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Incomplete charge transfer stability of organic donor-acceptor compounds

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The conditions required to establish the stability of incomplete charge transfer in the ground state of a 1:1 segregated-stack organic compound have been examined for a system involving finite-transfer integral between nearest-neighbor molecules along the donor and acceptor stacks. Molecular ionization energy, crystalline Madelung energy, as well as band or delocalization energy have been included. The three cases investigated, namely, no correlation between electrons on a stack, strong on-site correlation as well as strong nearest-neighbor correlation suggest that correlation between electrons (holes) on the same stack is important in establishing incomplete charge transfer in an organic compound such as TTF-TCNQ (tetrathiafulvalenium-tetracyanoquinodimethanide).

I. INTRODUCTION

TTF-TCNQ (tetrathiafulvalenium-tetracyanoquinodimethanide) and related segregated-stack donor-acceptor compounds have been the subject of extensive investigation in the recent past.[1] This work has been motivated not only by the interesting electric and magnetic properties[2] exhibited by these materials but also by the thought that these highly anisotropic organic compounds could be the physical embodiment of theoretical models used to discuss phase transitions and other phenomena in one dimension.[3]

One important physical quantity that holds significant consequences for the behavior of these materials is the amount of charge q transferred per donor-acceptor pair. This quantity determines the lattice periodicity that develops at a Peierls transition.[4] The electrical conductivity as well as other properties also depend, in general, upon the amount of charge that is transferred between the donor and acceptor molecules. In fact, it has been suggested[5] that incomplete charge transfer ($q<1$) in 1:1 segregated-stack donor-acceptor complexes is required to establish the relatively high conductivities observed as well as certain features in the optical-absorption spectrum. It is therefore of interest that recent diffuse x-ray[6] and inelastic-neutron[7]-scattering measurements performed on TTF-TCNQ indicate that this material is less than fully charge transferred with $q\approx 0.59$. Interpretation of the results of less direct measurements[5,8,9] have also suggested that TTF-TCNQ is incompletely charge transferred. TTF-TCNQ is therefore closer to a state in which one electron is transferred for two donor-acceptor pairs ($q=0.5$) than to the state of full charge transfer ($q=1.0$). Other studies[5,10] of NMP-TCNQ have suggested that this material is also incompletely charge transferred. In view of the importance of the amount of charge transfer in these materials it is surprising that relatively little effort has been devoted to determining how the charge transfer can be stabilized at values different from $q=1.0$. It has been previously shown[11] that with consideration of only the ionization and Madelung energies such systems can be understood to be either fully charge transferred or not charge transferred at all. Subsequently, a number of Madelung calculations[12-14] have been performed for segregated-stack as well as non-segregated-stack charge-transferred compounds to determine whether the Madelung energy is sufficiently strong to stabilize a charge-transferred ground state.

Other investigations[13,15,16] have focused on the electrostatic energies associated with various configurations of charge (Wigner lattice) chosen in such a way as to reduce the electrostatic repulsion between sheets of charge normal to the stacking direction in the 1:1 segregated-stack organic compounds. It has been shown that strong correlation between such sheets of charge could in principle lead to a stable charge transfer state with $q<1.0$. One of these calculations[15] has clearly illustrated the electrostatic origin of the nonstochiometric mixed-valence character of the TTF halides. It has also pointed out the importance of a relatively open structure normal to the stacking axis, leading to weak Madelung binding energy and incomplete charge transfer in a material such as TTF-TCNQ. Whether the existence of such a three-dimensionally-ordered charge transfer state as proposed is, however, consistent with the observed value of the conductivity in these materials or with the details of other measurements, e.g., x-ray and neutron scattering, is still open to question. The implication of on-site correlation with respect to the observation of diffuse x-ray scattering at "$4k_F$" has also recently been discussed,[17] and such correlation will be examined in connection with charge transfer stability.

The purpose of the present work is to examine the question of the stability of charge transfer away from $q = 1.0$ in the ground state of a 1:1 conducting organic compound with the use of several simple models involving finite transfer integral between molecules along the stack and no interstack correlation of charge. Attention will be focused on intrastack correlation and its implications with respect to charge transfer. This work differs in an essential way from the investigations[13,15,16] utilizing a correlated three-dimensional charge distribution (Wigner lattice) since finite transfer integral t is required in the present work to establish the stability of incomplete charge transfer.

From the results we will obtain, one can infer that the existence of a 1:1 segregated-stack donor-acceptor compound with less than full charge transfer is a consequence of the physical parameters satisfying a very special set of constraints that determine the stability of the system. It is therefore not surprising that the majority of the 1:1 compounds are fully charge transferred.

Klymenko *et al.*[16] have previously treated a similar model in connection with the question of charge transfer stability of these materials. The conclusions drawn in that work were, however, rather general and no discussion was devoted to the implications of nearest-neighbor electronic correlation along the stack (extended Hubbard model). Other recent work[18] has examined the possibility of charge transfer transitions at finite temperature. Such work, while interesting, is apparently inappropriate for TTF-TCNQ since there is no clear experimental evidence indicating significant change in the charge transfer in the vicinity of the several phase transitions observed in this material.

One striking feature of the 1:1 donor-acceptor compounds is that nearest-neighbor molecules along a particular stack have an average charge with the same sign. The molecules along a stack therefore repel each other electrostatically. This situation is unlike that encountered in simpler ionic inorganic structures such as sodium chloride for which there is an attraction between nearest-neighbor atoms with charge of opposite sign. The repulsion between like ionized molecules is presumably counterbalanced by the delocalization of electrons along the stack or, in other words, the stack is held together by a metallic bond. The models that we will investigate will therefore include a nonvanishing transfer integral t between molecules along the stack. The tight-binding model will, however, be generalized to include strong on-site correlation (Hubbard model; $U = \infty$) as well as strong nearest-neighbor correlation (extended Hubbard model; $U = \infty$, $V = \infty$). It will be shown, as might be expected, that Madelung repulsion as well as electron correlation on the stack favor charge transfer states with $q < 1$.

II. COHESIVE ENERGY

The energy per donor-acceptor pair of a 1:1 segregated stack organic compound can be written

$$E(q) = (I - A)q - E_M q^2 + E_c(q) . \tag{2.1}$$

I and A are the ionization energy and electron affinity of the donor and acceptor molecule, respectively. E_M is the Madelung energy per donor-acceptor pair at full charge transfer. The Madelung energy has been written for a uniform charge distribution along each stack, i.e., atomic charges obtained from molecular orbital calculations are scaled linearly with the charge transfer, q, for each molecule on the stack. The Madelung energy will then vary quadratically with the charge transfer q if we neglect the energy associated with the neutral configuration ($q = 0$). The last term in Eq. (2.1), $E_c(q)$, is the binding energy gained as a result of electronic delocalization along the stack. This will be treated in the tight-binding approximation with generalizations to include on-site as well as nearest-neighbor correlation.

Equation (2.1) is an approximation to the total energy per donor-acceptor pair and a number of implicit assumptions have been made in obtaining it. For example, the donor ionization energy I and the acceptor electron affinity A are assumed to be independent of the amount of charge transfer q. This is not true in principle since molecular single-particle energies depend upon the degree of electron occupation through direct-Coulomb, exchange, and correlation contributions. Calculation of the Madelung energy E_M neglects effects resulting from the delocalization of electronic charge. Significant delocalization of electronic charge along the stacking direction could modify the calculated value of the Madelung energy E_M. The delocalization energy $E_c(q)$ will be written for a simple tight-binding band with no electronic correlation, perfect on-site electronic correlation, and perfect nearest-neighbor correlation. Even though the model is highly idealized it exhibits some interesting properties.

In the discussion that follows we will be guided by previous estimates of the magnitudes of the three terms of Eq. (2.1). Measurements[19] indicate that $I - A$ for TTF-TCNQ is approximately 4 eV. Calculations[12-16] of the Madelung energy of TTF-TCNQ performed with the use of several molecular charge distributions obtained from different molecular orbital calculations have yielded approximately 2 eV of binding energy per fully ionized donor-acceptor pair. On the other hand, bandwidths for TTF and TCNQ segregated stacks have been estimated[20,21] at approximately "half a volt." It has therefore been commonly stated that such estimates clearly indicate that these contributions to the energy are not sufficient to provide the binding energy required to form a stable charge-transferred ground state.[22] Such argument has motivated a number of suggestions concerning the not-yet-considered contribution to the energy that could be responsible for providing this binding. One such contribution, the dipolar polarization energy, has been calculated[13,23] for TTF-TCNQ and shown to contribute[23] approximately 0.1 eV at most to the binding of TTF-TCNQ. It has been pointed out[24] however that this mean-field estimate represents a lower bound to the polarization energy since fluctuations of charge that remove the center of symmetry on any given molecule should significantly enhance this contribution. Interstack Van der Waals interactions have also been suggested[25] to make a significant contribution to the cohesive energy of the crystal.

In the present paper, we will defer any detailed examination of the magnitude of the cohesive energy of the crystal and implicitly assume the crystal to be bound by the three contributions to the energy considered in Eq. (2.1). In connection with this we will point out in Sec. V why some of the current estimates of the cohesive energy of TTF-TCNQ are sufficiently inaccurate so as to preclude the possibility of making a definitive statement about the cohesion of the crystal. It is certainly true that Eq. (2.1) does not include all contributions to the energy that bind the crystal. It is also certainly important that the three contributions appearing in Eq. (2.1) be estimated accurately before one is convinced that these contributions namely, the ionization energy, monopolar energy, and delocalization energy, do not provide a net negative energy or positive cohesion. In Sec. V electronic repulsion along a stack will be discussed and correlation will be argued to be important in increasing the cohesive energy over previous estimates. The treatment of correlation in three dimensions (Wigner lattice) has also been shown[13,15,16] to increase the cohesive energy over that calculated for a uniform distribution of charge at a fixed value of charge transfer q.

The emphasis of the present paper is to focus attention on the conditions required to establish partial or incomplete charge transfer when band delocalization is important. Certain general relationships will be obtained which should prove useful in understanding how mixed-valence or incompletely charge-transferred stacks are formed. Again we emphasize that in what follows we will assume that the ionization and Madelung energies are on the order of electron volts. The ionization energy will also be assumed to be larger than the Madelung energy in Secs. III and IV. The band energy will therefore play an important role in contributing to the stabilization of the charge transfer.

III. TIGHT-BINDING MODEL

Figure 1 illustrates the tight binding energies associated with the donor and acceptor stacks. The minimum in the acceptor band energy has been chosen at $k=0$ as indicated by transfer-integral calculations using molecular orbitals.[20] The results for this model are, however, identical to those for a model assuming parallel bands since no hybridization has been introduced in the vicinity of the band crossing. The model can be simply generalized to include effects of hybridization. There are q electrons per molecule on the acceptor stack (q holes per molecule on the donor stack). Equation (2.1) implies that the band centers are shifted only by the ionization and Madelung energies. Some evidence for the approximate validity of such an assumption in treating electronic levels in inorganic crystals has been obtained[26] from photoemission measurements on alkali and alkaline-earth fluorides.

Using this tight-binding model to obtain an expression for $E_c(q)$, Eq. (2.1) can be written

$$E(q)=(I-A)q-E_M q^2-(8t/\pi)\sin(\tfrac{1}{2}\pi q)\,, \qquad (3.1)$$

where t, the transfer integral, is an average of the transfer integrals on the donor and acceptor stacks.

For small values of the charge transfer such that $q\approx 0$,

$$E(q)\approx(I-A-4t)q\,. \qquad (3.2)$$

Since we assume that the ionization energy $I-A$ is greater than the bandwidth $E_B=4t$, the energy

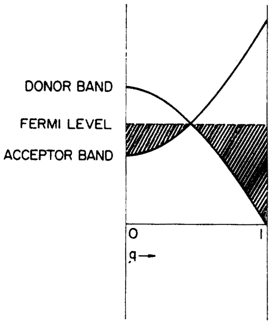

FIG. 1. Tight-binding model for donor and acceptor stacks.

$E(q)$, initially increases with q at small values of q.

The condition for the extrema is written

$$(I-A)-2E_M q=4t\cos(\tfrac{1}{2}\pi q)\,. \qquad (3.3)$$

The solutions of this equation will be discussed with use of the graphical construction shown in Fig. 2. The solutions are given by the intersections of the straight line of negative slope $-2E_M$ with the cosine function. To fix our ideas, we have assumed that the intercept of the straight line at $q=0$ which is $I-A$, is greater than the intercept of the cosine function, namely, the bandwidth $4t$. As discussed in Sec. II, this is certainly consistent with estimates of these quantities for TTF-TCNQ. Since $E(q)$ starts off by increasing with increasing q, the first intersection must be at a maximum of the function. One is therefore interested in those cases for which there are two intersections, since the second intersection will be at a minimum in the energy. Also, since we believe the ionization energy to be several electron volts and the bandwidth or transfer integral to be tenths of eV for TTF-TCNQ, we want to look for solutions such that the ratio of the intercept of the straight line to the intercept of the cosine function at $q=0$ reflects this estimate. The largest such ratio can be obtained by drawing the straight line tangent to the cosine curve at $q=1$. This is shown by the dashed line in Fig. 2. An infinitesimal counterclockwise rotation and displacement of this line can result in two intersections of this line with the cosine curve in the vicinity of $q=1$. An arbitrary straight line is drawn in Fig. 2 to illustrate two possible extrema. The conditions leading to a stable solution in the vicinity of $q=1$ can be written

$$E_M<\pi t\,, \qquad (3.4)$$

$$I-A>2E_M\,. \qquad (3.5)$$

Inequality (3.4) is obtained by requiring that the stable extremum has positive curvature in the vicinity of $q=1$. Inequality (3.5) follows from the requirement that the straight line have a positive value at $q=1$. This is the condition necessary to provide two intersections of the two curves. Both inequalities appear to be inconsistent with the estimates for TTF-TCNQ. The first inequality (3.4) states that the average of the donor and acceptor bandwidths is larger than the Madelung energy. This is just the opposite of what is expected. Inequality (3.5) states that the ionization energy is greater than twice the Madelung energy at full charge transfer. As we have pointed out, previous estimates of these two quantities indicate that at full charge transfer the ionization energy is at most twice the Madelung energy. As the stable point of intersection is made to move away from the vicinity of $q=1$, the conditions analogous to inequalities (3.4) and (3.5) become even more restrictive.

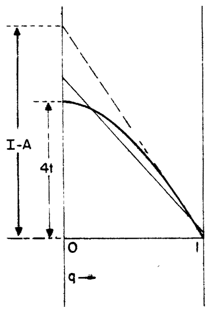

FIG. 2. Graphical solution for extrema of the tight-binding model.

In the vicinity of $q=1$ the inequality requiring the total energy to be negative or to bind the crystal can be written

$$(I-A)-E_M-8t/\pi<0\,, \qquad (3.6)$$

and since

$$I-A\approx 2E_M\,, \qquad (3.7)$$

one can write

$$E_B=4t>(\tfrac{1}{2}\pi)E_M\,. \qquad (3.8)$$

Therefore, if the total energy is negative, the bandwidth must even be greater than that required from the condition of positive curvature [inequality (3.4)]. On the other hand, any additive constant will modify inequality (3.8), whereas the second derivative of any contribution that has been left out will change inequality (3.4).

Even though the simple tight-binding model may be inappropriate for TTF-TCNQ, it is interesting to obtain an analytic expression for the charge transfer by linearizing in the vicinity of full charge transfer.

If we let

$$q=1-\Delta \qquad (3.9)$$

and assume Δ to be small,

$$\Delta\ll 1\,,$$

we can write

$$q=[2\pi t-(I-A)]/[2\pi t-2E_M]\,. \qquad (3.10)$$

An increase in the transfer integral t or the Madelung energy E_M therefore increases the charge transfer, as expected. An increase in the ionization energy $I-A$ decreases the charge transfer.

If there is a single intersection between the curves shown in Fig. 2 the system will be fully charge transferred if

$$(I-A)-E_M-8t/\pi<0\,, \tag{3.11}$$

or not charge transferred at all if

$$(I-A)-E_M-8t/\pi>0\,. \tag{3.12}$$

In Sec. IV, we will show that strong on-site correlation sets certain constraints on the physical parameters which indicate that it is more reasonable for the value of charge transfer of TTF-TCNQ to be stabilized in the vicinity of $q=0.5$ than in the vicinity of $q=1.0$. Certain unreasonable restrictions will still remain, however, namely, inequalities similar to inequalities (3.4) and (3.8). In Sec. V, strong nearest-neighbor correlation will be treated and shown to relax these unrealistic constraints significantly.

Secs. IV and V will therefore demonstrate the importance of electronic correlation within a stack in providing for the stability of nonintegral or incomplete charge transfer for narrow-band segregated-stack organic compounds.

IV. STRONG ON-SITE CORRELATION: HUBBARD MODEL

In this section we will assume that double occupancy of electrons (holes) on the molecules of the acceptor (donor) stacks is not allowed. In other words we will write the energy $E_c(q)$ for a Hubbard model[27] having infinite on-site correlation energy U.

The total energy can then be written

$$E(q)=(I-A)q-E_Mq^2-(4t/\pi)\sin\pi q\,. \tag{4.1}$$

The condition defining the extremum is

$$(I-A)-2E_Mq=4t\cos\pi q \tag{4.2}$$

and the graphical solution is illustrated in Fig. 3. Again, we are interested in a case for which there are at least two intersections of the straight line with the cosine curve. We also want to examine the case for which the straight line has the largest intercept at $q=0$ or, in other words, the largest value of $I-A$ consistent with a solution of incomplete charge transfer. This can be obtained by letting the straight line intersect the cosine curve at $q=0.5$ and setting the slopes of both curves equal at this point. An infinitesimal counterclockwise rotation and translation of the straight line will then result in three intersections of the two curves. The middle intersection in the vicinity of $q=0.5$ will represent the minimum. An arbitrarily drawn straight line is illustrated in Fig. 3 to represent the general case having three intersections.

Conditions leading to a stable solution in the vicinity of $q=0.5$ can be written

$$E_M<2\pi t\,, \tag{4.3}$$

$$I-A\approx E_M\,. \tag{4.4}$$

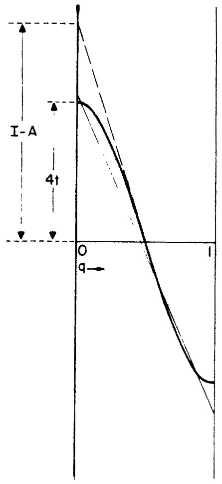

FIG. 3. Graphical solution for extrema of the Hubbard model.

Inequality (4.3) results from the condition that the slope of the straight line become no larger than the slope of the cosine curve at $q=0.5$. The approximate equality (4.4) results from requiring the middle intersection of the straight line with the cosine curve to be at a value approximately equal to 0.5.

These conditions on the values of the physical parameters are significantly relaxed from what was obtained for the tight-binding model (Sec. III), namely, inequalities (3.4) and (3.5). First, the equivalent tight-binding bandwidth $4t$ is not required to be greater than the Madelung energy as in the previous section. Also, the ionization energy is not required to be greater than twice the Madelung energy. As we have previously mentioned, the charge transfer is most easily stabilized in the vicinity of $q=0.5$. Such stabilization could not realistically be provided by the tight-binding model.

It is of interest to note that the condition of positive curvature relating the ionization energy, and equivalent bandwidth or transfer integral remains unchanged in this section and Sec. III, namely,

$$E_B=4t>(2/\pi)(I-A)\,. \tag{4.5}$$

This occurs even though we have doubled the slope $-2E_M$ of the straight line in going from Fig. 2 to 3: the intercept at $q=0$ remains the same since the intercept on the abscissa goes from 1 to 0.5. Therefore, the introduction of strong on-site correlation does not relax the constraint requiring relatively low ionization energy with respect to equivalent bandwidth $4t$ to achieve nonintegral charge transfer.

It should also be remarked that for net negative total energy at $q=0.5$, or, in other words, for positive cohesive energy at this value of the charge transfer one requires

$$(I-A)(0.5)-E_M(0.5)^2-4t/\pi<0\,, \tag{4.6}$$

which can also be written

$$E_B=4t>(\tfrac{1}{4}\pi)(I-A)\,. \tag{4.7}$$

This condition is also the same as obtained for the tight-binding model treated in Sec. III and is somewhat more restrictive than the condition obtained by requiring positive curvature at the minimum [inequality (4.5)].

An analytic expression for the charge transfer in the vicinity of $q=0.5$ can be obtained by setting $q=0.5+\Delta$ and assuming that $\Delta\ll 1$.

This yields

$$q=(0.5)\{[2\pi t-(I-A)]/[2\pi t-E_M]\}. \tag{4.8}$$

As in the tight-binding case, a decrease in $I-A$ or an increase in E_M leads to increased charge transfer. The dependence of the charge transfer q on the transfer integral is, however, somewhat different from the tight-binding case. Whether the charge transfer is less than or greater than 0.5, an increase in t, the transfer integral, will make q approach the value of 0.5. This occurs simply since the delocalization energy $E_c(q)$ for this case is lowest at $q=0.5$. An increase in t just lowers the value of the energy at this minimum. The system then becomes stable at a value closer to this minimum.

To conclude this section, we emphasize that strong on-site correlation has been shown to stabilize the system in the vicinity of $q=0.5$. This results simply since the delocalization energy is a minimum at this value of the charge transfer q. Finite U will result in a delocalization energy with a minimum somewhere between $q=0.5$ and $q=1.0$ and will therefore stabilize the system somewhere in this range.

The constraints on the physical parameters are still, however, not completely consistent with estimates of the magnitude of these parameters for TTF-TCNQ. The ratio of the ionization energy to equivalent bandwidth that is required from the condition of positive curvature [inequality (4.5)] and the condition of negative total energy [inequality (4.7)] is much smaller than that expected for TTF-TCNQ. In the next section, in which strong nearest-neighbor correlation along a stack is examined, it will be seen that this constraint is significantly relaxed.

V. STRONG NEAREST-NEIGHBOR CORRELATION: EXTENDED HUBBARD MODEL

In the present section we will examine the consequences of assuming that the nearest-neighbor interaction between ionized molecules on a stack is very strong, in fact infinite. If the nearest-neighbor interaction energy V is infinite as well as the on-site correlation energy U, then no more than one electron for every two donor-acceptor pairs ($q=0.5$) can be transferred. Each electron (hole) on the acceptor (donor) chain will, therefore, have a correlation hole around it consisting of two neutral molecules. In the presence of such strong nearest-neighbor correlation, the repulsive energy between nearest-neighbor ionized molecules along a stack must be removed from the Madelung sum. One can show simply that such intrastack correlation could significantly lower the total energy with respect to that calculated for an uncorrelated uniform charge distribution along each stack.

The ionization and Madelung energy contributions to the total energy can be written

$$E(q)=(I-A)q-E_M q^2\,. \tag{5.1}$$

As previously mentioned, the ionization energy has been estimated to be approximately four volts. At full charge transfer the Madelung energy is approximately two volts. Therefore,

$$4(1)-2(1)=2\text{eV}\,,$$

which is the familiar result indicating that full charge transfer should not be achieved. At a value of half-charge-transfer there is a similar difficulty, namely,

$$4(0.5)-2(0.5)^2=1.5\text{eV}\,,$$

and it is not apparent why the incomplete charge-transferred ground state should be stable.

The inclusion of strong nearest-neighbor correlation changes the picture drastically! In Fig. 4(b) we illustrate schematically an approximate correlated charge distribution for $q\approx 0.5$. Adjacent to each ionized molecule is a neutral molecule. The second nearest neighbor from the ionized molecule is chosen to have an occupation probability of 0.75 and every site beyond the second neighbor is chosen to be uncorrelated with an occupation probability of 0.5. Since the nearest-neighbor and second-nearest-neighbor electrostatic repulsive

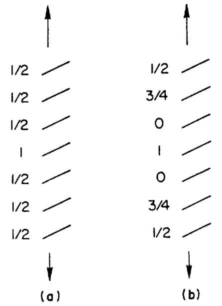

FIG. 4. Correlated charge distributions along a stack: (a) no correlation; (b) strong nearest neighbor correlation.

energies between ionized molecules[14] on the donor stack are 2.85 and 1.72 eV respectively, and those on the acceptor stack are 2.37 and 1.59 eV respectively, the energy of the correlated charge distribution [Fig. 4(b)] per donor-acceptor pair is lower than the energy of the uncorrelated charge distribution [Fig. 5(a)] by 1.8 eV. The total energy at half-charge-transfer is then approximately −0.3 eV. This simple argument, even though admittedly a crude approximation to what actually occurs, shows that the assumption of strong electronic correlation on the individual stacks significantly lowers the energy with respect to the values calculated in the absence of such correlation.

The state of incomplete charge transfer described in this section is different from the correlated states previously discussed.[13,15,16] In the present section the charge carriers on each stack are viewed as highly correlated over nearest-neighbor sites with no correlation between charge carriers on different stacks. This picture is consistent with the relatively high values of conductivity observed. It would also be consistent with an observation of x-ray or neutron scattering from one-dimensional charge density waves characterized by strong intrastack Coulomb correlations.[17,28]

For the case of infinite interaction energy V between nearest-neighbor ionized molecules on both donor and acceptor chains, as well as infinite on-site energy U the energy per donor-acceptor pair can be written[29]

$$E(q)=(I-A)q-E_M'q^2-\frac{4t}{\pi}(1-q)\sin\frac{\pi q}{1-q}. \qquad (5.2)$$

The prime on E_M indicates that electrostatic interactions between nearest-neighbor ionized molecules have been removed from the Madelung energy.

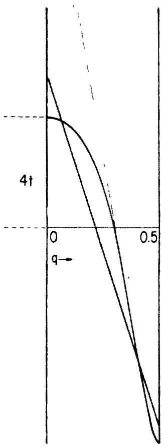

FIG. 5. Graphical solution for extrema of the extended Hubbard model.

The condition defining the extrema is now

$$(I-A)-2E_M'q=\frac{4t}{1-q}\cos\frac{\pi q}{1-q}-\frac{4t}{\pi}\sin\frac{\pi q}{1-q}. \qquad (5.3)$$

The graphical solution is illustrated in Fig. 5. One significant difference between the transcendental function for this case and the previous two cases is the much steeper slope (in the vicinity of $q=0.4$) for this curve. The value of q for which the slope is maximum is given by the solution of

$$\tan[\pi q/(1-q)]=-\pi/3(1-q). \qquad (5.4)$$

Again, if we draw the straight line tangent to this point, an infinitesimal rotation of this line will lead to three intersections, the middle one being at a minimum in the energy function. If the minimum in the energy is at the point of steepest slope on the transcendental curve, then the condition defining the extrema can be written

$$(I-A)-2E_M'q=-(16t/\pi)\sin(\tfrac{1}{2}\pi q). \qquad (5.5)$$

From the equality of the slopes of both curves at this value of q one can write

$$2E_M'=[4\pi t/(1-q)^3]\sin[\pi q(1-q)]. \qquad (5.6)$$

A relation between $I-A$ and E_M' can be obtained by eliminating the transfer integral from Eqs. (5.5) and (5.6):

$$I-A=2E_M'[q-(4/\pi^2)(1-q)^3] \qquad (5.7)$$

or

$$I-A\approx(.62)E_M', \qquad (5.8)$$

one also obtains

$$I-A\approx16t. \qquad (5.9)$$

The most significant difference from the previous two models, which did not include the nearest-neighbor interaction between ionized molecules, is the modification of the relation involving the ionization energy and equivalent bandwidth [Eq. (5.9)]. The system can now be stabilized at a value of incomplete charge transfer such that the ionization energy is approximately four times the value of the equivalent bandwidth. It should be emphasized that infinite values of U and V are not particularly physical. Finite values of these parameters as well as the inclusion of correlation associated with longer-range interactions could well lead to stabilization of the charge transfer at some larger value, say, in the range between $q=0.5$ and $q=1.0$ and perhaps result even in a larger allowed value of $I-A$.

From Eq. (5.8) we see that stabilization of the state of incomplete charge transfer requires a

Madelung constant E'_M somewhat larger than the ionization energy $I-A$. This is consistent with the removal of the nearest-neighbor electrostatic repulsion from the Madelung sum. Again if $I-A \approx 4$ eV, then Eq. (5.6) yields $E'_M \approx 6.5$ eV. Our simple argument involving the correlation hole illustrated in Fig. 4 resulted in $E'_M \approx 9$ eV. Assuming $I-A \approx 4$ eV, the total energy, Eq. (5.2), near the minimum at $q \approx 0.4$ is approximately equal to 0.5 eV. Therefore, strong nearest-neighbor correlation leads to a significant increase in the binding energy of the crystal over previous estimates.

To conclude, the importance of on-site as well as nearest-neighbor correlation has been demonstrated in connection with establishing incomplete charge transfer stability for the narrow-band 1:1 segregated-stack organic compounds. While it is certainly true that a more realistic model is required before the cohesive energy and value of the actual charge transfer can be calculated for any given compound, the preceding discussion illustrates in a qualitative manner some of the important issues involved in developing such a model.

VI. CONCLUSIONS

In the present paper we have addressed the question of charge transfer stability in a conducting 1:1 segregated-stack organic compound such as TTF-TCNQ. Particular attention was given to the conditions required to establish incomplete charge transfer in such a material. It was shown that such a partially ionic narrow-band system appears to require significant on-site as well as nearest-neighbor correlation in order for one to qualitatively understand how electronic delocalization can provide the charge transfer stability that is observed. Such a picture, if truly applicable to TTF-TCNQ, would therefore require electron-electron interactions to be important in this material.

There has been some discussion concerning the strength of electron-electron interactions in TTF-TCNQ and the inference that can be drawn concerning this strength from the results of experiment. The interpretation of the early photoemission measurements[30] in terms of the observation of ionized and neutral molecular species would seem to imply significant electronic correlation. This interpretation has been the subject of some severe criticism[31] and it appears that the issue is not presently settled.[8] Also, the magnetic susceptibility of TTF-TCNQ which was initially claimed[32] to be unenhanced from the Pauli value, therefore implying weak electron-electron interaction has recently been claimed[33] to be enhanced. Also, the recent claim,[17] if substantiated, that spin waves have been observed in the inelastic neutron scattering from TTF-TCNQ would indicate that electron-electron interactions are important in this material. On the other hand a recent review[34] of the results of inelastic electron-scattering and nuclear spin-lattice relaxation measurements has concluded that Coulomb interactions are not dominant in TTF-TCNQ. The linear dependence of the thermopower[35] on temperature over the metallic regime of this material also does not clearly indicate the presence of strong Coulomb interactions. Another recent review[28] has summarized evidence for the strength of electron-electron interactions in TTF-TCNQ. It should be emphasized that the present work was not initiated with any motivation to say something definitive about electron-electron interactions in TTF-TCNQ. It was initiated by a desire to examine the conditions required to establish incomplete charge transfer stability when the delocalization of electrons along the stack is solely responsible for such stability. The question of interest was: could delocalization energies with magnitudes of tenths of volts contribute significantly to such stability in the presence of ionization energies and apparent Madelung energies having the magnitudes of volts? The answer is that under the appropriate conditions they can, and that under these conditions, electronic correlation brought about by the electron-electron interaction appears to be essential. If, as suggested in the present paper, such a model is appropriate for TTF-TCNQ then the implications are clear. At present, however, there appears to be no consistent picture of the physical behavior of this material.

One can briefly speculate about a future direction for calculations aimed at elucidating the charge transfer stability in organic materials. One must certainly calculate the electrostatic energy associated with different configurations of charge in ionic structures. Certain subtle questions must, however, be resolved, e.g., if there is significant delocalization of electronic charge along a stacking direction, how valid is it to assume that the charges on two adjacent molecules along the stack are accurately characterized by nonoverlapping, spherically symmetric charge distributions centered on the atoms. One expects that delocalization or overlapping of electronic charge along the stack should reduce the electrostatic repulsion as presently calculated. One must also be able to reasonably estimate transfer integrals in the various crystalline directions. This estimate can be obtained from molecular orbital calculations for the dimer as has been done[20,21] in the case of TTF-TCNQ. Finally, and certainly the most difficult part of such program would be to include Coulomb correlation in the essential way that it should be included. It would certainly be of interest to generalize the results of this paper to include the case of finite U and V. The role of interstack correlation should also be examined. Future investigations of the importance of screening[36] in quasi-one-dimensionally conducting organic materials should help to elucidate the general importance of correlation. The results of such a program should help enable one to understand observed differences between organic materials and provide insight with respect to the synthesis of new materials.

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