

Electric-field-induced Mott insulating states in organic field-effect transistors

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We consider the possibility that the electrons injected into organic field-effect transistors are strongly correlated. A single layer of acenes can be modeled by a Hubbard Hamiltonian similar to that used for the κ -(BEDT-TTF)₂X family of organic superconductors. The injected electrons do not necessarily undergo a transition to a Mott insulator state as they would in bulk crystals when the system is half-filled. We calculate the fillings needed for obtaining insulating states in the framework of the slave-boson theory and in the limit of large Hubbard repulsion U . We also suggest that these Mott states are unstable above some critical interlayer coupling or long-range Coulomb interaction.

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I. INTRODUCTION

Recent advances in producing organic field-effect transistors¹ and the growth of single crystals of acenes^{2,3} raises the possibility of using an electric field to inject charge into a single layer of a layered molecular crystal such as pentacene. Recent theoretical papers have considered the possibility of superconductivity due to the electron-phonon interaction.^{4,5} Superconductivity might appear when the filling of the layer at the interface between the molecular crystal and the dielectric reaches half filling.⁴ In that theory, this would be the consequence of the existence of a van Hove singularity in the density of states and the pairing is described by the conventional BCS theory involving the electron-phonon interaction.⁴ However, in other organic materials, such as the κ -(BEDT-TTF)₂X family, the proximity of the superconducting phase with various other ground states (a Mott insulating state for example⁶) may suggest a more exotic type of pairing, involving the Coulomb interaction between the electrons.^{7,8} It is therefore important to study whether the injected carriers could form a strongly correlated state (at half filling, for example).

The first question we have to study is whether a Mott insulating state could be induced. Naively, one might expect that if the repulsion between two electrons on the same molecule is strong enough an insulating state will occur at half filling. The effect of disorder on such an insulating state in C₆₀ crystals doped by charge injection was recently considered theoretically.⁹ Here, even though we consider a clean system, it is not obvious that the effects of correlation will appear in a field effect geometry.

In a field-effect transistor, the charges are confined near the interface between the molecular crystal and the dielectric, because of the strong electric field used to inject the charges. The issue of how far extended from the interface the electronic wave functions are is very important. As the doping increases, it is indeed not clear whether the electrons will remain confined to the first layer or whether the electrons will occupy other states extended far from the interface. There is clearly a competition between the Coulomb repulsion that pushes the electrons apart and the electric field that forces the electrons to stay close to the interface. Then, if the electric field is not strong enough, the Mott transition will

not occur. In the following, we will adopt the slave-boson approach to study the Mott transition in the presence of the electric field. Slave-boson theory is the simplest theory which generically gives a Mott transition, and it will allow us to show that such Mott states could occur at non-half-integer fillings.

In Sec. II, we will estimate the Coulomb interaction for two electrons on the same acene molecule, such as pentacene, tetracene, and anthracene since these are important examples. We will then give a brief review of the physics of a single layer of such molecules. However, the presence of a finite electric field in field-effect transistors allows the electrons to hop onto the neighboring layers, thus modifying the dynamics. In Sec. III, by applying the slave-boson theory, we will show that the Mott state could occur at larger fillings, that we calculate in the limit of strong interaction. In Secs III B and III C, we give a discussion of the effect of the interactions we neglected first, such as the interlayer hopping, and the long-range Coulomb interactions. Those interactions could in fact destroy the Mott state, and we will calculate the critical strength above which the Mott state is no longer stable.

II. A STRONGLY CORRELATED MODEL FOR A SINGLE LAYER IN ACENE MOLECULAR CRYSTALS

In this section, we consider a model for a layer of acene molecules. Band structure calculations have shown that, for large electric fields applied to pentacene⁴ or C₆₀ (Ref. 10) field-effect transistors, the electrons are confined to a single layer.

For acene-based materials, we now argue that a single layer can be described by a Hubbard model on an anisotropic triangular lattice. Such a short-range Coulomb interaction is more valid in the strong doping regime where the screening of the Coulomb interaction by the other electrons is more efficient. This is the regime we are interested in. The Hamiltonian is written

$$\mathcal{H} = - \sum_{ij,\sigma} t_{ij} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{H.c.}) + U \sum_{\mathbf{i}} n_{\mathbf{i},\uparrow} n_{\mathbf{i},\downarrow}, \quad (1)$$

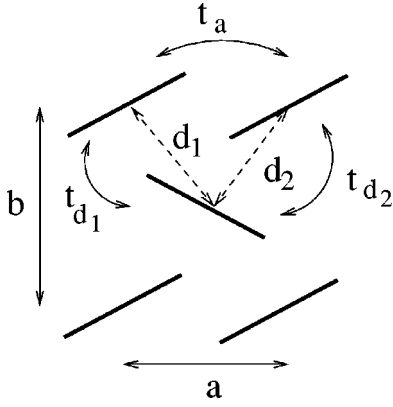


FIG. 1. Model for a layer of pentacene molecules, according to Refs. 11,13. The thick lines represent the pentacene molecules. t_a , t_{d_1} , and t_{d_2} denotes the different hopping integrals between neighboring molecules.

where $c_{i\sigma}^\dagger$ creates an electron (hole) at site \mathbf{i} in the lowest unoccupied molecular orbital (LUMO) [highest occupied molecular orbital (HOMO)]. t_{ij} are the tight-binding hopping integrals between molecular orbitals (t_{d_1} , t_{d_2} , t_a), as shown in Fig. 1, and U is the Hubbard repulsion for two electrons on the same molecule that we will estimate below. The kinetic part of the Hamiltonian can be rewritten

$$\mathcal{H}_0 = \sum_{\mathbf{k}, \sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$$

$$\epsilon_{\mathbf{k}} = -2t_{d_1} \cos(k_1 d_1) - 2t_{d_2} \cos(k_2 d_2) - 2t_a \cos(k_1 d_1 + k_2 d_2), \quad (2)$$

where $t_{d_{1,2}}$, t_a are the hopping parameters in the $d_{1,2}, a$ directions. For example, $t_{d_1} = 59$ meV, $t_{d_2} = 88$ meV, $t_a = 47$ meV for the LUMO orbital of pentacene.¹¹

We note that this band structure is similar to that for the κ -(BEDT-TTF)₂X family.⁸ A similarity between the band structure of α -sexithiophene and this family has been pointed out previously.¹²

Importantly, the coupling between the layers has been found to be negligible, thus showing the strongly two-dimensional character of these materials.¹¹ There are two molecules per unit cell but the band structure reduces to one band due to the equivalence of the crystal environment up to a rotation.

Correlation effects are known to be important for single isolated acene molecules, as has been discussed in the quantum chemistry literature.^{15,16} For the purpose of estimating the Hubbard repulsion, we have calculated the Hückel energies and wave functions of the electrons in benzene, naphthalene, anthracene, tetracene, and pentacene molecules. We have then estimated the cost in Coulomb energy of two additional electrons (or holes) on the molecule

$$U = \int d^3 r_1 d^3 r_2 \phi_\uparrow^*(\vec{r}_1) \phi_\downarrow(\vec{r}_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \phi_\uparrow^*(\vec{r}_2) \phi_\downarrow(\vec{r}_2), \quad (3)$$

where $\phi_\sigma(\vec{r})$ is the lowest unoccupied molecular orbital (LUMO) of the molecule. Using the Hückel approach, we found the coefficients c_i defined by

$$|\phi_\sigma\rangle = \frac{1}{\sqrt{N}} \sum_i c_i |i, \sigma\rangle, \quad (4)$$

where $|i\rangle$ is the atomic orbital of the i th carbon atom. Inserting this into Eq. (3) leads us to estimate the following expression for U :

$$U = \frac{U_0}{N^2} \sum_i |c_i|^4, \quad (5)$$

where the expression is written as a function of the *local* Coulomb interaction on a single carbon atom $U_0 \equiv \langle i, \uparrow; i, \downarrow | e^2 / |r_1 - r_2| | i, \uparrow; i, \downarrow \rangle$. We have calculated the Hückel parameters c_i for the four isolated molecules. For the benzene molecule, the electron is uniformly delocalized on the ring. The effective U is therefore U_0/N . For the other molecules, there is incomplete delocalization and $\sum_i |c_i|^4 > \sum_i |c_i|^2 = N$. Therefore $U > U_0/N$. The explicit calculation gives $U/U_0 = 0.14$ for naphthalene ($N=10$), 0.12 for anthracene ($N=14$), 0.10 for tetracene ($N=18$), and 0.09 for pentacene ($N=22$). Assuming a value of $U_0 = 12$ eV for the Coulomb interaction on a carbon atom,¹⁵ one can estimate that $U = 1.7$ eV for anthracene, $U = 1.2$ eV for tetracene, and $U = 1$ eV for pentacene. Although this calculation neglects the screening effects due to the other electrons, it suggests that the Coulomb interaction ($U \sim 1$ eV) may be comparable to the kinetic energy [with a bandwidth given by $W \sim 0.5$ eV (Ref. 11)]. This is consistent with other similar organic materials based, for example, on the BEDT-TTF or BETS molecules.⁸ Although our estimate of U is rather crude (especially because it neglects screening effects), it seems plausible to view a single layer in isolation as a strongly correlated system.

We first review the physics of the one-layer model at half filling⁸ and low temperatures before considering the effects due to the next layers. At small $U \ll t$, the single layer system, described by the Hamiltonian (1), is metallic, because the frustration of the lattice gives an imperfect nesting of the Fermi surface (see Fig. 2). At large $U \gg t$, the system is a Mott insulator and has a charge gap U . The interaction between the spins defines a smaller energy scale $\sim t^2/U$. In the intermediate regime of $U \sim t$, the question of the nature of the ground state remains to be settled. As previously suggested on theoretical grounds,¹⁷ a superconducting phase may appear near the metal-Mott insulator boundary. This may explain the phase diagram of half-filled organic materials.^{17,8} As the model (1) is essentially the same as the one which describes κ -(BEDT-TTF)₂X,⁸ it is tempting to suggest that superconductivity may appear in acene field-effect transistors, at half filling. In such an approach, the T_c is expected to increase with the Coulomb interaction.¹⁸ Meanwhile, the larger the molecule, the smaller the U is. Therefore, a larger T_c is expected for smaller molecules such as tetracene and anthracene (if screening effects can be ig-

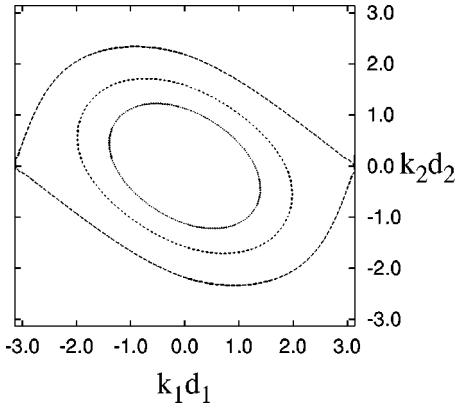


FIG. 2. Fermi surfaces for the band structure given in Eq. (2), for different band fillings, 1/8, 1/4, 1/2.

nored). However, the same trend is found within the electron-phonon mechanism.⁵ If such strongly correlated superconducting phases appear, Mott insulating states should also appear in other acenes with a larger U/t . This could be achieved in principle in materials based on a smaller acene molecule (to increase U), such as naphthalene. Alternatively, t might be decreased by pushing the molecules further apart by intercalation or attaching side groups to the molecules.¹⁹

III. A MODEL FOR LAYERED FIELD-EFFECT TRANSISTORS

We now examine how the single layer approach is modified when one takes into account the existence of the next layers. We have discussed above the example of acene-based materials to give an idea of the order of magnitude of the parameters, but the following considerations do not actually depend on the details of these materials.

Our aim is to study the case $U \gg t$ to see whether the Mott state we have discussed for a single layer can really be induced when the system has many layers. As it turns out to be the case, we may then speculate that superconductivity in field-effect transistors would probably be of the same origin as that observed in bulk crystals of κ -(BEDT-TTF)₂X. Conversely, the existence of superconductivity in those materials should encourage the search for superconductivity in field-effect transistors.

According to the band structure calculations,^{4,10} the electrons are confined to a single layer for the largest electric fields applied. Nevertheless, we do not restrict ourselves to a single band for two reasons. First, even when the charges are confined to a single layer, the next layers offer virtual states that make the system different from bulk crystals. This is precisely what we study in the next paragraph, where the interlayer coupling is set to zero, so that there is no mixing of the bands. Second, when the electric field is small enough with respect to the interlayer coupling t_{\perp} , the charges are partly delocalized onto the next layers. So the question is then: can we still have a Mott insulating state in the first layer?

We now take into account the next layers away from the interface. The Hamiltonian includes the kinetic energy of the

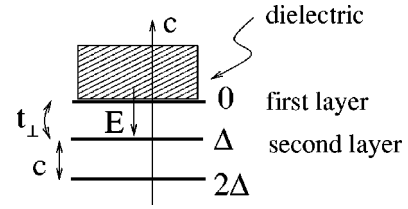


FIG. 3. Schematic picture for the first layers near the interface with the dielectric crystal. $\Delta = eEc$ is the energy associated with the electric field.

electrons within a layer, the strong interaction between them, the electric field imposed by the gate (but we neglect the modification of the electronic orbital by the electric field) and the interlayer hopping

$$\mathcal{H} = \sum_{\mathbf{k}, i, \sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}, i, \sigma}^{\dagger} c_{\mathbf{k}, i, \sigma} + U \sum_{\mathbf{i}, j} n_{\mathbf{i}, j, \uparrow} n_{\mathbf{i}, j, \downarrow} + \Delta \sum_{\mathbf{k}, i, \sigma} i n_{\mathbf{k}, i, \sigma} - t_{\perp} \sum_{\mathbf{k}, i, \sigma} (c_{\mathbf{k}, i, \sigma}^{\dagger} c_{\mathbf{k}, i+1, \sigma} + \text{H.c.}), \quad (6)$$

where $c_{\mathbf{k}, i, \sigma}^{\dagger}$ creates an electron in a state of momentum \mathbf{k} , in the layer i and spin state σ . $\epsilon_{\mathbf{k}}$ is the electronic dispersion within a layer, characterized by a bandwidth W . $\Delta = eEc$ is the energy spacing between the orbitals which belong to different layers, due to the electric field E imposed by the gate. c is the distance between the layers (see Fig. 3). We also define $\gamma = 2\Delta/W$. The Hamiltonian is then a multiband Hubbard model with the set of parameters U/W , γ , t_{\perp}/W and the total filling n .

A. No interlayer hopping

First, we will consider the case of decoupled layers $t_{\perp} = 0$, which is in fact a good approximation for acene materials. The only additional ingredient compared to Sec. II is the existence of additional states in the next layers at energies $[\Delta_i - W/2, \Delta_i + W/2]$ (where $\Delta_i = i\Delta$), which possibly overlap with the first band. We now discuss the effects of these additional states for both the case of half filling and arbitrary fillings.

Half filling. As long as $\Delta > W/2$, no additional states are filled [Fig. 4(a)] and due to the absence of coupling between the bands, the system behaves as a single layer in isolation, i.e., there is a metal-insulator transition at finite U , as we explained above. The only difference with the single layer problem is the existence of additional excited states, which will affect the transport and magnetic properties of the system. Thus, depending on the strength of U/Δ , the system is either a Mott insulator ($U/\Delta < 1$, the charge gap is roughly given by U) or a charge-transfer insulator ($U/\Delta > 1$), for which the excited states consist of a charge transfer to the next layer (the charge gap is given by Δ). Thus, the gap can be much smaller than U if the electric field is not large enough. The magnetic properties of the layer are given by superexchange processes. In the case of the Mott insulator, the effective antiferromagnetic exchange is given as usual by $J = 4t^2/U$. In the case of the charge-transfer insulator, a

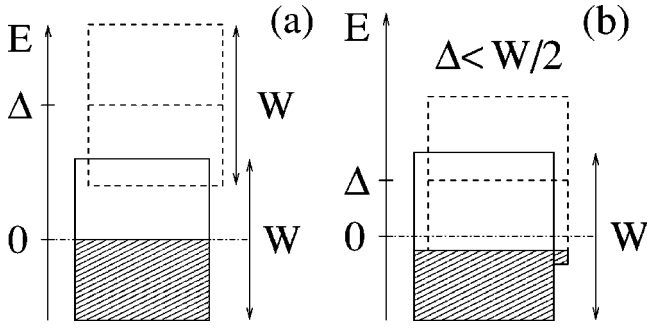


FIG. 4. Noninteracting band picture with the first two bands for a total filling of one electron per molecule, i.e., a total of N carriers where N is the number of sites within a layer, W the bandwidth, and $\Delta = eEc$ the midenergy of the conduction states of the second layer. (a) $\Delta > W/2$. The lower band is half filled. (b) $\Delta < W/2$. The lower band is no longer half filled: some electrons occupy the states of the second band.

given electron would not necessarily hop virtually to a neighboring site in the same layer because it costs the energy U but would rather hop onto the next layer which costs a smaller energy $\Delta = eEc$. Then, in this case, the exchange J between two spins would explicitly depend upon the strength of the electric field. Note, however, that if we change E , we would not only change J , but also the total filling of the system. Above half filling, some carriers will occupy states in the next layer. As long as the layers are weakly coupled, these extra carriers will not change the magnetic properties of the first layer. Therefore, the net effect of the electric field will be to decrease the interaction between the spins. This effect can not be detected through the change of the critical temperature of the antiferromagnetic transition because such transition is prevented by the Mermin-Wagner theorem in a strictly two-dimensional system. However, measurement of the magnetic susceptibility would provide information about spin-spin interaction and how they change with the electric field. When $\Delta < W/2$ [see Fig. 4(b)], however, the second layer starts to be filled before the first one gets to half filling (the chemical potential is negative). The entire system is less than half filled and no metal-insulator transition is then expected. The critical value $\Delta = W/2$ is very schematic here because $t_{\perp} = 0$. In Sec. III B, we will see that for finite t_{\perp} , the critical value of Δ actually increases.

Arbitrary fillings. In the case $\Delta < W/2$, some states in the second band have a negative energy and need to be filled before the first band becomes half filled [see Fig. 4(b)], thus possibly allowing for a localization of the charges in the first layer if U is large enough. To assure that the first band is half filled, we fix the chemical potential at zero energy $\mu = 0$. In the next paragraph, we calculate, in the framework of the slave-boson theory, the total number of carriers needed to have $\mu = 0$.

In slave-boson mean-field theory,²⁰ the effect of the Coulomb interaction is to renormalize the hoppings by quantities denoted by z_j^2 (for the layer j). z_j is the mean field value of the operator $\hat{z}_{i,j}$ which is given by a combination of auxiliary boson operators $e_{i,j}^{\dagger} p_{i,j,\sigma} + p_{i,j,-\sigma}^{\dagger} d_{i,j}$, that tell if the site (i,j) is empty (operator $e_{i,j}$), single occupied ($p_{i,j,\sigma}$), or

double occupied ($d_{i,j}$).¹⁴ The many-body Hamiltonian (6) for the layer j reduces in the mean-field approximation to free fermions with renormalized bandwidths

$$\mathcal{H}_j = - \sum_{\mathbf{i},\sigma} t_{\mathbf{i}} z_j^2 (c_{\mathbf{i},j,\sigma}^{\dagger} c_{\mathbf{i},j,\sigma} + \text{H.c.}) + U d_j^2 + \Delta \sum_{\mathbf{i},\sigma} j n_{i,j,\sigma}, \quad (7)$$

where d_j is the mean-field value of the double occupancy operator $d_{i,j}$. In the following, we will restrict ourselves to $U \rightarrow +\infty$, so that $d_j = 0$ (the double occupancies are forbidden). The layers are all decoupled and the total Hamiltonian is the sum over all the layers. However, the quantities z_j^2 , which determines the bandwidths, are coupled together because they depend on the fillings of the band j , which is determined by the chemical potential of the entire system.

For free electrons ($U = 0$, $z_j^2 = 1$), the number of states below zero energy in the second layer is denoted by $(1 - \gamma)N$ ($\gamma < 1$ and N is the number of sites). When we take into account the Coulomb interaction within the slave-boson picture, the bandwidths are reduced ($W \rightarrow W z_2^2$). The number of states given above becomes $(1 - \gamma/z_2^2)N$, that is smaller than $(1 - \gamma)N$ and depends upon z_2^2 that we have to determine. Therefore, we note that the total filling needed to have $\mu = 0$ in the interacting system must be smaller than that for free electrons. We now calculate the filling explicitly.

We first calculate the value of z_2^2 for $\gamma < 1$ when the carriers of the first layer become localized. For that, we consider just the first two layers ($j = 0, 1$) and take a *constant* density of states in the layers to simplify the calculation. At $\mu = 0$, the fillings n_j are given by

$$n_1 = \frac{1}{2} + \frac{(n-1)z_2^2 + \gamma/2}{z_1^2 + z_2^2}, \quad (8)$$

$$n_2 = n - n_1, \quad (9)$$

where n is the total filling of the system and $W z_1^2$ and $W z_2^2$ are the bandwidths of the two bands. In the limit of large U (i.e., $U \gg W, \Delta$), $z_1^2 = (1 - 2n_1)/(1 - n_1)$. Charge localization in the first layer is characterized by $z_1^2 = 0$ or $n_1 = 1/2$. First, Eq. (8) gives the bandwidth of the second band $z_2^2 = \gamma/[2(n-1)]$. On the other hand, in the limit of large U , the bandwidth is given by $z_2^2 = (1 - 2n_2)/(1 - n_2)$, where $n_2 = n - 1/2$. Equating the two expressions, we find the total filling n , $n_c(\gamma)$, for which $n_1 = 1/2$ and the bandwidth z_2^2 :

$$z_2^2 = \frac{1}{2} (\sqrt{\gamma^2 + 8\gamma} - \gamma), \quad (10)$$

$$n_c(\gamma) = 1 - \frac{1}{\sqrt{1 + 8/\gamma} - 1} \equiv 1 - f(\gamma). \quad (11)$$

Note that this solution is valid as long as the third band is not involved, that is to say, if we define the energy of the middle of the third band by $\Delta_2 = \alpha_2 \Delta$, $\Delta_2 - W/2 > 0$ or in terms of γ , $\gamma > 1/\alpha_2$.

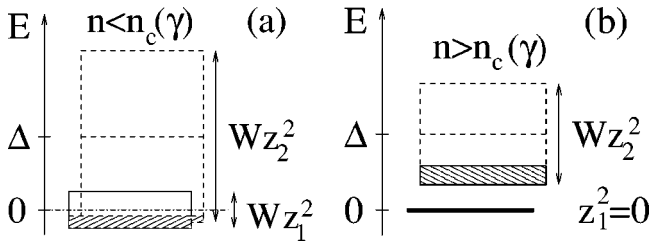


FIG. 5. Interacting band picture for the first two bands within the slave-boson mean-field theory (here $2\Delta < W \ll U$). (a) The first two bands are partially filled with electrons and the bandwidths are renormalized by the interaction. (b) As soon as $n > n_c(\gamma)$, the lower band is half filled, so that $z_1^2 = 0$. Then, there is one electron localized on each site of the first layer. The second band is partially filled.

Therefore, in the regime $1/\alpha_2 < \gamma < 1$, the total filling needed to get the first band half filled is given by Eq. (11). Above this filling, $z_1^2 = 0$, so that we have one localized electron on each site of the first layer. The additional $[2n_c(\gamma) - 1]N$ electrons fill the band of the second layer which bandwidth is Wz_2^2 [given by Eq. (10), see Fig. 5].

More generally, in order to consider the regime with $\gamma < 1/\alpha_{N_b}$, we have to consider N_b additional bands. Generalization to many bands with energies $\Delta_i = \alpha_i \Delta$ ($\alpha_0 = 0$, $\alpha_1 = 1$, α_2, \dots) and bandwidth W is straightforward. Performing the same steps as above, in the regime $1/\alpha_{N_b+1} < \gamma < 1/\alpha_{N_b}$, the filling at which the N_b first bands are half filled is given by

$$n_c(\gamma) = \frac{N_b + 1}{2} - \sum_{p=1}^{N_b} f(\alpha_p \gamma). \quad (12)$$

Let us recall that N_b is the number of bands partially filled. For a given system with a fixed γ , N_b bands are involved when the bottom of the N_b^{th} band crosses the zero energy. It occurs when γ gets smaller than $1/\alpha_{N_b}$. The shape of this curve depends on the positions of the bands $\Delta_p = \alpha_p \Delta$.

Furthermore, the generalization to higher fillings is also very similar. If we consider such a filling that P bands are completely half filled and N_b bands are partially filled. In the regime where $1/(\alpha_{P+N_b} - \alpha_{P-1}) < \gamma < 1/(\alpha_{P+N_b+1} - \alpha_{P-1})$, the critical n_c to get the P^{th} band half-filled is given by

$$n_c(\gamma) = \frac{N_b + P}{2} - \sum_{j=P}^{N_b+P-1} f[(\alpha_j - \alpha_{P-1})\gamma]. \quad (13)$$

Note that this equation reduces to Eq. (12) for $P=1$. Examples of the first two curves ($P=1$ and $P=2$) are given in Fig. 6.

In conclusion, when $\gamma > 1$, only one band is involved. When the band gets to half filling ($n=1/2$), it undergoes a transition to a Mott state at large U in which all the electrons are localized on the first layer. Doping the system further leads to filling of the states of the second layer, eventually up to half filling when the total density is $n=1$, then localizing

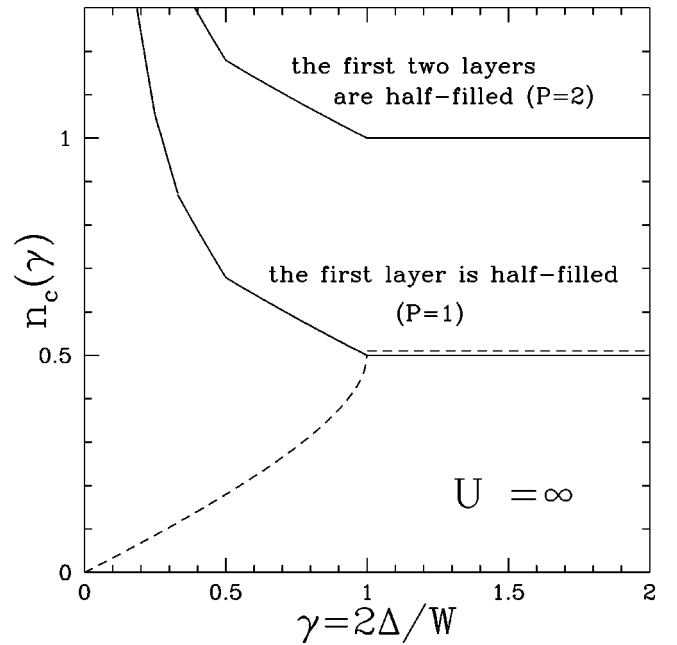


FIG. 6. Phase diagram (filling n versus energy spacing between the bands due to the electric field γ) from slave-boson theory in the limit $U = \infty$ and $t_{\perp} = 0$. Solid lines show the critical fillings above which the first (second) band is half filled, i.e., the electrons are localized on each site of the first (second) layer in the limit of large U . The dashed line shows the critical filling above which the second band starts to be filled.

the electrons in the second layer, and so on (see Fig. 6). However, as soon as $\gamma < 1$ (the second band starts to be involved above some filling, see dashed line in Fig. 6), the Mott state needs a larger filling to occur. This filling $n_c(\gamma)$ is given by Eq. (12). In that case, the first band is half filled, and there is one electron localized on each site. As the total number of electrons is larger than the number of sites of the first layer, some of them occupy the states of the next layers. The system is metallic, but with a reduced number of carriers.

The condition on γ is nothing but a condition on the electric field since $\gamma = 2eEc/W$. The border $\gamma=1$ defines a critical field E_c . For instance, in the acenes, $W \sim 0.2$ eV and $c \sim 15$ Å gives $E_c \sim 10^8$ V m $^{-1}$, which is close to the dielectric breakdown field.²¹

However, this calculation neglects the interlayer hopping. It is known that such couplings are quite small in layered molecular crystals, in particular in those discussed above,^{11,13,12,19} but it is not obvious whether an infinitesimal coupling would destroy the charge localization in either layers. In the next section, we study whether such a state survives when one takes into account such interactions, such as the interlayer coupling or also the Coulomb interaction between nearest sites.

B. Effect of the interlayer hopping

The Mott state in a single layer of a field-effect transistor is not as stable as in a bulk crystal. The electrons have, indeed, other available conduction states in the next layers

away from the surface. This opens a way to avoid the strong on-site Coulomb interaction, though it costs the energy associated with the electric field eEc . Some interactions will actually act against the charge localization: the coupling between the layers favors extended states away from the surface. We just consider the hopping between the two layers closest to the surface

$$\mathcal{H}_\perp = -t_\perp \sum_{\mathbf{k},\sigma} (c_{\mathbf{k},1,\sigma}^\dagger c_{\mathbf{k},2,\sigma} + \text{H.c.}). \quad (14)$$

When $\gamma > 1$, the two bands are separated by a gap. Using the same Hamiltonian, but at half filling, Blawid *et al.* showed that, within the slave-boson theory, there is a Mott-metal transition when $t_\perp > W[\gamma(\gamma-1)/2]^{1/2}/2 \equiv t_{\perp,c}$ for $U = +\infty$.²² Note that, when $\gamma \rightarrow 1$, the critical t_\perp vanishes. This is consistent with the disappearance of the Mott state at half filling that we found when $\gamma < 1$.

On the other hand, in Sec. III A, we found that a total filling larger than $n_c(\gamma)$ ($> 1/2$) was needed, when $\gamma < 1$, to have the first layer half filled, thus allowing for a Mott state in the first layer. We now wonder if this state is still stable above $n_c(\gamma)$ when $t_\perp \neq 0$. If we think of the result given above, it seems that we need a real gap between the two bands ($\gamma > 1$). With the Coulomb interaction switched on, the bandwidth of the second band is reduced and a gap opens when $\Delta - Wz_2^2/2 > 0$. In the limit of large U , z_2^2 is given by $(1-2n_2)/(1-n_2)$, and $n_2 = n - 1/2$ as long as any other band can be safely ignored. Therefore, the gap opens when the density n satisfies $z_2^2 = \gamma = (2-2n)/(3/2-n)$. That gives $n = (2-3\gamma/2)/(2-\gamma) \equiv n'_c(\gamma) > n_c(\gamma)$. So we could think that the Mott state is unstable in the regime $n_c(\gamma) < n < n'_c(\gamma)$, but becomes stable as soon as a gap opens, i.e., when $n > n'_c(\gamma)$.

In fact, the case considered here is different from that of Blawid *et al.* because the second band is partially filled. We now show that, as soon as $n > n_c(\gamma)$, the Mott state is stable below a critical value for t_\perp . This is because we do not need a gap between the two bands, but a gap between the energy of the localized states and the energy of the available states in the second band. As soon as $\mu > 0$, the second band is partially filled and the gap opens.

We consider *two* coupled bands with dispersions given by ϵ_k and $\tilde{\epsilon}_k$ ($\tilde{\epsilon}_k = \Delta + \epsilon_k$ in the noninteracting picture). We neglect the other higher-energy bands in order to simplify the expressions. In the slave-boson picture, the effect of the interaction is just to renormalize the bandwidths by quantities denoted by z_1^2 and z_2^2 .

$$\mathcal{H}_0 = \sum_{\mathbf{k},\sigma} z_1^2 \epsilon_k c_{\mathbf{k},1,\sigma}^\dagger c_{\mathbf{k},1,\sigma} + \sum_{\mathbf{k},\sigma} \underbrace{(\Delta + z_2^2 \epsilon_k)}_{\tilde{\epsilon}_k} c_{\mathbf{k},2,\sigma}^\dagger c_{\mathbf{k},2,\sigma}. \quad (15)$$

It also renormalizes the coupling between the two bands such as

$$\mathcal{H}_\perp = -t_\perp z_1 z_2 \sum_{\mathbf{k},\sigma} (c_{\mathbf{k},1,\sigma}^\dagger c_{\mathbf{k},2,\sigma} + \text{H.c.}). \quad (16)$$

We again restrict ourselves to the limit of infinite U , where the z_i^2 are function of the fillings n_i :

$$z_i^2 = \frac{1-2n_i}{1-n_i}, \quad (17)$$

$$n_i = \frac{1}{2N} \sum_{\mathbf{k}\sigma} \langle c_{\mathbf{k},i,\sigma}^\dagger c_{\mathbf{k},i,\sigma} \rangle, \quad (18)$$

where the n_i are calculated as function of the parameters of the model. Near the metal-insulator boundary for the first layer (but in the metallic region), n_1 will be expanded as a function of $z_1^2 \rightarrow 0$:

$$n_1 = \frac{1}{2} - \beta z_1^2, \quad (19)$$

where we have introduced a parameter β that has to be determined. To satisfy Eqs. (17) and (19) at the same time, in the metallic regime, we need

$$4\beta = 1. \quad (20)$$

This gives a condition on the parameters of the model at the Mott-metal boundary. So all we have to do is to calculate this parameter β . We decompose $c_{\mathbf{k},1,\sigma}^\dagger$ as function of the eigenoperators

$$c_{\mathbf{k},1,\sigma}^\dagger = u_k \alpha_{\mathbf{k}\sigma}^\dagger + v_k \beta_{\mathbf{k}\sigma}^\dagger, \quad (21)$$

where u_k and v_k are given by the diagonalization of the Hamiltonian. We are interested in the limit $t_\perp \sim z_1 \rightarrow 0$. Then, these parameters are expanded as

$$|u_k|^2 \sim 1 - \frac{t_\perp^2}{(\epsilon_k - \tilde{\epsilon}_k)^2}, \quad (22)$$

$$|v_k|^2 \sim \frac{t_\perp^2}{(\epsilon_k - \tilde{\epsilon}_k)^2} \quad (23)$$

and n_1 can be rewritten

$$n_1 = \frac{1}{2N} \sum_{\mathbf{k}} |u_k|^2 \langle \alpha_{\mathbf{k}\sigma}^\dagger \alpha_{\mathbf{k}\sigma} \rangle + \frac{1}{2N} \sum_{\mathbf{k}} |v_k|^2 \langle \beta_{\mathbf{k}\sigma}^\dagger \beta_{\mathbf{k}\sigma} \rangle. \quad (24)$$

1. $\mu = 0$

We restrict ourselves to $\gamma > 1$, as the Mott state appears to be unstable when $\gamma = 1$. Then only the lower band is filled, i.e., $\langle \beta_{\mathbf{k}\sigma}^\dagger \beta_{\mathbf{k}\sigma} \rangle = 0$ and n_1 is given by

$$n_1 = \frac{1}{2} - \frac{1}{2N} \sum_{\mathbf{k}} \frac{t_\perp^2}{(\epsilon_k - \tilde{\epsilon}_k)^2}, \quad (25)$$

where the sum runs over all the k . At the first order in z_1^2 , we can replace ϵ_k by 0 in the expression above. $\tilde{\epsilon}_k$ has a bandwidth which depends on z_2^2 . As the second band β is empty, n_2 is of the order $\mathcal{O}(t_\perp^2)$. Then, using Eq. (17), z_2^2 is just $1 - \mathcal{O}(t_\perp^2)$. We can replace $\tilde{\epsilon}_k - \epsilon_k$ by $\Delta + \epsilon_k$:

$$n_1 = \frac{1}{2} - \frac{1}{2N} \sum_k \frac{t_\perp^2}{(\Delta + \epsilon_k)^2} \quad (26)$$

which can be expressed as a function of an integral

$$n_1 = \frac{1}{2} - \frac{1}{2} \int_{-W/2}^0 d\omega \rho_0(\omega) \frac{t_\perp^2}{(\Delta + \omega)^2} \quad (27)$$

with $\rho_0 = 2/W$, the density of states per site that we have taken constant. The upper limit is 0, because only half of the first band is filled. Now, we make the substitution $t_\perp \rightarrow t_\perp z_1$:

$$n_1 = \frac{1}{2} - \frac{t_\perp^2 z_1^2}{2\Delta(\Delta - W/2)} \quad (28)$$

therefore, the critical t_\perp , given by Eq. (20), is

$$t_{\perp c} = \sqrt{\Delta(\Delta - W/2)/2} \quad (29)$$

which is the expression found previously.²² Along the line $\gamma > 1$, $n = 1/2$, the Mott state is stable below a critical t_\perp which is given above. Note that it vanishes when the gap between the two bands vanishes, $\gamma \rightarrow 1$ ($\Delta \rightarrow W/2$).

2. $\mu > 0$

We have to fill the second band β with electrons. n_1 has an additional term, and is given by

$$n_1 = \frac{1}{2} - \frac{1}{2N} \sum_k \frac{t_\perp^2}{\tilde{\epsilon}_k^2} + \frac{1}{2N} \sum_k \frac{t_\perp^2}{\tilde{\epsilon}_k^2} \langle \beta_{k\sigma}^\dagger \beta_{k\sigma} \rangle, \quad (30)$$

where $\langle \beta_{k\sigma}^\dagger \beta_{k\sigma} \rangle = \theta[\tilde{\epsilon}_k - \mu + \mathcal{O}(t_\perp^2)]$. We have now to calculate the third term. The second one is, indeed, identical, provided that $W \rightarrow Wz_2^2$ in order to take into account the renormalized bandwidth of the second band due to its filling. We first calculate the integral and then make the substitution $W \rightarrow Wz_2^2$:

$$\int_{-W/2}^{\mu-\Delta} d\omega \rho_0(\omega) \frac{t_\perp^2}{(\Delta + \omega)^2} = \frac{t_\perp^2}{W} \frac{\mu - \Delta + W/2}{\mu(\Delta - W/2)}. \quad (31)$$

Therefore, after the substitution, we find

$$n_1 = \frac{1}{2} - \frac{t_\perp^2}{2\Delta(\Delta - Wz_2^2/2)} + \frac{t_\perp^2}{Wz_2^2} \frac{\mu - \Delta + Wz_2^2/2}{\mu(\Delta - Wz_2^2/2)}. \quad (32)$$

The next question is how μ is related to n :

$$n - n_1 = \frac{1}{2} \int_{-W/2}^{\mu-\Delta} d\omega \rho(\omega), \quad (33)$$

where $\rho(\omega)$ is the density of states of the second band, which is affected by the coupling t_\perp . At the leading order, however, we can replace $\rho(\omega)$ by $\rho_0(\omega)$ and n_1 by $1/2$. That gives the chemical potential

$$\mu = \Delta + (n-1)Wz_2^2 + \mathcal{O}(t_\perp^2). \quad (34)$$

The problem is that z_2^2 is also function of the filling n_2 . But here again, because we are looking for the leading order in z_1^2 , we can replace n_2 by $n - 1/2$. Then,

$$z_2^2 = \frac{1-2n_2}{1-n_2} = \frac{2-2n}{3/2-n}. \quad (35)$$

Putting all the terms together and noticing that t_\perp scales as $z_1 z_2$, n_1 is then given by

$$n_1 = \frac{1}{2} - \left(\frac{t_\perp z_1}{W} \right)^2 \frac{4-4n}{3/2-n} \left(\frac{1}{\gamma} - \frac{2n-1}{\gamma+2(n-1)} \frac{2-2n}{3/2-n} \right)$$

and the equation for the stability border $4\beta_c = 1$ is written as

$$\frac{t_{\perp c}}{W} = \left[\frac{4-4n}{3/2-n} \left(\frac{1}{\gamma} - \frac{2n-1}{\gamma+2(n-1)} \frac{2-2n}{3/2-n} \right) \right]^{-1/2}. \quad (36)$$

The resultant phase diagram is given in Fig. 7(a) for a particular value of $\gamma < 1$. Below the critical $t_{\perp c}$, the first layer is insulating. The $t_{\perp c}$ vanishes at a particular density. As shown in Fig. 7(a), it vanishes with μ , which corresponds to the density $n = n_c(\delta)$ that we calculated in the previous section [for the present problem of two bands, see Eq. (11) or Eqs. (12) or (13) when more bands are involved]. In other words, $t_{\perp c}$ vanishes when there is no gap between the energy of the localized states and the energy of the available states in the second band. In conclusion, as soon as $n > n_c(\delta)$, there is one electron localized on each site of the first layer for $t < t_{\perp c}$. Remember, however, that we are considering the $U = \infty$ limit. Note that, when $n = 1/2$, the second term in the brackets vanishes, leading to the expression (29) which is valid for $\Delta > W/2$ ($\gamma > 1$).

In Fig. 7(b), the critical $t_{\perp c}$ is given for several values of γ . When $\gamma > 1$ (see the case $\gamma = 1.2$), there is a critical t_\perp even at $n = 1/2$. When n increases above $1/2$, the bandwidth of the second band decreases according to Eq. (35) and the gap increases. Consequently, the mixing of the two bands decreases and we need a larger $t_{\perp c}$ to destroy the Mott state. At $n = 1$, it diverges. In the model we are considering, we have only two bands. When $n = 1$, the entire system is half filled and is therefore a Mott insulator. The $t_{\perp c}$ to destroy it is then infinite because we are in the limit of infinite U .

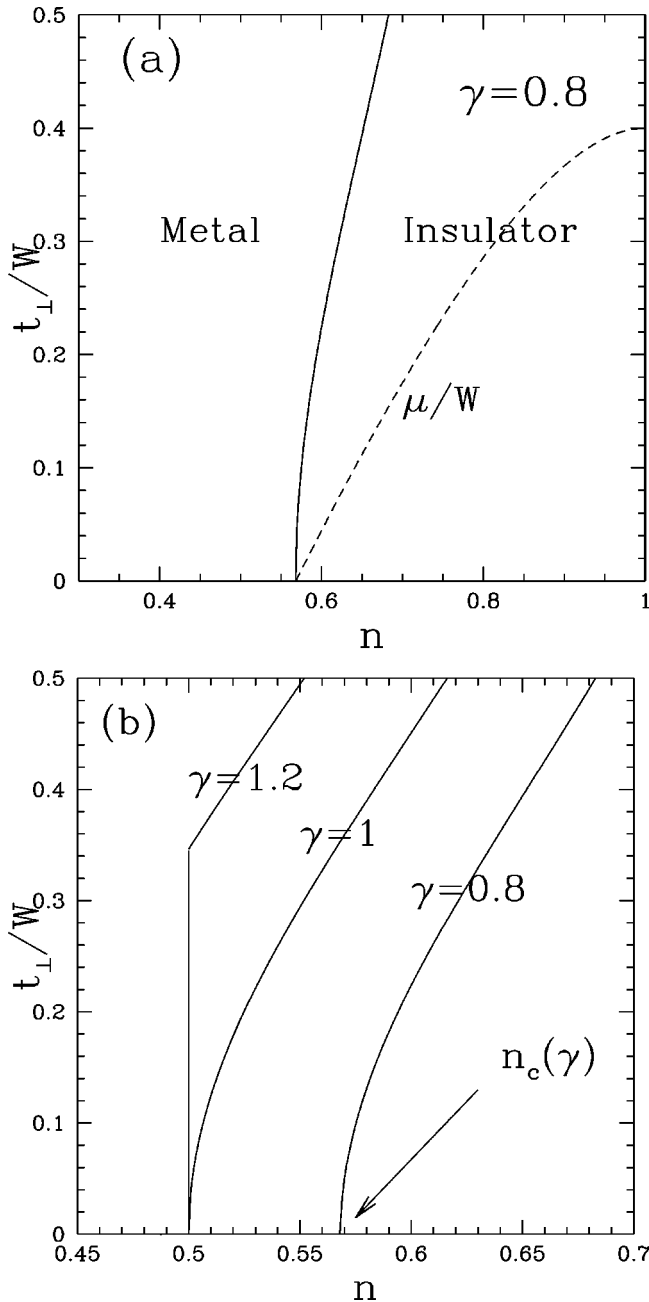


FIG. 7. (a) Example of the phase diagram when $t_{\perp} \neq 0$, for $\gamma = 0.8$. Charge localization on each site of the first layer occurs as soon as the chemical potential $\mu > 0$, i.e., as soon as there is a gap between the energy of the localized states and the energy of the available states in the second band. (b) The critical line for different values of γ . In every case, $U = \infty$.

C. Intersite Coulomb interaction

Another example of an interaction that can destroy the Mott state is given by the Coulomb interaction between the nearest neighbor sites

$$\mathcal{H} = V \sum_{\langle i,j \rangle} n_i n_j. \quad (37)$$

This term is diagonal in the basis of localized electrons. In the limit of large U and at half filling, the energy per electron

of the Mott insulating state is $E_0 = zV/2$, where z is the coordination number of the lattice. Therefore, we expect that if E_0 becomes larger than the energy spacing between bands Δ it will be energetically favorable to transfer carriers from the Mott insulating layer to the next band. The system will then be metallic. Therefore, in the limit of infinite U , we need $V < 2\Delta/z$ to get a Mott state.

IV. CONCLUSION

We have given an estimate of the on-site Coulomb interaction for the layered acene molecular crystals. It turns out that the interaction ($U \sim 1$ eV) may be comparable to the band width ($W \sim 0.5$ eV). However, whether the system is in the metallic or insulating regime, has to be determined experimentally. A prediction of the nature of the real ground state would indeed need a more accurate estimation of U/W . This is in fact a common feature of many organic materials.⁸

In bulk crystals, a large repulsive interaction leads to a Mott insulating state when there is one electron per site. In such a case, the hopping of the electrons to the other sites costs the large energy U . In field-effect transistors, however, when the first molecular layer at the interface reaches half filling, the electrons still have many empty states available on the next layers away from the surface, though these states are at higher energies depending on the strength of the electric field. When the electric field is smaller than a critical value $E_c = W/(2ec)$, the carriers occupy the conduction states of the next layer and the first layer is doped with holes. In this case, the Mott state is destroyed. However, above the critical electric field, the Mott state is stable at half-filling, at least below a critical value for the interlayer coupling $t_{\perp c}$ [given by Eq. (29)].

On the other hand, we have shown that it is possible to restore the Mott state below E_c provided that the system is further doped. This is in order to fill the first band up to half filling, to compensate for the loss of carriers which go onto the next layers. At $n = n_c(\gamma)$, the chemical potential vanishes and allows for a Mott state in the first layer. This is what we have found in Sec. III A, neglecting the coupling between the layers. This coupling, although small in the layered molecular crystals, is still present. In Sec. III B, we have calculated the critical value $t_{\perp c}$, below which the Mott state is stable. It turns out that as soon as n reaches $n_c(\gamma)$, $t_{\perp c}$ becomes nonzero.

In reality, in a field-effect transistor, the doping n and the gate voltage (or equivalently the electric field E) are not independent quantities. In Fig. 7(b), if we take a particular material with a fixed t_{\perp} and W , when the electric field increases, the metal-Mott boundary will be crossed at some stage (provided that U is large enough).

Finally, we speculate about the possibility of superconductivity in organic field-effect transistors. Since a Mott state can be induced in the first layer if the interaction is large enough, it is possible that superconductivity can occur due to the strong correlation between the electrons (though not strong enough to create a Mott insulating state). Is it possible to find a superconducting phase near the metal-insulator boundaries as in κ -(BEDT-TTF)₂X? Then, if the supercon-

ductivity is induced in the first layer, does it effect the next layers by the proximity effect? Experimentally, a strong electric field [$E \sim W/(ce)$], is needed, either to reach a sufficient doping or to get a sufficiently large energy separation between the bands. It is not obvious whether the regime in question can be experimentally reached or not because of dielectric breakdown; but it turns out that layered organic molecular crystals are good candidates to observe such ef-

fects because of their relatively small bandwidth and weak interlayer coupling.

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