied part of the t_{1u} band is, however, broader in K_3C_{60} than in K_6C_{60} according to PES.[21] This is in agreement with the present calculations, since the many-body effects should be small for K_6C_{60}, where the t_{1u} band is full. This suggests that there may be both phonon satellites and many-body contributions to the bandwidth of K_3C_{60}.

Doped C_{60} (M_3C_{60}, with M=K,Rb) has generally been assumed to be a metal, although the observation of a pseudogap in photoemission and inverse photoemission has been claimed.[3] For a Hubbard model, a Mott insulator is expected if the energy cost, $U - V$, for an electron to hop to the nearest-neighbor site is larger than the bandwidth W. According to our estimates of U and V and standard estimates of W,[19] $(U - V)/W \approx 1$. Recent band-structure calculations, going beyond the ASA, show, however, a larger bandwidth of the order $W \sim 0.65$ eV for K_3C_{60} in the fcc structure,[23] which probably makes $(U-V)/W$ slightly smaller than unity. It would be interesting to study a three-dimensional Hubbard model with a long-range interaction, to find out the exact criterion for a Mott transition for such a model.

We note that there are some indications of strong correlation effects for other doped C_{60} compounds. Thus it has been suggested that K_4C_{60} is an insulator although band theory predicts a metal,[24,25] and it has been reported that C_{60} TDAE is a ferromagnet.[26]

Finally, we remark that in a metallic system, the large U obtained here is efficiently screened. Thus it has been found that such a large value of U is not necessarily inconsistent with an electron-phonon mechanism for superconductivity.[16]

The calculations here provide parameters for the Coulomb interaction in a Hubbard-like model. Simple but realistic models for the hopping energy in different lattice structure have been given elsewhere.[19]

In conclusion, we have estimated the on-site Coulomb interaction U and the nearest-neighbor interaction V for C_{60} and found the values $U_0 = 2.7$ eV for a free molecule and $U = 0.8 - 1.3$ eV and $V = 0.3 - 0.5$ eV for a solid. These parameters were used for a Hubbard chain with orbital and spin degeneracy. For doped C_{60} it was shown that the associated many-body effects lead to a substantial increase in the width of the t_{1u} band seen in a photoemission spectrum. The calculations and a comparison of the experimental PES spectra for K_3C_{60} and K_6C_{60} (Ref. 21) suggest there may be both a phonon satellite and a many-body contribution to the large PES bandwidth for K_3C_{60}.

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[1] W. Krätschmer, L.D. Lamb, K. Fostiropoulos, and D.R. Huffman, Nature (London) **347**, 354 (1990).

[2] A.F. Hebard *et al.*, Nature (London) **350**, 600 (1991); M.J. Rosseinsky *et al.*, Phys. Rev. Lett. **66**, 2830 (1991).

[3] T. Takahashi *et al.*, Phys. Rev. Lett. **68**, 1232 (1992).

[4] R.W. Lof, M.A. van Veenendaal, B. Koopmans, H.T. Jonkman, and G.A. Sawatzky, Phys. Rev. Lett. **68**, 3924 (1992).

[5] O. Gunnarsson, Phys. Rev. B **41**, 514 (1990).

[6] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L.J. Sham, *ibid.* **140**, A1133 (1965); for a recent review see, e.g., R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[7] O. Gunnarsson, O.K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).

[8] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975); O.K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).

[9] M.R. Pederson, S.C. Erwin, W.E. Pickett, K.A. Jackson, and L.L. Boyer, in *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena *et al.* (Kluwer Academic, Amsterdam, 1992), Vol. II, p. 1323; M R. Pederson and A.A. Quong, Phys. Rev. B **46**, 12 906 (1992).

[10] V. de Coulon, J.L. Martins, and F. Reuse, Phys. Rev. B **45**, 13 671 (1992).

[11] R.L. Martin and J.P. Ritchie (unpublished).

[12] R.L. Hettich, R.N. Compton, and R.H. Ritchie, Phys. Rev. Lett. **67**, 1242 (1991).

[13] J. de Vries *et al.*, Chem. Phys. Lett. **188**, 159 (1992).

[14] G. Gensterblum *et al.*, Phys. Rev. Lett. **67**, 2171 (1991).

[15] P.W. Fowler, P. Lazzeretti, and R. Zanasi, Chem. Phys. Lett. **165**, 79 (1990).

[16] O. Gunnarsson and G. Zwicknagl, Phys. Rev. Lett. **69**, 957 (1992).

[17] A.F. Hebard, R.C. Haddon, R.M. Fleming, and R. Kortan, Appl. Phys. Lett. **59**, 2109 (1991).

[18] P.A. Bruhwiler, A.J. Maxwell, A. Nilsson, R.L. Whetten, and N. Mårtensson (unpublished).

[19] S. Satpathy, V.P. Antropov, O.K. Andersen, O. Jepsen, O. Gunnarsson, and A.I. Liechtenstein, Phys. Rev. B **46**, 1773 (1992).

[20] W.F. Brinkman and T.M. Rice, Phys. Rev. B **2**, 1324 (1970).

[21] C.T. Chen, L.H. Tjeng, P. Rudolf, G. Meigs, J.E. Rowe, J. Chen, J.P. McCauley, Jr., A.B. Smith III, A.R. McGhie, W.J. Romanow, and E.W. Plummer, Nature **352**, 603 (1991); P.J. Benning, J.L. Martens, J.H. Weaver, L.P.F. Chibante, and R.E. Smalley, Science **252**, 1417 (1991); G.K. Wertheim, J.E. Rowe, D.N.E. Buchanan, E.E. Chaban, A.F. Hebard, A.R. Kortan, A.V. Makhija, and R.C. Haddon, *ibid.* **252**, 1419 (1991).

[22] P. Baltzer, W.J. Griffiths, A.J. Maxwell, P.A. Bruhwiler, L. Karlsson, and N. Mårtensson (unpublished).

[23] V.P. Antropov *et al.* (unpublished).

[24] R.F. Kiefl *et al.*, Phys. Rev. Lett. **69**, 2005 (1992).

[25] P.J. Benning *et al.* (unpublished).

[26] P.-M. Allemand *et al.*, Science **253**, 301 (1991).