

## Neutral-ionic transitions in organic mixed-stack compounds

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Torrance *et al.* have made the interesting observation that several mixed-stack organic compounds undergo transitions from neutral states to ionic states as the temperature or pressure is varied. We examine a simple model of such transitions including Coulomb interaction and hybridization of neutral and ionic states. In the limit of weak hybridization and long-range repulsive interaction between ionic planes, it is proven that there is a *complete* devil's staircase where the degree of ionicity assumes an infinity of rational values. For attractive interactions between ionic planes, the neutral-ionic transition is shown to be *first order* for weak hybridization. Comparison with experiment indicates that this situation applies to tetrathiafulvalene chloranil. For strong hybridization the transition is continuous but goes through a metallic phase. It is shown, for the first time, that the spectrum of the charge-transfer Hamiltonian contains both a bound spectrum, the observed charge-transfer excitations, and a continuum.

## I. INTRODUCTION

Mixed-stack charge-transfer organic compounds consist of stacks of alternating donor (*D*) and acceptor (*A*) molecules.<sup>1</sup> They either come as mostly neutral ( $\cdots DADADA \cdots$ ) such as perylene-tetracyanoquinodimethane (TCNQ), or as mostly ionic ( $\cdots D^+A^-D^+A^-D^+A^- \cdots$ ) such as tetramethylphenylenediamine- (TMPD) TCNQ.<sup>2</sup> In both cases they are exceptional because the lowest excitation above the ground state is a charge transfer along the stack, which creates an ionic pair in a neutral material ( $\cdots DAD^+A^-DA \cdots$ ) or a neutral pair in an ionic material ( $\cdots D^+A^-DAD^+A^- \cdots$ ).

Recently, Torrance *et al.*<sup>2</sup> made the remarkable discovery that several neutral compounds undergo transitions to ionic states as the pressure or temperature is changed. The most extensively studied compound is tetrathiafulvalence (TTF) chloranil. The neutral-ionic transition in this material, which occurs at 84 K under ambient pressure, is accompanied by anomalies in vibrational spectra,<sup>3</sup> specific heat,<sup>4</sup> lattice constants,<sup>3,5</sup> and dielectric constant.<sup>6</sup> Both the neutral and the ionic phase were found to be substantially hybridized.<sup>3</sup> Optical, infrared, and

Raman measurements<sup>3</sup> indicate that the transition takes place over a finite-temperature region in which there is coexistence of neutral and ionic molecules. At the neutral-ionic transition the difference between donor ionization energy *I* and acceptor electron affinity *A* is compensated by the Madelung energy of the ionic lattice.

A simple theory, which does not include hybridization, gives a linear relationship between the charge-transfer excitation energy and *I-A*,<sup>7</sup> which indeed holds true for neutral compounds.<sup>2</sup> The theory leads to a sharp first-order phase transition. Hubbard and Torrance<sup>8</sup> have extended the model to include the repulsive Coulomb interaction between fully ionized *a-c* planes (Fig. 1) and they argue that this gives a gradual variation of the amount of ionic *a-c* planes.

A *D-A* pair, however, changes from neutral to ionic in a smooth way as *I-A* is varied if hybridization is included. Calculations on infinite *D-A* chains by Krugler *et al.*<sup>9</sup> found indeed that the degree of charge transfer  $\rho$  varies continuously with *I-A*, while the charge-transfer excitation energy  $E_{CT}$  is always finite. Afterwards, Strebel and Soos<sup>10</sup> found that  $\rho$  varied discontinuously at the neutral-ionic boundary although the gap in the excitation

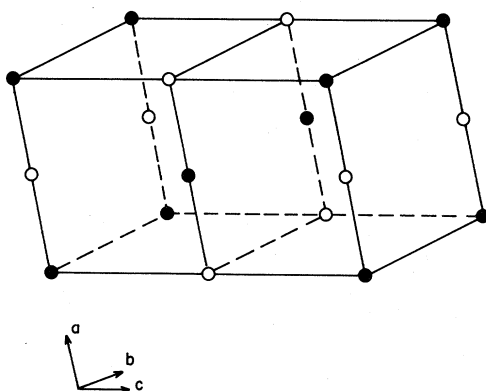


FIG. 1. Arrangement of donors (black) and acceptors (white) in the monoclinic unit cell of TTF chloranil (Ref. 22). The stacking direction is along the  $a$  axis.

spectrum vanishes. They used an extended Hubbard model. With the same model, Krivnov and Ovchinnikov<sup>11</sup> found a finite  $E_{CT}$  at the transition.

All of these authors, however, did not include in the Hamiltonian the Coulomb interaction between different sites but added a self-consistent Madelung energy afterwards. Because of this, they all found that the lowest excitations were extended plane waves ( $DAD^+ADADA^-DA$ ) while they really are *bound pairs* ( $DADAD^+A^-DADA$ ).

In this paper we introduce a model for neutral-ionic transitions including hybridization of neutral and ionic states in addition to Coulomb interaction. The Hamiltonian is essentially an  $XYZ$  model in a staggered magnetic field. This model can be solved exactly at the neutral-ionic boundary. If the  $D$ - $A$  transfer integral  $2\tau$  is less than the nearest-neighbor Coulomb interaction  $J$ , then the transition is first order with always a finite  $E_{CT}$ . TTF chloranil in fact shows a small discontinuity in the frequency of certain infrared, vibrational modes while the charge-transfer excitation energy is 0.9 eV at 81 K. If  $2\tau > J$ , the transition is found to be continuous with a vanishing  $E_{CT}$ . In addition it is shown that the spectrum of the Hamiltonian not only contains free states ( $DA^-DADAD^+A$ ), but also the expected localized charge-transfer excitations ( $DADAD^+A^-DADA$ ). In the limit of small mixing and repulsive interactions between planes our model reduces to the one studied by Hubbard and Torrance, which in turn is equivalent with a model proposed by Safran for staging in intercalation compounds.<sup>12</sup> We solve the model and prove that as the effective field is varied the ratio of  $a$ - $c$  planes that are ionized passes through all possible rational functions. This behavior is known as the complete

devil's staircase.<sup>13</sup>

Our paper is organized as follows: In Sec. II A we present our model, in Sec. II B we work out the phase diagram within the Hartree-Fock approximation, and in Sec. II C the excitation spectrum is calculated. In Sec. III we discuss the consequences of repulsive interactions in the limit of small mixing and prove the existence of the complete devil's staircase and in Sec. IV we give a short summary.

## II. THE NEUTRAL-IONIC TRANSITION

### A. Hamiltonian

The states of a charge-transfer compound can be described by specifying whether any given donor or acceptor is neutral or ionized.<sup>9</sup> We exclude the possibility that the molecules are doubly ionized, i.e., we work within the physically reasonable approximation that the strong Coulomb interaction between electrons with different spin excludes such configurations.

Every donor or acceptor is a two-state system and we will use the notation of a spin  $\frac{1}{2}$  quantum system:  $|\uparrow, i\rangle_A$  is a neutral acceptor at site  $i$ ,  $|\downarrow, i\rangle_A$  is a negatively ionized acceptor at site  $i$ ,  $|\uparrow, j\rangle_D$  is a neutral donor at site  $j$ , and  $|\downarrow, j\rangle_D$  is a positively ionized donor at site  $j$ . Note the different convention for donors and acceptors. The position of donors and acceptors is shown schematically in Fig. 1. Only configurations with total charge zero are allowed.

First, we construct the Hamiltonian along one stack with alternating donors and acceptors. It costs an energy  $I$  to ionize a donor while an acceptor gains an electronic affinity  $A$  on accepting an electron. The associated Hamiltonian is

$$\mathcal{H}_1 = I \sum_{n \text{ even}} S_z(n) + A \sum_{n \text{ odd}} S_z(n) + \mu \sum_n S_z(n), \quad (2.1)$$

with  $2S_x$ ,  $2S_y$ , and  $2S_z$  Pauli spin matrices and donors and acceptors on even and odd sites, respectively. The charge on a donor site  $j$  is given by

$$q_j = \langle \uparrow, j | [S_z(j) + \frac{1}{2}] | \uparrow, j \rangle,$$

and similarly for the acceptor. The chemical potential  $\mu$  is chosen such that the total charge  $\langle | [\sum_n S_z(n)] | \rangle$  is zero.

The next important contribution is the Coulomb

interaction. We consider in this section only the nearest-neighbor interaction. The effective nearest-neighbor Coulomb interaction  $\langle e^2/a \rangle$  was calculated approximately for TTF-TCNQ by Hubbard,<sup>14</sup> giving  $\langle e^2/a \rangle \sim 0.55$  eV. Including nearest-neighbor interaction only implies that the Madelung constant  $\alpha$  is 2. Realistic calculations<sup>15</sup> on TMPD<sup>+</sup>-TCNQ<sup>-</sup> give  $\alpha = 1.29$ . The Coulomb interaction is given by

$$\begin{aligned} \mathcal{H}_2 = & \langle e^2/a \rangle \sum_{n \text{ even}} [S_z(n) + \frac{1}{2}] [S_z(n+1) - \frac{1}{2}] \\ & + \langle e^2/a \rangle \sum_{n \text{ odd}} [S_z(n) - \frac{1}{2}] [S_z(n+1) + \frac{1}{2}]. \end{aligned} \quad (2.2)$$

Adding (2.1) and (2.2) we find

$$\begin{aligned} \mathcal{H} = & (I - \langle e^2/a \rangle + \mu) \sum_{n \text{ even}} S_z(n) \\ & + (A + \langle e^2/a \rangle + \mu) \sum_{n \text{ odd}} S_z(n) \\ & + \langle e^2/a \rangle \sum_n S_z(n) S_z(n+1). \end{aligned} \quad (2.3)$$

This is just the Ising antiferromagnetic with exchange  $J \equiv \langle e^2/a \rangle$  in a staggered field. If the field on donor sites,  $I - J + \mu$ , is exactly opposite to the field on the acceptor sites,  $A + J + \mu$ , then the total charge  $\langle |\sum_n S_z(n)| \rangle$  must be zero. The resulting Hamiltonian is

$$\mathcal{H} = H \sum_n (-1)^n S_z(n) + J \sum_n S_z(n) S_z(n+1), \quad (2.4)$$

with  $H = (I - A)/2 - J$ .

In fact, this Hamiltonian is equivalent to that proposed by Torrance *et al.*<sup>2</sup> The charge-transfer excitation energy  $E_{CT}$  corresponds to the spin flip of two neighboring spins:

$$E_{CT}^N = 2H + J = I - A - J, \quad (2.5)$$

for the neutral ground state ( $H > 0$ ), and

$$E_{CT}^I = -2H + J = 3J - (I - A), \quad (2.6)$$

in the ionic ground state ( $H < 0$ ).

The field  $H$  was found to be 0.1 eV at room temperature in TTF chloranil.<sup>2</sup> A first-order neutral-ionic transition occurs at  $H = 0$  where  $I - A = 2J$  and  $E_{CT} = J$ . These results coincide with those of Torrance *et al.*<sup>2</sup> for  $\alpha = 2$ . However, infrared measurements of certain vibrational modes indicate<sup>3</sup> that the actual transition involves a change in the degree of charge of charge transfer of only 45% from a quasineutral state to a quasi-ionic state and we need to consider mixing between neutral and ion-

ic donor-acceptor pairs. The only combination of spin matrices that mixes neutral and ionic pairs is

$$O^{12} \equiv 2\tau [S_x(1)S_x(2) + S_y(1)S_y(2)], \quad (2.7)$$

$$\begin{aligned} O^{12} | \uparrow, 1 \rangle_A | \downarrow, 2 \rangle_D \\ = \tau | \downarrow, 1 \rangle_A | \uparrow, 2 \rangle_D, \quad D^+ A^- \rightarrow D^0 A^0 \end{aligned} \quad (2.8a)$$

$$\begin{aligned} O^{12} | \downarrow, 1 \rangle_A | \uparrow, 2 \rangle_D \\ = \tau | \uparrow, 1 \rangle_A | \downarrow, 2 \rangle_D, \quad D^0 A^0 \rightarrow D^+ A^- \end{aligned} \quad (2.8b)$$

$$O^{12} | \uparrow, 1 \rangle_A | \uparrow, 2 \rangle_D = 0,$$

$$O^{12} | \downarrow, 1 \rangle_A | \downarrow, 2 \rangle_D = 0.$$

The operator  $O^{12}$  does not operate on  $D$ - $A$  pairs with a net charge. The resulting Hamiltonian is

$$\begin{aligned} \mathcal{H}_3 = 2\tau \sum_n [S_x(n)S_x(n+1) \\ + S_y(n)S_y(n+1)], \end{aligned} \quad (2.9)$$

where

$$\tau \equiv \langle D_1^+ A_2^- | \mathcal{H} | D_1^0 A_2^0 \rangle$$

is equivalent to the Milliken configuration integral<sup>1</sup> and is of the order of 0.1–0.3 eV. It is important to note that  $\mathcal{H}_3$  preserves the translational invariance along the chain. Our final single-stack Hamiltonian for  $N/2$   $D$ - $A$  pairs is

$$\begin{aligned} \mathcal{H} = H \sum_{n=1}^N (-1)^n S_z(n) + J \sum_{n=1}^N S_z(n) S_z(n+1) \\ + 2\tau \sum_{n=1}^N [S_x(n)S_x(n+1) \\ + S_y(n)S_y(n+1)]. \end{aligned} \quad (2.10)$$

The order parameter is<sup>16</sup>

$$\rho - \frac{1}{2} \equiv \frac{1}{N} \left\langle \sum_{n=1}^N (-1)^n S_z(n) \right\rangle, \quad (2.11)$$

where  $\rho$  is the degree of charge transfer from donor to acceptor. It changes from 0 in the neutral phase to 1 in the ionic phase.

Because of charge neutrality,  $\langle S_z \rangle = 0$  and we can only allow singlet excitations of the spin system. For  $H = 0$ , this Hamiltonian was solved<sup>16</sup> with the following result. For  $J > 2\tau$ , there is long-range order in the order parameter and a gap  $E_{CT}$  in the singlet excitation spectrum

$$E_{CT} = \pi \frac{\sinh \theta}{\theta} \sum_{n=-\infty}^{+\infty} \cosh^{-1} \frac{(2n+1)\pi^2}{2\theta}, \quad (2.12a)$$

with

$$\cosh\theta = J/2\tau. \quad (2.12b)$$

For  $J \gg 2\tau$ ,

$$E_{CT} = J(1 - 4\tau/J + \dots), \quad (2.13a)$$

and

$$|\rho - \frac{1}{2}| = \frac{1}{2} \left[ (1 - (2\tau/J)^2 - \frac{1}{4}(2\tau/J)^4 - \frac{1}{16}(2\tau/J)^6 + \dots) \right]. \quad (2.13b)$$

As  $J$  approaches  $2\tau$ ,  $E_{CT}$  goes rapidly to zero:

$$E_{CT} \simeq 8\pi\tau \exp \left\{ -\pi^2/2 \left[ 2 \left[ \frac{J}{2\tau} - 1 \right] \right]^{1/2} \right\}. \quad (2.14)$$

For  $J < 2\tau$ ,  $E_{CT}$  is zero and there is no long-range order:  $\rho = \frac{1}{2}$ . The singlet excitation spectrum is gapless. At  $J = 2\tau$ , the singlet spectrum is<sup>16</sup>

$$E_{CT}(q) = \pi\tau |\sin q|, \quad |q| < \pi. \quad (2.15)$$

In the next section we shall see how  $H$  affects these results.

### B. Phase diagram

We begin by considering only a single donor-acceptor pair (dimer) to be able to compare it later with an infinite chain. The wave function is a linear superposition of neutral  $|\uparrow\downarrow\rangle$  and ionic  $|\downarrow\uparrow\rangle$  states.<sup>1</sup> The Hamiltonian may be diagonalized with eigenvalues

$$E^\pm = \pm(H^2 + \tau^2)^{1/2}, \quad (2.16)$$

and eigenvectors

$$|\xi^+\rangle = \frac{\tau|\uparrow\downarrow\rangle + [H + (H^2 + \tau^2)^{1/2}]|\downarrow\uparrow\rangle}{\{\tau^2 + [H + (H^2 + \tau^2)^{1/2}]^2\}^{1/2}}, \quad (2.17a)$$

and

$$|\xi^-\rangle = \frac{\tau|\uparrow\downarrow\rangle + [H - (H^2 + \tau^2)^{1/2}]|\downarrow\uparrow\rangle}{\{\tau^2 + [H - (H^2 + \tau^2)^{1/2}]^2\}^{1/2}}. \quad (2.17b)$$

The upper level  $E^+$  is empty and the wave function of the lower level  $|\xi^-\rangle$  varies from  $|\uparrow\downarrow\rangle$  (neutral)

for  $H \gtrsim \tau$  to  $|\downarrow\uparrow\rangle$  (ionic) for  $H \lesssim -\tau$ . The degree of charge transfer  $\rho$  from donor to acceptor in the lower level is  $|\langle D^+A^- | \xi^- \rangle|^2$  or

$$\rho = \tau^2 / \{\tau^2 + [H + (\tau^2 + H^2)^{1/2}]^2\}. \quad (2.18)$$

The excitation energy from lower level to upper level  $E_{CT}$  is

$$E_{CT} = 2(H^2 + \tau^2)^{1/2}. \quad (2.19)$$

Note that  $\rho$  and  $E_{CT}$  are smooth functions of  $H$ . Next we turn to the infinite chain.

To find the phase diagram, we will treat the Coulomb interaction self-consistently. This is done by transforming  $\mathcal{H}$  first to a fermion Hamiltonian using the Jordan-Wigner transformation:

$$S^z(n) = \psi_n^\dagger \psi_n - \frac{1}{2}, \quad (2.20a)$$

$$S^+(n) = \psi_n^\dagger \exp \left[ i\pi \sum_{m=0}^{n-1} \psi_m^\dagger \psi_m \right]. \quad (2.20b)$$

The spinless fermion operators obey anticommutation relations,

$$\psi_m \psi_n^\dagger + \psi_n^\dagger \psi_m = \delta_{mn}, \quad (2.21)$$

and the resulting Hamiltonian is

$$\begin{aligned} \mathcal{H} = & H \sum_n (-1)^n \psi_n^\dagger \psi_n + J \sum_n \psi_n^\dagger \psi_{n+1}^\dagger \psi_{n+1} \psi_n \\ & - \tau \sum_n (\psi_n^\dagger \psi_{n+1} + \text{c.c.}) \end{aligned} \quad (2.22)$$

Since  $\langle S_z \rangle = 0$ , we have  $N/2$  particles. It is important to note that the spinless fermion operators entering  $\mathcal{H}$  are not the electrons of the  $D-A$  system.

In the Hartree-Fock approximation<sup>17</sup> to the ground state  $\Psi(n_1, n_2, \dots, n_{N/2})$ , it is assumed that  $\Psi$  is the Slater determinant of  $N/2$  single-particle wave functions  $\phi_i(n)$ . If  $\xi_i^\dagger$  creates a fermion in the state  $\phi_i$  then

$$|\Psi_{\text{HF}}\rangle = \prod_{i=1}^{N/2} \xi_i^\dagger |0\rangle, \quad (2.23)$$

where  $|0\rangle$  is the vacuum. The wave functions  $\phi_i$  are determined by minimizing the energy

$$E_{\text{HF}} = \langle \Psi_{\text{HF}} | \mathcal{H} | \Psi_{\text{HF}} \rangle. \quad (2.24)$$

This gives the Hartree-Fock self-consistency equations

$$\begin{aligned} -\tau[\phi_i(n+1) + \phi_i(n-1)] + (-1)^n H \phi_i(n) + J \sum_j [\phi_j^\dagger(n+1)\phi_j(n+1) + \phi_j^\dagger(n-1)\phi_j(n-1)]\phi_i(n) \\ - J \sum_j [\phi_j^\dagger(n+1)\phi_i(n+1) + \phi_j^\dagger(n-1)\phi_i(n-1)]\phi_j(n) = E_i \phi_i(n), \end{aligned} \quad (2.25)$$

where  $E_i$  is the energy cost of removing a fermion from state  $\phi_i$ . For  $J=0$ , the solution is found immediately, and

$$\phi_i^\pm(n) = \frac{1}{\sqrt{N}} (u_i^\pm e^{ik_i n} + v_i^\pm e^{i(k_i + \pi)n}), \quad (2.26)$$

where  $u_i^2 + v_i^2 = 1$  and

$$k_i = (2\pi/N)i, \quad i = 0, \pm 1, \dots, \pm N/2. \quad (2.27)$$

The eigenvalues  $E_i$  are

$$E_i^\pm = \pm (4\tau^2 \cos^2 k_i + H^2)^{1/2} \quad (2.28)$$

and the eigenfunctions

$$(v_i/u_i)^\pm = (E_i^\pm + 2\tau \cos k_i)/H. \quad (2.29)$$

We have found two bands,  $E_i^+$  and  $E_i^-$ , of  $N/2$  states. The lower one will be filled; the upper one empty. The ground-state wave function is the

Slater determinant of  $\phi_i^-(n)$ . We assume that for the *interacting* case, the  $\phi_i(n)$  still have the form of Eq. (2.26) and we solve for  $u_i^\pm$  and  $v_i^\pm$ :

$$(v_i/u_i)^\pm = (E_i^\pm + 2\tau p \cos k_i) / [H - 2J(\rho - \frac{1}{2})], \quad (2.30)$$

where

$$p = 1 + \frac{J}{\tau N} \sum_j (u_j^{-2} - v_j^{-2}) \cos k_j \quad (2.31)$$

and  $\rho$  is the degree of charge transfer. The energy eigenvalues  $E_i^\pm$  are

$$E_i^\pm = \pm \{4\tau^2 p^2 \cos^2 k_i + [H - 2J(\rho - \frac{1}{2})]^2\}^{1/2}. \quad (2.32)$$

Since we know the ground-state wave function, we can calculate the ground-state energy from Eq. (2.24):

$$\begin{aligned} E_{\text{HF}} &= \sum_i E_i^- - J \sum_{i,j,n} [\phi_i^{-*}(n) \phi_i^-(n) \phi_j^{-*}(n+1) \phi_j^-(n+1) - \phi_i^{-*}(n) \phi_j^{-*}(n) \phi_i^-(n+1) \phi_j^-(n+1)] \\ &= N \left[ -\frac{1}{\pi} \{4\tau^2 p^2 + [H - 2J(\rho - \frac{1}{2})]^2\}^{1/2} E \left[ \frac{4\tau^2 p^2}{4\tau^2 p^2 + [H - 2J(\rho - \frac{1}{2})]^2} \right] - J\rho(1-\rho) + \frac{\tau^2}{J}(p-1)^2 \right], \end{aligned} \quad (2.33)$$

where  $E(m)$  is a complete elliptic integral of the second kind with modulus  $m$ . We still need to determine  $\rho$  and  $p$ . From Eqs. (2.30) and (2.31) it follows that for  $|H|/\tau$  large or  $J/\tau$  large,  $v_i/u_i = \pm 1$  so  $p=1$ . If both  $|H|/\tau$  and  $J/\tau$  are small then  $v_i^- = 0$  and

$$p = 1 + \frac{J}{\tau\pi}. \quad (2.34)$$

The degree of charge transfer  $\rho$  is determined by a self-consistency equation,

$$\begin{aligned} \rho &= \frac{1}{2} + \frac{1}{N} \frac{\partial}{\partial H} \langle \mathcal{N} \rangle \quad (2.35) \\ &= \frac{1}{2} - \frac{1}{\pi} \frac{[H - 2J(\rho - \frac{1}{2})]}{\{4\tau^2 p^2 + [H - 2J(\rho - \frac{1}{2})]^2\}^{1/2}} \\ &\quad \times K \left[ \frac{4\tau^2 p^2}{4\tau^2 p^2 + [H - 2J(\rho - \frac{1}{2})]^2} \right], \end{aligned} \quad (2.36)$$

where  $K(m)$  is a complete elliptic integral of the first kind. If  $\tau/J \ll 1$  then  $p=1$  and

$$\rho \simeq \frac{1}{2} - \frac{1}{2} \text{sgn}(H) \left[ 1 - \frac{\tau^2}{(|H| + J)^2} \right], \quad (2.37)$$

and at  $H=0$  a *first-order* transition occurs from a mostly neutral to a mostly ionic phase. So, as long as  $\tau/J$  is small, the simple theory remains valid. On the other hand, for  $\tau/J$  large and  $H$  small we find

$$\rho \simeq \frac{1}{2} - \frac{1}{\pi} \frac{H}{2\tau p} \ln \left[ \frac{8\tau p}{|H|} \right], \quad (2.38)$$

and the degree of charge transfer varies continuously, as in the dimer but more rapidly. In conclusion, for  $J > 2\tau$ ,  $\rho$  undergoes a first-order transition at  $H=0$ , while for  $J < 2\tau$  the transition is continuous. The resulting phase diagram is shown in Fig. 2.

It should be noted that the Hartree-Fock approximation underestimates fluctuations and thus overestimates  $|\rho - \frac{1}{2}|$ . In fact, for  $J > 2\tau$  and  $H=0$ , Eq. (2.36) gives

$$|\rho - \frac{1}{2}| \sim \exp(-\pi\tau p/J),$$

which is small but not zero, as would follow from the exact solution. On the other hand,  $|\rho - \frac{1}{2}|$  will be enhanced somewhat by interchain Coulomb interaction.

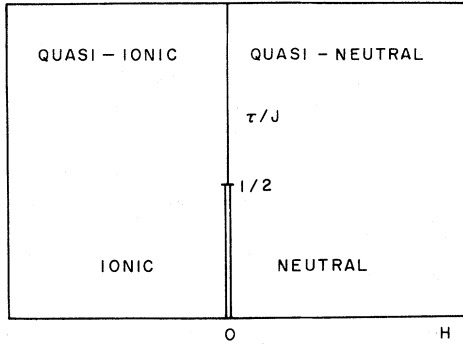


FIG. 2. Phase diagram for mixed-stack compounds. When  $H > 0$ , the compound is largely neutral, while for  $H < 0$  it is largely ionic. The transition at  $H = 0$  is first order if  $2\tau$  is less than  $J$ .

### C. Excitation spectrum

The lowest-lying optical excitation is a charge transfer of an electron from a donor to a neighboring acceptor (neutral phase). For  $\tau = 0$ , this costs an energy

$$E_{CT} = 2 |H| + J \sim 1 \text{ eV}. \quad (2.39)$$

If we compare this with Eq. (2.32) we see that it lies about halfway between the empty and the filled band. In the fermion model, it corresponds to a

$$(E_K - E_{CT})a_j^+ = \sum_{j'}^+ \langle j | \mathcal{H}' \frac{1}{E_K - \mathcal{H}_0} \mathcal{H}' | j' \rangle^+ a_{j'}^+ + \sum_{j'}^+ \langle j | \mathcal{H}' \frac{1}{E_K - \mathcal{H}_0} \mathcal{H}' | j' \rangle^- a_{j'}^-, \quad (2.42a)$$

$$(E_K - E_{CT})a_j^- = \sum_{j'}^- \langle j | \mathcal{H}' \frac{1}{E_K - \mathcal{H}_0} \mathcal{H}' | j' \rangle^- a_{j'}^- + \sum_{j'}^- \langle j | \mathcal{H}' \frac{1}{E_K - \mathcal{H}_0} \mathcal{H}' | j' \rangle^+ a_{j'}^+, \quad (2.42b)$$

where

$$\psi_K = \sum_j a_j^+ |j\rangle^+ + \sum_j a_j^- |j\rangle^-$$

is the eigenstate with energy  $E_K$ .

The intermediate state on which  $1/E - \mathcal{H}_0$  operates is either the neutral ground state or a doubly excited state. Two excited states  $|j\rangle^+$  and  $|j'\rangle^+$  have an energy  $2E_{CT}$  if  $j' \neq j \pm 2$ . If  $j' = j \pm 2$  the energy cost is only  $E_{CT} + 2H$ . A dipole at site  $j$  will polarize the stack nearby making it easier for another dipole to be formed. By assuming that  $E_K \sim E_{CT}$ , one finds

$$(E_K - E_{CT})a_j^+ \simeq -\frac{\tau^2}{2H}(a_{j+2}^+ + a_{j-2}^+), \quad (2.43a)$$

$$(E_K - E_{CT})a_j^- \simeq -\frac{\tau^2}{2H}(a_{j+2}^- + a_{j-2}^-). \quad (2.43b)$$

tightly bound particle-hole pair or Frenkel exciton.<sup>18</sup>

In the following we consider the neutral phase. There are two types of Frenkel excitons: one with an ionized donor at site  $j$  and an ionized acceptor at site  $j+1$  ( $DAD_j^+ A_{j+1}^- DA$ ) and one with an ionized donor at site  $j$  and an ionized acceptor at site  $j-1$  ( $DAD_j A_{j-1}^- D_j^+ A$ ). They will be denoted by  $|j\rangle^+$  and  $|j\rangle^-$ . They have the same energy but opposite dipole moment. Their degeneracy is a consequence of the reflection invariance of the stack.

Since there are  $N/2$  sites for  $j$ , we have an  $N$ -fold degenerate excitation spectrum with energy  $E_{CT}$ . The effective Hamiltonian is

$$\begin{aligned} \mathcal{H}_0 = & \frac{E_{CT}}{2} \sum_{n \text{ even}} (\psi_{n+1}^\dagger \psi_{n+1} - \psi_n^\dagger \psi_n) \\ & + \frac{E_{CT}}{2} \sum_{n \text{ even}} (\psi_{n-1}^\dagger \psi_{n-1} - \psi_n^\dagger \psi_n). \end{aligned} \quad (2.40)$$

The first term counts the number of  $|j\rangle^+$  excitations, the second the number of  $|j\rangle^-$  excitations. Next we include the hopping term

$$\mathcal{H}' = \tau \sum_n (\psi_n^\dagger \psi_{n+1} + \text{c.c.}), \quad (2.41)$$

perturbatively. Because of the  $N$ -fold degeneracy we need to solve  $N$  secular equations.<sup>19</sup> To lowest order

The exciton motion thus goes in three steps

- (1)  $DAD^+ A^- DADA$ ,
- (2)  $DAD^+ A^- D^+ A^- DA$ ,
- (3)  $DADAD^+ A^- DA$ ,

similar to molecular excitons.<sup>1</sup> In fact, for a strongly dimerized chain, the Frenkel excitons would reduce to molecular excitons.

In Eqs. (2.43), terms of order  $\tau^2/E_{CT}$  were ignored since  $E_{CT} \sim 1$  eV and  $H \sim 0.1$  eV. The resulting equations can be solved by plane waves and the eigenvalues are

$$E_i = E_{CT} - \frac{\tau^2}{H} \cos k_i + O(\tau^3/H^2), \quad (2.44)$$

$$k_i = (2\pi/N)i, \quad i = 1, \dots, N/2 \quad (2.45)$$

both for the  $|j\rangle^+$  and the  $|j\rangle^-$  excitation.

In the ionic phase the eigenvalues are

$$E_i = E_{CT} - \frac{\tau^2}{|H|} \cos k_i + O(\tau^3/|H|^2). \quad (2.46)$$

If we now fix  $H$  and increase  $\tau$ , then the perturbation breaks down. This can be understood as follows. The binding energy  $E_B$  of the bound state is the difference in energy of a free particle-hole pair and an exciton:

$$E_B \simeq 4J \left| \rho - \frac{1}{2} \right| - J. \quad (2.47)$$

If we fix  $H$  and increase  $\tau$ , then  $\rho \simeq \frac{1}{2}$  when  $\tau > J/2$ ,

$$\begin{aligned} E_K \psi_K(k_1, k_2) &= \sum_{k'_1, k'_2} \langle k_1, k_2 | H | k'_1, k'_2 \rangle \psi_K(k'_1, k'_2) \\ &= [E_{HF} + E^+(k_1) - E^-(k_2)] \psi_K(k_1, k_2) \\ &\quad - \frac{J}{N} \sum_{\substack{k_1, k_2 \\ k'_1 + k'_2 = k_1 + k_2}} [(1 - u_{k'_1}^+ v_{k'_1}^+ u_{k_2}^- u_{k_2}^-) \\ &\quad - \cos(k_1 - k_2)(u_{k_1}^{+2} - v_{k_1}^{+2})(u_{k_2}^{-2} - v_{k_2}^{-2})] \psi_K(k'_1, k'_2) \end{aligned} \quad (2.49)$$

with  $E^\pm(k)$  and  $u_k^\pm, v_k^\pm$  given in Eqs. (2.30) and (2.32). For small  $H$  and  $\tau > J/2$ ,  $u_i^\pm = 1$  and  $v_i^\pm = 0$  so

$$\begin{aligned} E_K \psi_K(k_1, k_2) &= [E_{HF} + E^+(k_1) - E^-(k_2)] \psi_K(k_1, k_2) \\ &\quad - \frac{J}{N} \sum_{\substack{k'_1, k'_2 \\ k'_1 + k'_2 = k_1 + k_2}} [1 - \cos(k_1 - k_2)] \\ &\quad \times \psi_K(k'_1, k'_2) \end{aligned} \quad (2.51)$$

and the strongest attraction occurs if  $k_1 - k_2 \simeq \pi$ . If we define

$$k_1 = \frac{\pi}{2} + \bar{k}_1, \quad (2.52a)$$

$$k_2 = -\frac{\pi}{2} + \bar{k}_2, \quad (2.52b)$$

with  $k_1$  and  $k_2$  small, then the effective Hamiltonian is

$$\begin{aligned} H_{\text{eff}} &= E_{HF} + 2|H| + 4J \left| \rho - \frac{1}{2} \right| \\ &\quad + \frac{1}{2} \frac{\hbar^2 \bar{k}_1^2}{ma^2} + \frac{1}{2} \frac{\hbar^2 \bar{k}_2^2}{ma^2} - 2Ja \delta(x_p - x_h), \end{aligned} \quad (2.53)$$

and  $E_B$  becomes negative. The bound state is lying above the band edge. The radius of the exciton will become large compared to a lattice constant. The bound state, now similar to a Wannier exciton, should be constructed from extended Hartree-Fock states.<sup>18</sup> The wave function of a particle with momentum  $k_1$  in the upper band and a hole  $k_2$  in the lower band is

$$|k_1, k_2\rangle = \xi_{k_1}^\dagger \xi_{k_2} |\psi_{HF}\rangle. \quad (2.48)$$

To find the particle-hole excitation energy  $E_K$  we diagonalize  $H$  in the subspace  $|k_1, k_2\rangle$ . We will find that  $E_K$  is close to the band gap if  $J \ll \tau$  and we can ignore mixing with the ground state. Thus we need to solve

$$m = \hbar^2 (|H| + 2J \left| \rho - \frac{1}{2} \right|) / 4\tau^2 p^2 a^2, \quad (2.54)$$

with  $p$  given by Eq. (2.34).

This is the effective-mass equation for a Wannier exciton with a short-range interaction. Separating out the center of mass motion, one finds a Schrödinger equation for a particle with reduced mass  $m/2$ . There is a bound state with binding energy

$$E_B = \frac{4ma^2 J^2}{\hbar^2} \quad (2.55)$$

and wave function

$$\begin{aligned} \psi(x_p - x_h) &= \left[ \frac{2maJ}{\hbar^2} \right]^{1/2} \\ &\quad \times \exp \left[ -\frac{2mJa}{\hbar^2} |x_p - x_h| \right]. \end{aligned} \quad (2.56)$$

The charge-transfer excitation energy is

$$E_{CT}^0 = (|H| + 2J \left| \rho - \frac{1}{2} \right|) [2 - (J/\tau p)^2]. \quad (2.57)$$

The charge-transfer excitation spectrum is shown in

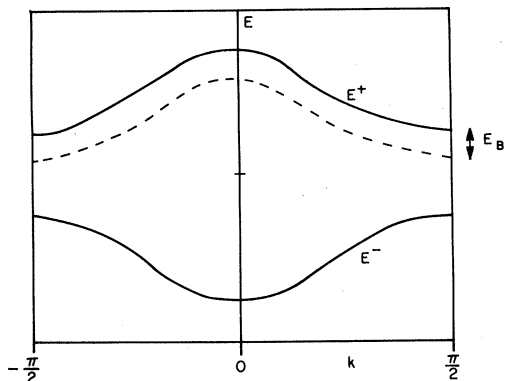


FIG. 3. Charge-transfer excitation spectrum. The lower band  $E^-(k)$  is filled; the upper band  $E^+(k)$  is empty. The lowest-lying charge-transfer excitation creates an exciton with binding energy  $E_B$  indicated by the dotted line.

Fig. 3. For  $\tau \gg 2J$  the effective mass becomes small and the bound state lies just below the empty band. The size of the bound state now becomes very large. However, when this happens, one really should use the Coulomb interaction. Then, there will be an infinite series of bound states just below the empty band.

Finally, when  $\tau$  is fixed and  $H$  goes to zero, we approach the neutral-ionic transition and the perturbation series for the bound-state energy [Eq. (2.46)] again breaks down. At  $H=0$ , the charge-transfer excitation energy is given by the exact solution, Eq. (2.12). So  $E_{CT}$  goes through a minimum at  $H=0$ . The charge-transfer excitation for  $J \gg \tau$  now corresponds to changing a string of  $m$   $D$ - $A$  molecules from neutral to ionic. The excitation energy

$$E_{CT} \approx J + 2 |H| m \quad (2.58)$$

is independent of  $m$  at the transition. So just as the case for  $\tau > J/2$ , the size of the bound state diverges as  $H$  goes to zero.

So far we considered only neutral excitations. The energy cost of adding a single charge to the system is  $E^+(k)$  [Eq. (2.32)]. Since  $E^+(\pi/2)$  is zero for  $\rho = \frac{1}{2}$ , we find that for  $\tau > J/2$  and  $H=0$ , the mixed stack must become *metallic* at the transition. Although this does not happen for TTF

chloranil it could occur for other mixed-stack compounds. The localized charge-transfer states, discussed in this section, will mix into the ground state and further reduce the order parameter  $|\rho - \frac{1}{2}|$ .

### III. INTERACTION BETWEEN PLANES AND THE DEVIL'S STAIRCASE

In the limit where  $\tau$  is small compared to  $J$  the mixing term in (2.10) plays no role except for reducing slightly the value of  $|\langle S_z \rangle|$  in the ionic and neutral phases. The model reduces to an antiferromagnetic Ising model in a field. For simplicity we introduce ferromagnetic spins  $S_z(n) \rightarrow (-1)^n S(n)$ :

$$\mathcal{H} = H \sum_{n=1}^N S(n) - J \sum_{n=1}^N S(n)S(n+1). \quad (3.1)$$

Now  $S(n) = \frac{1}{2}$  is the ionic state,  $S(n) = -\frac{1}{2}$  is the neutral state, and the energy per site for these states

$$\mathcal{H} = HS - JS^2, \quad S = \pm \frac{1}{2}. \quad (3.2)$$

It has been argued by Hubbard and Torrance<sup>8</sup> that the interactions between stacks *within*  $a$ - $c$  planes are attractive whereas the interactions *between*  $a$ - $c$  planes are repulsive (Fig. 1), and  $a$ - $c$  planes should always be completely ionized or completely neutral. The energy per spin in the absence of interplane interaction will again be on the form (3.1) where the summation includes interactions between stacks, and the energy per spin is given by (3.2).

The energy of a system of planes is

$$\mathcal{H} = \sum_i HS_i + \frac{1}{2} \sum_{ij} J(i-j) (S_i + \frac{1}{2})(S_j + \frac{1}{2}), \quad (3.3)$$

where  $J(i-j)$  is the Coulomb interaction between planes  $i$  and  $j$ . This is exactly the Ising Hamiltonian investigated by Torrance and Hubbard, and also by Safran<sup>12</sup> in a study of staging in intercalation compounds.

To estimate  $J(i-j)$  let us calculate the Coulomb interaction energy between a mixed stack of alternating ions with period  $a/2$ , and a charge  $e$  located at a distance  $r$  from the stack

$$\begin{aligned} J(i-j) &= e^2 \sum_n \frac{1}{[r^2 + (na)^2]^{1/2}} - \frac{1}{\{r^2 + [(n + \frac{1}{2})a]^2\}^{1/2}} \\ &= 2e^2 \sum_m \int_{-\infty}^{\infty} dn [1 + (-1)^{m+1}] \frac{\cos 2\pi mn}{[r^2 + (na)^2]^{1/2}} = \frac{4e^2}{a} \sum_{m=1}^{\infty} [1 + (-1)^{m+1}] K_0 \left[ 2\pi m \frac{r}{a} \right]. \end{aligned} \quad (3.4)$$



Since  $r \sim a$  for nearest-neighbor stacks, and  $K_0$  decays exponentially, it is sufficient to include only the first term in the expansion (3.4) and represent the interaction with a given plane with the interaction with the nearest stack within the plane:

$$J(i-j) \sim \frac{8e^2}{a} K_0 \left[ 2\pi \frac{r}{a} \right] \sim \frac{8e^2}{a} (a/4r)^{1/2} \exp \left[ -2\pi \frac{r}{a} \right]. \quad (3.5)$$

The nearest-neighbor interaction  $J(1) \sim 0.005e^2/r$  and is thus very small compared with the in-plane interaction  $J$ .

The ground state of (3.3) for a given  $\langle S_i \rangle$  was studied by Hubbard.<sup>14</sup> The ground states are quasi-periodic arrangements of spins. The fraction of "up" spins (or ionized planes) may assume any rational value,  $m/n$ . Figure 4 shows some configurations. Let  $X_i^0$  denote the position of the  $i$ th up spin, and let  $X_i^1$  denote the nearest-neighbor distance to the following up spin,  $X_i^1 = X_{i+1}^0 - X_i^0$ . Similarly,  $X_i^p$  is the  $p$ th-nearest-neighbor distance  $X_i^p = X_{i+p}^0 - X_i^0$ .

For a given value of  $q$  it can be shown that

$$\begin{aligned} X_i^1 &= r_1 \text{ or } r_1 + 1, \\ &\vdots \\ X_i^p &= r_p \text{ or } r_p + 1, \end{aligned} \quad (3.6)$$

where  $r_p$  and  $r_p + 1$  are the two integers nearest to  $np/m$ . For  $np/m$  integer,  $X_i^p = np/m$ .

The sum of all  $p$ th-nearest-neighbor distances

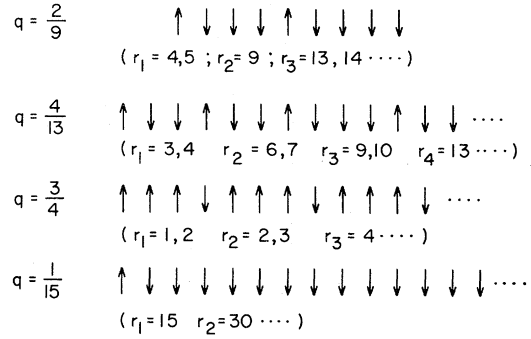


FIG. 4. Ground-state configurations for (3.3). The fraction of ionized planes is given by  $q$ .

must necessarily fulfill the relation

$$\sum_i X_i^p = pN, \quad (3.7)$$

where  $N$  is the total number of spins (planes). This is all we need to know to *exactly* calculate the stability intervals for all possible rational periods.

Consider the situation where the chain is deformed into a loop of length  $N$ , and  $q = m/n$ . This phase is stable as long as it costs energy to flip one up spin, or to flip one down spin. We calculate first the energy cost of flipping one down spin (i.e., ionizing one more plane). In the new configuration (3.6) and (3.7) still hold. Hence  $r_p$   $p$ th-nearest-neighbor distances  $r_p + 1$  will be replaced by  $r_p + 1$   $p$ th-nearest-neighbor distances  $r_p$  in order to keep Eq. (3.7) constant, and the total change in energy will be

$$\begin{aligned} U(\downarrow \rightarrow \uparrow) &= H + (r_1 + 1)J(r_1) - r_1 J(r_1 + 1) + (r_2 + 1)J(r_2) - r_2 J(r_2 + 1) + \cdots \\ &\quad + nJ(n - 1) - (n - 1)J(n) + (r_{m+1} + 1)J(r_{m+1}) - r_{m+1} J(r_{m+1} + 1) + \cdots \\ &\quad + 2nJ(2n - 1) - (2n - 1)J(2n) + \cdots, \end{aligned} \quad (3.8a)$$

where  $r_m = n$ ,  $r_{2m} = 2n$ , ... has been inserted. Similarly the energy cost of flipping one spin from up to down is

$$\begin{aligned} U(\downarrow \rightarrow \uparrow) &= -H - (r_1 + 1)J(r_1) + r_1 J(r_1 + 1) - (r_2 + 1)J(r_2) + r_2 J(r_2 + 1) + \cdots \\ &\quad + nJ(n + 1) - (n + 1)J(n) - (r_{m+1} + 1)J(r_{m+1}) + r_{m+1} J(r_{m+1} + 1) + \cdots \\ &\quad + 2nJ(2n + 1) - (2n + 1)J(2n) + \cdots. \end{aligned} \quad (3.8b)$$

The value of  $H, H_1(m/n)$ , for which  $U(\downarrow \rightarrow \uparrow)$  becomes zero defines the upper limit of the stability interval for the phase  $q = m/n$ . Similarly, the value  $H_2(m/n)$ , where  $U(\uparrow \rightarrow \downarrow)$  becomes zero gives the lower limit of stability. The number  $r_n$  can be calculated in a trivial way, so (3.8a) and (3.8b) allow us to calculate the stability of all possible phases. The stability interval of the configuration with  $q = m/n$  is

$$\begin{aligned} \Delta H \left[ \frac{m}{n} \right] = & H_1 \left[ \frac{m}{n} \right] - H_2 \left[ \frac{m}{n} \right] = nJ(n+1) + nJ(n-1) - 2nJ(n) \\ & + 2nJ(2n+1) + 2nJ(2n-1) - 4nJ(2n) + \dots \\ & + pnJ(pn+1) + pnJ(pn-1) - 2pnJ(pn) + \dots \end{aligned} \quad (3.9)$$

Note that  $\Delta H$  is independent of the numerator  $m$ . If we make the ansatz that the interaction  $J$  is of infinite range and convex,

$$J(i+1) + J(i-1) - 2J(i) > 0,$$

$\Delta H(m/n)$  is positive and *finite* for all values of  $m$  and  $n$ . Note that this width is independent of the numerator  $m$ . We have thus explicitly shown that  $q(H)$  form a complete devil's staircase<sup>20</sup> and we have calculated the stability intervals of all phases. The neutral phase is stable for  $H > 0$ ; the completely ionized phase is stable for

$$H < -J_0^1 \equiv -\sum_i J(i).$$

Figure 5 shows the resulting ionicity versus  $H$ . An interaction  $J(i) = e^{-i}$  was chosen. Only phases that are stable in an interval  $\Delta H/J(1) > 10^{-3}$  are shown. For  $J(i)$  given by (3.5) even fewer phases will be visible. The total width of the mixed phase is  $\Delta H \sim 0.005e^2/a \sim 0.005$  eV. Since a variation of  $\Delta T = 200$  K corresponds to  $\Delta H \sim 0.1$  eV for TTF chloranil,<sup>2</sup> the width of the mixed phase in temperature space is  $\sim 10$  K. This is in fair agreement with the observed smearing.<sup>3</sup> The problem lies in the *shape* of  $q(T)$ . The theoretical curve is *steep* near the boundaries to the completely ionic and to the

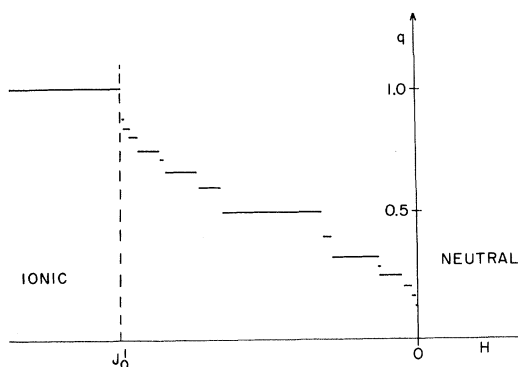


FIG. 5. Charge transfer vs effective field for  $\tau=0$  and repulsive interaction between planes. The fraction of ionized planes  $q$  exhibits a complete devil's staircase, locking into all possible rational values. Only the phases which are stable in an interval  $\Delta H/J(1) > 10^{-3}$  are shown.

completely neutral phases, and locks into the phase  $q = \frac{1}{2}$  over a substantial interval. Experimentally, the curve has the opposite shape: It is rounded near the boundaries, steep in the middle. This looks more like the impurity smearing that often obscures first-order transitions. It might well be that the small repulsive Coulomb interaction is overcome by other attractive forces; in this case we would expect a sharp first-order transition for the ideal system.

#### IV. CONCLUSION

We may summarize the results of the previous sections as follows. Three parameters are needed to describe neutral to ionic transitions.

(i) The chemical potential difference  $H$  between a neutral donor-acceptor pair and an ionic pair. It measures how close we are to the transition.

(ii) The Coulomb interaction  $J$  between ionic pairs. It is a measure of the "collective" nature of the transition.

(iii) The overlap integral  $\tau$  between the wave function of a neutral pair and that of an ionic pair. It is a measure of the importance of quantum fluctuations.

In Sec. II we studied single stacks of donor and acceptors and we found that for  $2\tau$  less than  $J$  a first-order transition occurs at  $H=0$  with a discontinuous change in the degree of charge transfer  $\rho$ . The appropriate order parameter is  $\rho - \frac{1}{2}$ . For  $2\tau$  larger than  $J$ , the transition is continuous while at  $H=0$  the stack becomes metallic. The lowest-lying electronic excitation is always a bound charge-transfer state. For  $2\tau$  larger than  $J$ , the bound state becomes mobile and extended near  $H=0$ . In Sec. III we included, for  $\tau=0$ , the long-range interstack Coulomb interaction and found a sequence of partially ionized phases between  $H=0$  and  $H = -\sum_i J(i)$ .

This description has some limitations. We have ignored the spin degree of freedom. In the neutral phase every donor has two electrons with paired spins in its highest occupied orbital. In the ionic phase both donor and acceptor have a single electron in their highest occupied orbital. Neighboring

spins are correlated antiferromagnetically with an exchange constant of order  $\tau^2/E_{CT}$ . From this we expect a substantial increase in magnetic susceptibility in the ionic phase. This was not observed, possibly due to donor-acceptor dimerization. We also ignored *double* charge-transfer excitations, relying on strong on-site Coulomb repulsion.

One may further question to what extent the one-dimensional description of Sec. II is valid. From the polarization of the infrared absorption it is known that the charge-transfer only occurs along stacks. Coulomb interaction, however, gives rise to interstack interaction and its effect was discussed in Sec. III for  $\tau=0$ . For  $\tau > 2J$ , the Coulomb interaction will cause the metallic phase at  $H=0$  to disappear at sufficiently low temperatures.<sup>21</sup>

Beside Coulomb interaction there is also the possibility of hydrogen bonding.<sup>22</sup> This would counteract the Coulomb repulsion between *a-c* planes and perhaps remove the partially ionized phases. The magnitude of the hydrogen bonding interaction is not known.

In comparing our results with experiment, care must be taken that no charged impurities are present. A computer simulation of their effect showed that they locally polarize the stack and thereby smear out the phase transition. They also gave rise to a large increase in the dielectric constant near  $H=0$ .

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