Deducing correlation parameters from optical conductivity in the Bechgaard salts

Frédéric Mila

Laboratoire de Physique Quantique, Université Paul Sabatier
31062 Toulouse (France)

Abstract

Numerical calculations of the kinetic energy of various extensions of the one-dimensional Hubbard model including dimerization and repulsion between nearest neighbours are reported. Using the sum rule that relates the kinetic energy to the integral of the optical conductivity, one can determine 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 TMTSF and TMTTF series.

PACS Nos: 71.10.+x, 75.10.-b, 71.30.+h, 72.15.Nj
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, which 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 model. 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

\[ H = -t_1 \sum_{\text{even},\sigma} (c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}) - t_2 \sum_{\text{odd},\sigma} (c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1} \]  

(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 $U$; iv) a repulsion between nearest neighbours $V$. 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 $K_\rho$, can take any value from 0 to $+\infty$. However, for the quarter-filled, extended Hubbard model, which is the appropriate description of (TMTSF)$_2$PF$_6$ as far as quantum chemistry is concerned, it was possible to show that $K_\rho$ cannot be smaller than $1/4$. It is actually possible to calculate $K_\rho$ as a function of the correlation parameters with a reasonable accuracy using standard numerical techniques \[6,7,5\], 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 to answer 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]. An analysis of the charge-transfer spectra of many charge-transfer salts by Mazumdar and Dixit led them to the general conclusion that \( U \) is about 1.5 eV and \( V \) is 0.5 eV [10]. This analysis is certainly relevant, but in view of the very numerous experimental results that are now available for the Bechgaard salts, an analysis more specific to these compounds, including in particular the effect of dimerization, should be performed. The interpretation of the temperature dependence of the susceptibility [11] and of the resistivity [12] 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. Finally, quantum chemistry calculations of the correlation parameters have also been performed for these systems [13], but the reliability of the calculation 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 details by Jacobsen [14]. 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

\[
T = -t_1 \sum_{\text{even},\sigma} (c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.}) - t_2 \sum_{\text{odd},\sigma} (c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.})
\]  

(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 $E_{\text{kin}}$ 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 $E_{\text{kin}}^0$ calculated in the ground-state of $T$, i.e. without correlations, the integral of the conductivity provides an estimate of $E_{\text{kin}}$, and the reduction of kinetic energy is defined as the ratio $E_{\text{kin}}/E_{\text{kin}}^0$. 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 systems are essentially quarter-filled. In that case, it was shown by Maldague [16], and recently confirmed by Eskes and Oles [17], 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 only are accurate to within a few percents.

Performing such an analysis for the Bechgaard salts, Jacobsen reached the conclusion that $E_{\text{kin}}/E_{\text{kin}}^0$ is about 0.85 for $(\text{TMTSF})_2\text{ClO}_4$ and 0.73 for $(\text{TMTTF})_2\text{PF}_6$. Various estimates of the hopping integrals for $(\text{TMTTF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{ClO}_4$ 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 $(\text{TMTTF})_2\text{PF}_6$, the ratio $t_2/t_1$ is believed to be approximately equal to 0.9 for $(\text{TMTSF})_2\text{ClO}_4$ and 0.7 for $(\text{TMTTF})_2\text{PF}_6$ [15]. So to extract information about the correlation parameters from Jacobsen 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 2 particles on 4 sites. Motivated by Jacobsen’s results, Baeriswyl et al [18] 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 finite clusters 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

\[ E_{\text{kin}} = t_1 \partial_{t_1} E_{G.S.} + t_2 \partial_{t_2} E_{G.S.} \]

where the ground-state energy \( E_{G.S.} \equiv \langle H \rangle \) is evaluated with Lanczos algorithm. \( E_{\text{kin}} \) is then obtained from a finite-size scaling analysis of \( E_{\text{kin}}/L \). For non-interacting 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 \( E_{\text{kin}}/L \) 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 favour 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 \( L = 12 \) 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
neighbours). The ratio $E_{\text{kin}}/E_{\text{kin}}^0$ 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 the 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 maybe 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 $U/t_1 \to +\infty$ 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 $t_2/t_1 = .7$ for (TMTTF)$_2$PF$_6$, a reduction of 0.73 is incompatible with on-site repulsion only. This can be considered as a proof that repulsion on neighbouring sites is important in these systems.

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 $E_{\text{kin}}/E_{\text{kin}}^0$ for (TMTSF)$_2$ClO$_4$ and (TMTTF)$_2$PF$_6$? The most convenient thing to do is to plot the curves of constant $E_{\text{kin}}/E_{\text{kin}}^0$ 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 a special comment is the reentrant behaviour 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 $[19]$, and which become lighter when $U/t_1$ increases.

There is now no problem to find parameters that give a reduction of kinetic energy of 0.85 for (TMTSF)$_2$ClO$_4$ and of 0.73 for (TMTTF)$_2$PF$_6$. 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 neighbouring 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 in the range 1.0 - 1.25. We also know from different sources \cite{14,15} 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 2. 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 \cite{14}, leading to smaller values of $\epsilon_{\text{kin}}/\epsilon_{\text{kin}}^0$ (0.67 for (TMTTF)$_2$PF$_6$, 0.80 for (TMTSF)$_2$ClO$_4$). Another source of uncertainty lies in the values used for the ratios $t_2/t_1$, but the dependence of $\epsilon_{\text{kin}}/\epsilon_{\text{kin}}^0$ on this parameter is smooth (see Fig. 4). Finally, the location on the curves is only approximative because the arguments derived from quantum chemistry are only qualitative or, at best, semi-quantitative.

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 neighbours is not negligible. Second, $U/t_1$ is larger in TMTTF than in TMTSF. If that was 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 lead them to conclude that $U/t_1$ is about the same in both series. Recent calculations of the susceptibility [11] 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,...) lies in the presence of a relatively large value of the repulsion between nearest neighbours. 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.
REFERENCES

[1] J. Solyom, Adv. Phys. 28, 201 (1979).

[2] V. Emery, in Highly Conducting One-Dimensional Solids, edited by J. T. Devrese et al (Plenum, New York, 1979), p. 327.

[3] C. Bourbonnais, J. Phys. (Paris) I 3, 143 (1993).

[4] P. Wzietek, F. Creuzet, C. Bourbonnais, D. Jérôme, K. Bechgaard and P. Batail, J. Phys. (Paris) I 3, 171 (1993).

[5] F. Mila and X. Zotos, Europhys. Lett. 24, 133 (1993).

[6] H. J. Schulz, Phys. Rev. Lett. 64, 2831 (1990); Int. J. Mod. Phys. B 5, 57 (1991).

[7] M. Ogata et al, Phys. Rev. Lett. 66, 2388 (1991).

[8] G. A. Sawatzky in High Temperature Superconductivity, eds. D. P. Tunstall and W. Barford, published by Adam Hilger, Bristol (1991).

[9] B. Dardel et al, Europhys. Lett. 24, 687 (1993).

[10] S. Mazumdar and S. N. Dixit, Phys. Rev. B 34, 3683 (1986).

[11] F. Mila and K. Penc Phys. Rev. B 51, xxxx (1995).

[12] K. Penc and F. Mila, Phys. Rev. B 50, 11429 (1994).

[13] A. Fritsch and L. Ducasse, J. Physique I 1, 855 (1991).

[14] See C. S. Jacobsen, J. Phys. C 19, 5643 (1986), and references therein.

[15] L. Ducasse et al, J. Phys. C 19, 3805 (1986).

[16] P. F. Maldague, Phys. Rev. B 16, 2437 (1977).

[17] H. Eskes and A. M. Oles, Phys. Rev. Lett. 73, 732 (1994).

[18] D. Baeriswyl, J. Carmelo, A. Luther, Phys. Rev. B 33, 7247 (1986).
[19] K. Penc and F. Mila, Phys. Rev. B 49, 9670 (1994).
FIGURES

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) $t_2/t_1 = 0.7$

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

FIG. 4. Constant kinetic energy plots from $E_{\text{kin}}/E_{\text{kin}}^0 = 0.99$ (bottom left) to $E_{\text{kin}}/E_{\text{kin}}^0 = 0.50$ (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)$_2$ClO$_4$ ($t_2/t_1 = 0.9$, $E_{\text{kin}}/E_{\text{kin}}^0 = 0.85$); Squares: (TMTTF)$_2$PF$_6$ ($t_2/t_1 = 0.7$, $E_{\text{kin}}/E_{\text{kin}}^0 = 0.73$)
### 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 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $\varepsilon_{\text{kin}}/\varepsilon_{\text{kin}}^0$ | 0.707 | 0.711 | 0.720 | 0.733 | 0.752 | 0.777 | 0.808 | 0.845 | 0.889 | 0.940 | 1.0 |

### TABLE II.

| Compound          | $t_2/t_1$ | $U/t_1$ | $V/t_1$ |
|--------------------|-----------|---------|---------|
| (TMTSF)$_2$ClO$_4$ | 0.9       | 5.0     | 2.0     |
| (TMTTF)$_2$PF$_6$  | 0.7       | 7.0     | 2.8     |