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Deducing correlation parameters from optical conductivity in the Bechgaard salts

Frédéric Mila
Laboratoire de Physique Quantique, Université Paul Sabatier, 31062 Toulouse, France

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Numerical calculations of the kinetic energy of various extensions of the one-dimensional Hubbard model including dimerization and repulsion between nearest neighbors are reported. Using the sum rule that relates the kinetic energy to the integral of the optical conductivity, one can detemine which parameters are consistent with the reduction of the infrared oscillator strength that has been observed in the Bechgaard salts. This leads to improved estimates of the correlation parameters for both the tetramethyltetraselenafulvalene and tetramethyltetrathiafulvalene series.

The problem of finding an accurate description of the electronic properties of quasi-one-dimensional organic conductors has a long history. Even for the one-dimensional properties that can be observed at not too low temperatures there is no consensus. One of the origins of the difficulty is that one can work within two different kinds of models. The first one is the Fermi-gas model, also known as g-ology.[1,2] This is the appropriate framework to describe the low-energy properties, which are not of the usual Fermi-liquid type but of the Luttinger-liquid type. Most of the low-energy properties have been extensively analyzed within this type of model, and some information on the size of the parameters is available.[3,4] The second kind of model is the Hubbard model and its extensions. They are described by the Hamiltonian

$$\begin{aligned}H=&-t_1\sum_{i\ \mathrm{even},\sigma}(c^{\dagger}_{i,\sigma}c_{i+1,\sigma}+\mathrm{H.c.})\\&-t_2\sum_{i\ \mathrm{odd},\sigma}(c^{\dagger}_{i,\sigma}c_{i+1,\sigma}+\mathrm{H.c.})\\&+U\sum_i n_{i\uparrow}n_{i\downarrow}+V\sum_i n_i n_{i+1}\ .\end{aligned}\tag{1}$$

The parameters of this model are (i) a hopping integral t_1 for the short bonds; (ii) a hopping integral t_2 ($\leq t_1$) for the long bonds; (iii) an on-site repulsion U; and (iv) a repulsion between nearest neighbors V. In the following, energies will be measured in units of t_1, and the basic dimensionless parameters are t_2/t_1 for the dimerization and U/t_1 and V/t_1 for the Coulomb interactions. These parameters are large-energy scales, and such a description is the natural framework to make contact with quantum chemistry or to analyze high-energy properties of the materials.

Recently, it has been shown that, even for the low-energy properties, this description in terms of high-energy scales can be very useful.[5] In the context of the Luttinger-liquid theory, the central parameter that describes the low-energy physics, the exponent K_ρ, can take any value from 0 to $+\infty$. However, for the quarter-filled, extended Hubbard model, which is the appropriate description of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (where TMTSF is tetramethyltetraselenafulvalene) as far as quantum chemistry is concerned, it was possible to show that K_ρ cannot be smaller than $\frac{1}{4}$. It is actually possible to calculate K_ρ as a function of the correlation parameters with a reasonable accuracy using standard numerical techniques,[5–7] and an accurate determination of these parameters will be an important step toward a good understanding of the low-energy properties of the Bechgaard salts.

How can one determine the correlation parameters? In systems like transition-metal compounds, the combination of photoemission and Auger spectroscopy has proved to be the most powerful tool for answering that question,[8] but this is hopeless in the case of the Bechgaard salts because the photoemission spectrum is itself the subject of much controversy.[5,9] For charge-transfer salts, more specifically, for TTF-TCNQ (where TTF is tetrathiafulvalene and TCNQ is tetracyanoquinodimethane) and related compounds, a lot of work had been done on that question in the early 1980s, based on diffuse scattering experiments and susceptibility measurements. The competition between $2k_F$ and $4k_F$ in the charge response function, and the enhanced Pauli susceptibility observed in some compounds, have been shown by Mazumdar and co-workers[10] to be consistent with the nondimerized version of Eq. (1) if U is about 1.5 eV and V is 0.5 eV. A detailed study of charge and spin response functions by Hirsch and Scalapino with quantum Monte Carlo simulations confirmed the important role of the repulsion between nearest neighbors.[11] Finally, this description was also shown to be able to account for the charge-transfer spectra of many salts.[12]

Part of this analysis can be transposed to the Bechgaard salts. However, given the important role played by dimerization in these compounds, a more specific analysis that includes different values of t_1 and t_2 would be welcome. The interpretation of the temperature dependence of the susceptibility[3,13] and of the resistivity[14] has given some preliminary information, but it is not very precise: Quantitative calculations are already very difficult for the Hubbard model with only on-site repulsion, and accurate estimates for the model of Eq. (1) as a function of t_2/t_1, U/t_1,and V/t_1 are not available. Quantum-chemistry calculations of the correlation pa-

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rameters have also been performed for these systems,[15] but the reliability of the calculations is again very controversial.

There is however one set of experimental data that has not been systematically used, namely, the reflectivity measurements. That these results contain information on the local correlations has already been explained in great detail by Jacobsen.[16] The idea is the following. On one hand, one can determine the plasma frequency from a Drude fit of the reflectivity spectrum. On the other hand, one can extract the optical conductivity through a standard procedure. Comparing the integral of the real part of the conductivity with the plasma frequency yields an estimate of the reduction of the kinetic energy due to correlations. To be more precise, let us denote by T the kinetic-energy operator defined by

$$T=-t_1\sum_{i\ \text{even},\sigma}(c^{\dagger}_{i,\sigma}c_{i+1,\sigma}+\text{H.c.})$$

$$-t_2\sum_{i\ \text{odd},\sigma}(c^{\dagger}_{i,\sigma}c_{i+1,\sigma}+\text{H.c.})\ . \tag{2}$$

The kinetic energy is given by $E_{\text{kin}}=\langle T\rangle$, where the expectation value is calculated in the ground state of the full Hamiltonian H. The kinetic energy per site $\mathcal{E}_{\text{kin}}$ is then defined as $\lim_{L\to+\infty}E_{\text{kin}}/L$, where L is the number of sites. The plasma frequency provides an estimate of the kinetic energy $\mathcal{E}^0_{\text{kin}}$ calculated in the ground state of T, i.e., without correlations, the integral of the conductivity provides an estimate of $\mathcal{E}_{\text{kin}}$, and the reduction of kinetic energy is defined as the ratio $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}$. The main difficulty is where to stop in performing the integral of the conductivity. This can be a serious problem because, for strongly correlated systems, spectral weight coming from the conduction band can be found at high energy—typically around U—and it is impossible to disentangle this weight from other contributions to the conductivity. In the case of the Bechgaard salts, this is not too serious because the system are essentially quarter filled. In that case, it was shown by Maldague[18] and recently confirmed by Eskes and Oles[19] that the sum rule is almost exhausted by the lower band, and the estimates of the kinetic energy obtained by integrating over the lower band are only accurate to within a few percent.

Performing such an analysis for the Bechgaard salts,

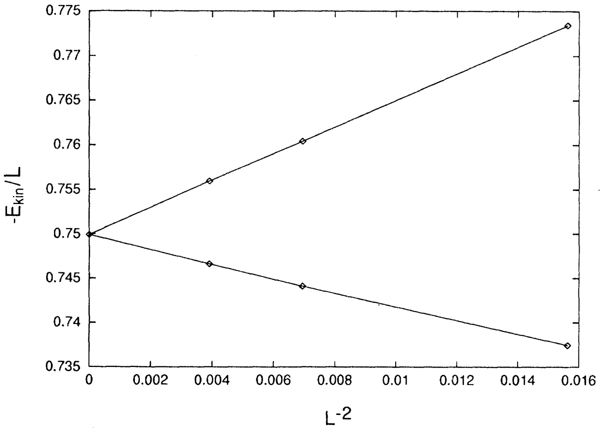


FIG. 1. Finite-size scaling of the kinetic energy for $t_2/t_1=1$, $U/t_1=10$, and $V/t_1=0$. Upper curve, closed shell; lower curve, open shell.

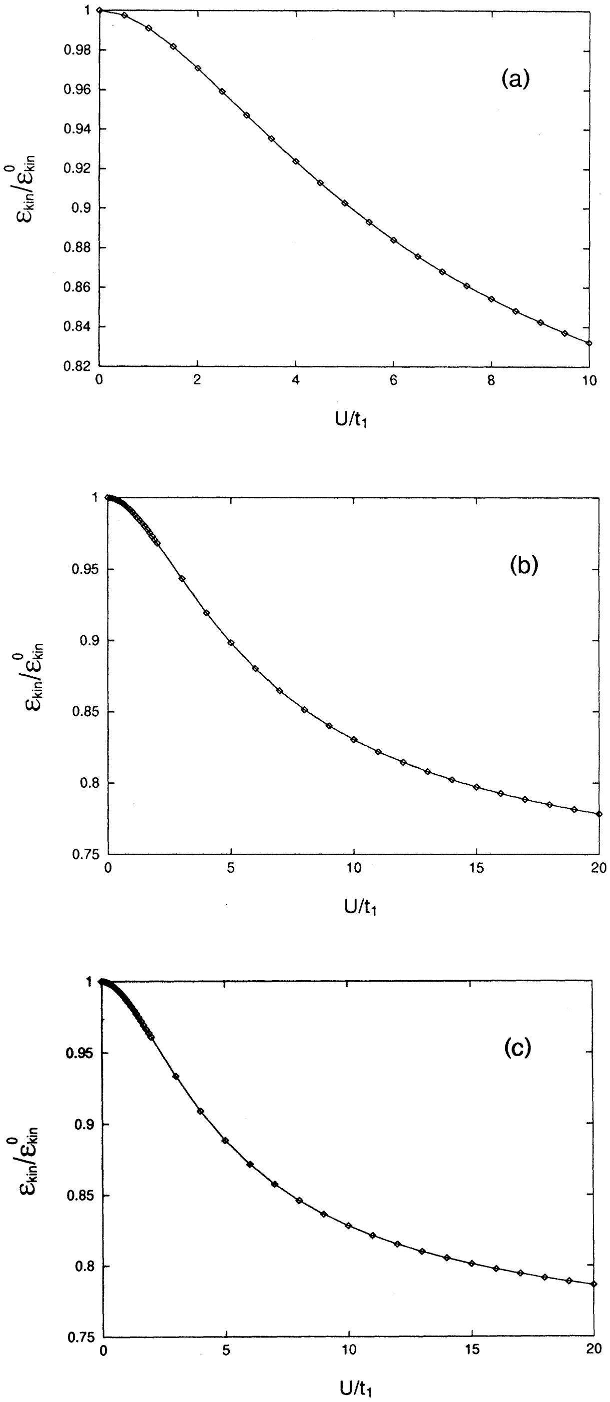


FIG. 2. Kinetic energy as a function of U/t_1 for $V/t_1=0$. (a) $t_2/t_1=1$; (b) $t_2/t_1=0.9$; (c) $t_2/t_1=0.7$.

TABLE I. Reduction of kinetic energy for $U/t_1 \to +\infty$ and $V/t_1=0$.

t_2/t_1	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
$\mathcal{E}_{\rm kin}/\mathcal{E}^0_{\rm kin}$	0.707	0.711	0.720	0.733	0.752	0.777	0.808	0.845	0.889	0.940	1.0

Jacobsen reached the conclusion that $\mathcal{E}_{\rm kin}/\mathcal{E}^0_{\rm kin}$ is about 0.85 for (TMTSF)$_2$ClO$_4$ and 0.73 for (TMTTF)$_2$PF$_6$ (where TMTTF is tetramethyltetrathiafulvalene). Various estimates of the hopping integrals for (TMTTF)$_2$PF$_6$ and (TMTSF)$_2$ClO$_4$ have been proposed on the basis of experimental results and quantum-chemistry calculations. While there is still some uncertainty concerning their absolute value, especially in the case of (TMTTF)$_2$PF$_6$, the ratio t_2/t_1 is believed to be approximately equal to 0.9 for (TMTSF)$_2$ClO$_4$ and 0.7 for (TMTTF)$_2$PF$_6$.[17] So, to extract information about the correlation parameters from Jacobsen's measurements, one just needs accurate estimates of the kinetic energy in the ground state of the Hamiltonian of Eq. (1) as a function of U/t_1 and V/t_1. When Jacobsen published his results nothing of the sort was available, and he could not go beyond a qualitative analysis of the results based on the numerical study of a system of two particles on four sites. Motivated by Jacobsen's results, Baeriswyl, Carmelo, and Luther[20] calculated the kinetic energy of the standard Hubbard model using the Bethe ansatz solution at half filling and the Gutzwiller ansatz away from half filling. Their results confirm the trends, namely, that correlations have to be invoked to explain the reduction of oscillator strength, but they do not allow for a precise interpretation of the experimental results. We are not aware of any further work on that problem.

In this paper, we calculate the kinetic-energy on the basis of numerical results obtained on finite clusters by exact diagonalization. For a given cluster, the expectation value of the kinetic energy is most easily obtained using the Hellmann-Feynman theorem as

$$E_{\rm kin}=t_1\partial_{t_1}E_{\rm G.S.}+t_2\partial_{t_2}E_{\rm G.S.}\ , \qquad (3)$$

where the ground-state $E_{\rm G.S.}\equiv\langle H\rangle$ is evaluated with the Lanczos algorithm. $\mathcal{E}_{\rm kin}$ is then obtained from a finite-size scaling analysis of $E_{\rm kin}/L$. For noninteracting electrons, it is easy to show that the finite-size corrections go as $1/L^2$, where L is the number of sites. This remains true for the total energy per site for Luttinger liquids. So it is quite natural to assume that this is also true for the derivatives of this quantity with respect to the hopping integrals, and thus for the kinetic energy. Our numerical results clearly support this assumption. A typical example is given in Fig. 1, where we have plotted $E_{\rm kin}/L$ as a function of $1/L^2$ for $L=8$, 12, and 16. The two curves have been obtained for different boundary conditions corresponding to closed and open shells, respectively. The scaling law is quite accurately satisfied, and the two boundary conditions give estimates in very good agreement, which lends further support in favor of the assumption that the scaling is in $1/L^2$. In most cases where we have tried both types of boundary conditions, the slope was smaller for the boundary conditions corresponding to open shells, and all the results given in the rest of the paper have been obtained with such boundary conditions. Besides, we have compared the results obtained by using only $L=8$ and 12 with estimates obtained using also the results for $L=16$ for a few cases, and the error was always less than 1%. So, unless one needs a very accurate value of the kinetic energy, it is sufficient to use systems with 8 and 12 sites to perform the $1/L^2$ extrapolation. This has been systematically done in the following.

Let us start with the results obtained in the case $V/t_1=0$ (no repulsion between first neighbors). The ratio $\mathcal{E}_{\rm kin}/\varepsilon^0_{\rm kin}$ is plotted as a function of U/t_1 for three values of t_2/t_1 in Fig. 2 for a quarter-filled system. In all cases it decreases with U,in agreement with the intuitive idea that correlations make the motion more difficult and lead to a reduction of kinetic energy. What is perhaps

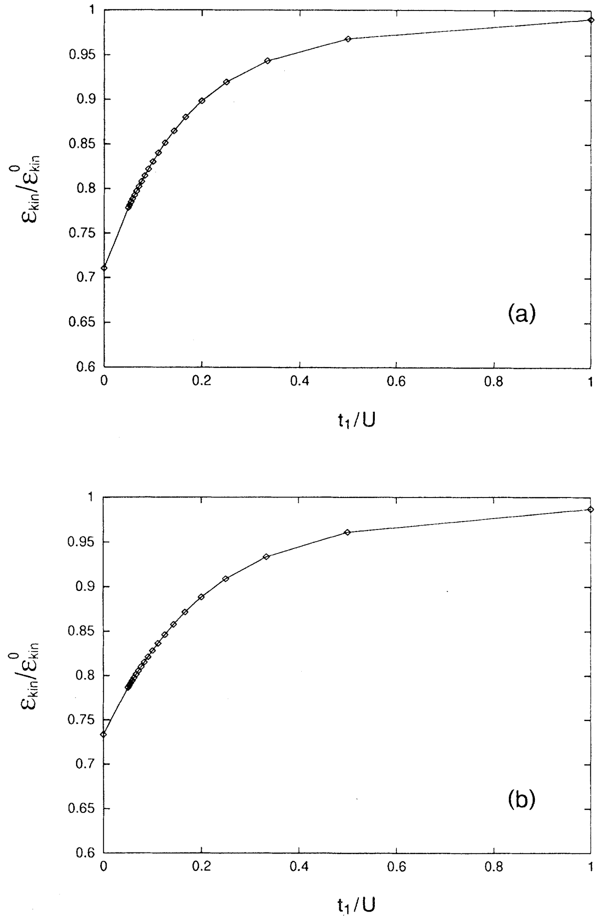
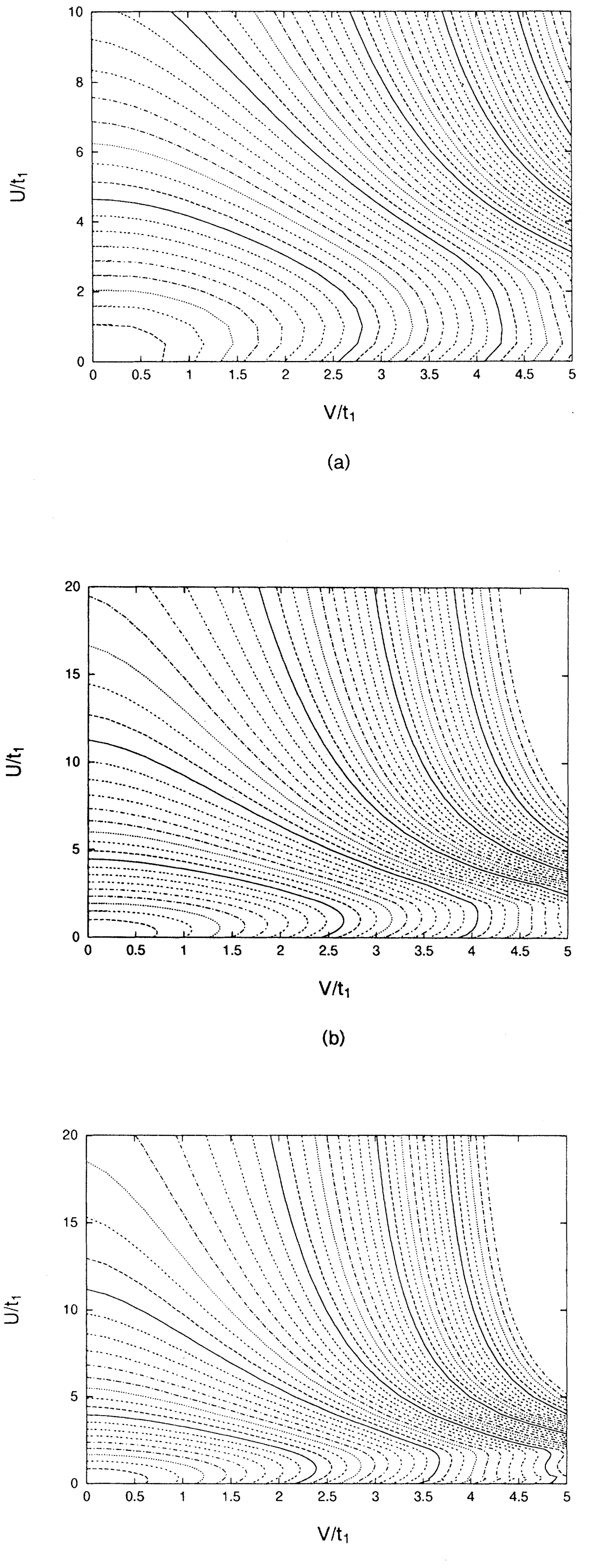


FIG. 3. Large-U behavior of the kinetic energy for $V/t_1=0$. (a) $t_2/t_1=0.9$; (b) $t_2/t_1=0.7$.

more surprising is that, even for very large values of U/t_1, the reduction is not so big. That our results are still valid for large U/t_1 can actually be checked quite easily. The value for $U/t_1 \rightarrow +\infty$ is the same as for spinless fermions at half filling (see Table I), and our results plotted as a function of t_1/U extrapolate nicely toward that limiting value [see Fig. 3]. So, taking for granted that $t_2/t_1=0.7$ for $(TMTTF)_2PF_6$, a reduction of 0.73 is incompatible with on-site repulsion only. This can be considered as an alternative proof to that given in Refs. 10–12 that repulsion on neighboring sites is important in these systems. This conclusion depends of course on the actual value of $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}$ in $(TMTTF)_2PF_6$, and a slightly larger value of this ratio would be compatible with on-site repulsion only, provided the value of U/t is large enough. This would be incompatible however with resistivity and susceptibility measurements.[13,14] So, in spite of the experimental uncertainty about the actual value of $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}$, the fact that a repulsion between nearest neighbors has to be invoked to understand these data seems quite firmly established.

Let us now consider the general case described by Eq. (1). The question we would like to answer is the following: What are the values of U/t_1 and V/t_1 that are compatible with the known values of t_2/t_1 and of $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}$ for $(TMTSF)_2ClO_4$ and $(TMTTF)_2PF_6$? The most convenient thing to do is to plot the curves of constant $\mathcal{E}_{\text{kin}}/\varepsilon^0_{\text{kin}}$ in the $(U/t_1, V/t_1)$ plane for the values of t_2/t_1 of interest. Such plots for quarter-filled systems are given in Fig. 4 for $t_2/t_1=1$, 0.9, and 0.7. The basic features of these curves are again quite natural. The only one that deserves special comment is the re-entrant behavior for large V/t_1 and small U/t_1. Another way of looking at the same effect is to notice that, for a given value of V/t_1, the kinetic energy first increases before it decreases for U/t_1 large enough. This presumably comes from local pairs, which are known to exist and to be very heavy objects in the small-U/t_1, large-V/t_1 limit,[21] and which become lighter when U/t_1 increases.



(a)

(b)

(c)

FIG. 4. Constant kinetic energy plots from $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}=0.99$ (bottom left) to $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}=0.50$ (top right). (a) $t_2/t_1=1$; (b) $t_2/t_1=0.9$; (c) $t_2/t_1=0.7$.

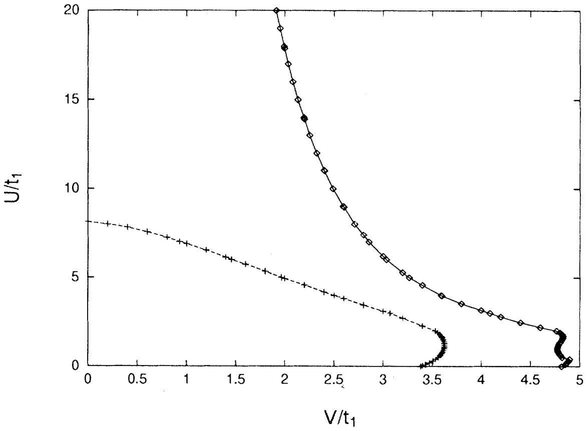


FIG. 5. Comparison of the curves giving the correct reduction of kinetic energy. Crosses, $(TMTSF)_2ClO_4$ $(t_2/t_1=0.9$, $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}=0.85)$; squares, $(TMTTF)_2PF_6$ $(t_2/t_1=0.7$, $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}=0.73)$.

There is now no problem to find parameters that give a reduction of kinetic energy of 0.85 for $(TMTSF)_2ClO_4$ and of 0.73 for $(TMTTF)_2PF_6$. The corresponding curves of possible pairs $(U/t_1, V/t_1)$ are reproduced in Fig. 5. This is not very useful unless we can decide where the actual parameters are located on these curves. This is actually possible on the basis of general arguments coming from quantum chemistry. Unlike the g parameters of the Fermi-gas model, U and V have a simple microscopic meaning: U is the energy needed to put two particles on the same site, and V is the energy needed to put them on neighboring sites. Now, the molecules TMTSF and TMTTF are very similar, the only difference being that the $3p$ orbitals of sulfur in TMTTF are more concentrated than the $4p$ orbitals of selenium in TMTSF, and quantum-chemistry calculations predict that the ratio U(TMTTF)/U(TMTSF) is the range 1.0–1.25. We also know from different sources[16,17] that t_1(TMTTF)/t_1(TMTSF) is in the range 0.7–0.8. So the ratio U/t_1 is at most 80% larger for TMTTF than for TMTSF. But from Fig. 5 we know that this ratio is at most 8 for TMTSF, so it is at most 15 for TMTTF. Looking again at Fig. 5, this means that V/t_1 is at least equal to 2 for TMTTF. Now, on the basis of quantum chemistry, V is expected to be roughly the same for both types of compounds, which implies that V/t_1 is at least 1.5 for TMTSF. But, according to Fig. 5, this means that U/t_1 cannot be larger than 6 in that compound. This again puts a constraint on U/t_1 in TMTTF, and so on. Finally, if we use the constraints given by quantum chemistry, we end up with the parameters given in Table II. These values are just estimates, and one should put error bars on them. The main source of uncertainty probably comes from the experimental results. In particular, the saturation value of the integral of the loss function generally gives numbers in good agreement with the plasma frequency deduced from a Drude fit of the reflectivity spectrum. However, in the present case, the values obtained from the loss function are slightly larger,[16] leading to smaller values of $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}$ [0.67 for $(TMTTF)_2PF_6$, 0.80 for $(TMTSF)_2ClO_4$]. Another source of uncertainty lies in the values used for the ratios t_2/t_1, but the dependence of $\mathcal{E}_{\text{kin}}/\mathcal{E}^0_{\text{kin}}$ on this parameter is smooth (see Fig. 4). Finally, the location on the curves is only approximate because the arguments derived from quantum chemistry are only qualitative or, at best, semiquantitative.

Anther legitimate question about the parameters of Table II is whether they are consistent with the spin Peierls transition that takes place in $(TMTTF)_2PF_6$ at low temperature. As pointed out by Ung, Mazumdar, and Toussaint,[22] this is incompatible with a $4k_F$ charge-density wave (CDW), a natural instability of the extended Hubbard model at quarter filling. For the nondimerized version of the model of Eq. (1), and for U infinite, it was shown by Ovchinnikov[23] that a metal-insulator transition to this type of order takes place at $V_c = 2t$. The generalization of that result to finite values of U has been performed by Mila and Zotos,[5] and for $U = 7t$, the transition is at $V_c = 2.6t$, a value smaller than our estimate of V. This does not imply, however, that the ground state of Eq. (1) with the parameters of $(TMTTF)_2PF_6$ is a $4k_F$ CDW because of dimerization. In fact, when $t_2 \neq t_1$, the system is effectively half filled, and the ground state of Eq. (1) is already insulating for infinitesimal values of the repulsion parameters, the instability corresponding to a $2k_F$ spin-density wave as in the case of the half-filled Hubbard model. In the weak-coupling case, electrons sit on dimers and there is no CDW. However, it is likely that a $4k_F$ CDW will appear when V is large enough. Whether the critical value for $t_2/t_1 = 0.7$ and $U/t_1 = 7$ is larger than our estimate is unknown at the moment, and more work is needed to decide whether a value of V/t_1 slightly smaller than 2.8 is appropriate for $(TMTTF)_2PF_6$.

TABLE II. Estimates of the basic parameters t_2/t_1, U/t_1 and V/t_1.

Compound	t_2/t_1	U/t_1	V/t_1
$(TMTSF)_2ClO_4$	0.9	5.0	2.0
$(TMTTF)_2PF_6$	0.7	7.0	2.8

In spite of these sources of uncertainty, two points seem to be clearly established. First, the reduction of oscillator strength reported for TMTTF implies that the repulsion between first neighbors is not negligible. Second, U/t_1 is larger in TMTTF than in TMTSF. If that were not the case, V would have to be much larger in TMTTF than in TMTSF, which can be rejected on the basis of quantum chemistry. This last conclusion should be contrasted with the interpretation of the temperature dependence of the susceptibility of Wzietek *et al.*,[4] which led them to conclude that U/t_1 is about the same in both series. Recent calculations of the susceptibility[13] suggest, however, that the temperature dependence is actually consistent with our present conclusion that U/t_1 is larger in TMTTF than in TMTSF.

In conclusion, the reduction of oscillator strength reported for the Bechgaard salts by Jacobsen leads to precise and useful information on the size of the correlation parameters in these compounds. The main difference with respect to the microscopic models used so far in the interpretation of various experimental results (susceptibility, minimum of resistivity, etc.) lies in the presence of a relatively large value of the repulsion between nearest neighbors. Whether the estimates proposed in the present paper are consistent with the other experimental data remains to be seen.

I am very grateful to Jean-Paul Pouget, who encouraged me to look at the optical data of Jacobsen.

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