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A valence-bond approach to the electronic localization in 3/4 filled systems

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Résumé. — Nous avons utilisé la méthode Diagrammatic Valence Bond (DVB) pour analyser les propriétés électroniques de clusters monodimensionnels (1D), dont les solutions exactes ont été obtenues au moyen d'un hamiltonien du type Hubbard (étendu). Un essai de calcul par des méthodes SCF semi-empiriques des paramètres de corrélation intrasite U , intersites V (premier voisin) et V_2 (second voisin) a été mené et les valeurs obtenues ont été comparées aux données tirées de l'expérience. Une classification possible des sels M_2X (M : molécule organique, X^- anion), découle des structures cristallographiques et des mesures de conductivité: les composés d'un premier groupe ont une structure dimérisée et un comportement semi-conducteur à 300 K tandis que ceux d'un deuxième groupe s'empilent de manière régulière ou quasi-régulière, sont métalliques à 300 K et leur localisation électronique est modifiée entre 100-200 K. Dans le premier cas, les calculs DVB conduisent à une description de l'état fondamental localisé en termes d'une forte onde de densité de liaison. L'effet du terme entre second voisins V_2 demeure faible bien qu'il puisse modifier les corrélations de charge à longue distance ainsi que le comportement magnétique. Les susceptibilités magnétiques χ calculées sur un cycle de 8 sites sont en bon accord avec l'expérience à 300 K et c'est pour V_2 voisin de $V/2$ que la dépendance de χ avec la température est reproduite de façon la plus satisfaisante. Dans le second cas, des calculs *ab initio* modèles tendent à montrer que la dimérisation électronique pourrait être modifiée par le potentiel des anions. Une modification des intégrales de transfert intra- et inter-dimères rend compte qualitativement de la variation de la résistivité en fonction de la température. Les résultats DVB sur des anneaux de 12 sites montrent que cette différence entraîne une nette augmentation de la localisation lorsque les corrélations sont prises en compte, en comparaison du cas régulier observé à haute température.

Abstract. — The Diagrammatic Valence Bond (DVB) method has been used to investigate the electronic properties of one-dimensionnal (1D) clusters, for which exact solutions were obtained within the framework of an (extended) Hubbard hamiltonian. The correlation parameters, U , V and V_2 are tentatively calculated by means of SCF semi-empirical methods and compared to the data issued from experiment. From the crystal structures and the conductivity data, the M_2X salts

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(M : organic molecule, X^- anion) may be classified in two groups : on one hand, the compounds with a dimerized structure which are semi-conductor at 300 K and, on another hand, the systems with a regular or quasi-regular 1D stacking which are metallic at 300 K and which exhibit a change in the electronic localization around 100-200 K. For the first class, the DVB calculations lead to a strong bond order wave picture for the localized ground state. The effect of the next nearest neighbor V_2 is small although it may affect long distance charge correlations and the magnetic behavior. The magnetic susceptibility χ calculations on a 8 sites ring lead to a good agreement with 300 K experimental data and the temperature dependence of χ is best reproduced with V_2 close to $V/2$. For the second class, it is shown that, the electronic dimerization might be modified by the anion potential, as indicated by model *ab initio* calculations. The behavior of the resistivity as a function of temperature is qualitatively described by a change in the intra and interdimer transfer integrals. The DVB results on 12 sites rings indicate that this difference leads to an enhanced localization when the correlations are turned on compared to the high temperature regular system.

Introduction.

Since the discovery of organic superconductivity in the Bechgaard salts $TMTSF_2X$ ($TMTSF$ = tetramethyltetraselenafulvalene ; X^- : anion) [1], a large amount of experimental and theoretical work has been devoted to this family of organic conductors [2]. However, the small number of organic salts exhibiting this property, the fact that the maximum critical temperature T_c does not exceed 11 K, and the quite noteworthy discovery of the high T_c oxides, have cooled the initial enthusiasm. But, contrary to the $TMTSF$ and $BEDTTTF$ ($BEDTTTF$ = bisethylenedithio-tetrathiafulvalene) salts, the low T superconductivity appears to be quite « common » in the so-called κ salts [3], which show a well defined two-dimensional packing and some properties recalling the high T_c oxides. Moreover, for the first time, the superconductivity has been quite recently discovered in some salts based on molecules containing oxygen [4]. These exciting results have revived the interest of the scientific community for these materials.

The dimensionality of these systems governs for a large part their electronic properties. Concerning the superconductivity, it is important to note that the two-dimensional (2D) character increases in the series : $TMTSF_2X$ [6], β [5] and κ [3, 7] phases of the M_2X salts (M : organic molecule). In the last two cases, the low temperature metallic regime competes only with the superconducting state. However, an antiferromagnetic state might coexist with the superconducting state although no clear experimental evidence supports this assumption [3]. The superconductivity and its origin (BCS or not-BCS mechanism, microscopic nature of the screening of the electron-electron repulsion) is not the single property to which has been devoted a large literature in the past few years. The phase diagram of the 1D or quasi-1D salts, represented by the Bechgaard salts $TMTSF_2X$ [6] and their sulfur analogs $TMTTF_2X$ ($TMTTF$ = tetramethyltetrathiafulvalene) [8], is more complicated : insulator (antiferromagnetic, AF ; non magnetic, spin-Peierls, SP), metal or superconducting states have been observed. Moreover, the ordering of non-centrosymmetrical anions may modify the electronic distributions [9]. For example, a physical constraint makes a SP state to evolve into an AF one (pressure in the case of $TMTTF_2PF_6$ [10] ; temperature for $TMDTDSF_2PF_6$ [11]).

The difficulty in a theoretical analysis of these salts lies on their complex microscopic structure (one, two or more large molecules per unit cell, partial filling of the one-electron band resulting from the transfer between the anion and the cation, ...) and on the possible interplay between various terms (kinetic part of the hamiltonian, Coulomb interaction, electron-phonon coupling, disorder of the anion, ..). Therefore, it is a challenge to single out

the relevant parameters controlling the behavior of these salts, as it is equally difficult to provide a very accurate calculation of their electronic structure. An *ab initio* determination of the energies and wavefunctions of the ground and excited states of the organic conductors is virtually untractable. Moreover, a unified theoretical description, at a more empirical level, of the behavior of every organic salt is even still lacking.

Among the factors which might influence the physical properties, the electronic correlations appear to be certainly a leading term (see for example [2]). It is noteworthy that the one-electron approach might lead to wrong results for such properties as the symmetries of the lower excited states in longer polyenes [12], the negative spin densities in radicals [13] or transpolyacetylene [14], excitations energies in organic ion-radicals or transition metal complexes [15]. Another example of the one-electron model limitation is given by the band structure results on the M_2X salts. This approach leads to a metallic behavior for every kind of salt based on the unit formula $M_2^+ X^-$, although the conductivity measurements show that the TMTTF salts undergo a progressive localization [8], without any structural distortion, and $DIMET_2SbF_6$ ($DIMET$ = dimethylethylenedithio-tetrathiafulvalene) is already localized at room temperature [16].

The effects of the electron-electron correlations have been investigated using different theoretical models. The *g*-ology models [17, 18], derived in the weak coupling limit where the correlation terms are considered as a perturbation of the one-electron formalism, have been applied to the study of the phase transitions, the localization processes and the NMR relaxation times. In the opposite limit of strong coupling, the Hubbard hamiltonian is equivalent to a Heisenberg spin model. This model is currently used to fit the variation of the magnetic susceptibility of localized systems with the temperature, as done for example in reference [19]. Besides these approaches emphasizing the role of the infinite solid and thus requiring perturbative or group renormalization techniques, more local methods have been developed in an attempt to solve the Hubbard or extended Hubbard models for clusters of finite size. The difficulty of these local approaches lies mainly in the extrapolation to the solid, which represents a difficult task. The critical properties of spin-1/2 chains have been investigated, in the limit of infinite U , by a quantum Monte Carlo model [20], and by a combination of field theory techniques and numerical solution on finite chains [21]. Recently, the variational Diagrammatic Valence Bond (DVB) method [22] has been derived and applied to find correlated states in solid-state and quantum-chemical models. The (severe) restriction lies in the size of the complete basis set which requires extrapolation procedures if one is analyzing the solid state physics, but the DVB results are *exact* and this approach gives a very convenient representation of the wavefunction. The applications of the DVB method have been made in various fields as the study of the polyenes [22], non-linear optic results [23], electronic and magnetic properties of the complete family of segregated-stack charge transfer salts [24], ..

This paper first recalls the characteristics of the DVB formalism. Then, the values of the one- and two-electron terms taking place in an extended Hubbard model are discussed : the data derived from the experiments are compared to the values issued from the band structure approach (transfer integrals), or derived from semi-empirical quantum calculations on monomers or dimers. Finally, the analysis of the organic salts which present a localization, either at room temperature or at a temperature, T_p , typically between 100 K and 200 K, is given from the results obtained in the case of 1D clusters.

Method.

The DVB formalism applies to model systems with one orbital per site. A complete set of electronic configurations of N_e electrons on N sites ($N_e = 3 N/2$ for this 3/4 filled case) is built

up upon the site orbitals following the Rumer procedure which generates S^2 and S_z eigenfunctions [25]. A valence bond electronic configuration is thus defined from the occupancy of every site together with the spin-coupling of the electrons. The use of only one orbital per site allows us to draw simple diagrams to symbolize each configuration. Crosses and dots stand for doubly occupied and empty sites respectively. Two singly occupied sites are connected by a line in the case of a singlet spin coupling between the corresponding electrons.

In the second quantized formalism, each VB diagram is easily obtained by applying to the empty state the proper combination of the creation operators associated with the orbital basis [22]. As the VB basis is complete, the method is computationally limited by the size of the cluster : the larger studied system is built of 18 electrons on 12 sites (size of the singlet space is 15 730). In this case, the complete diagonalization of the matrix is not feasible and an algorithm of coordinate relaxation has been used to determine the lowest eigenvalues and eigenvectors [26].

It is important to note that, within this method, the site orbitals are orthogonal. This point is fully justified by the value of the overlap between first neighbor sites in the organic salts under study. This represents an intermolecular overlap which is only around 10^{-2} , in the intradimer case, and actually negligible.

We do not include in the calculation any electron-phonon or electron-molecular vibration coupling term. Some models emphasize the importance of such terms : analysis of the Raman and infrared spectra [27], possible mechanism of the organic superconductivity based on the coupling of the electrons with the molecular vibration [28]. On the contrary, the leading role of the correlation, in particular in the organic and high T_c oxides superconductivity, has been well argued by Mazumdar and Ramasesha [29] and we follow this proposal in this study of the localization.

The electronic Hamiltonian is a sum of a one and a two electron parts, H_1 and H_2 :

$$H = H_1 + H_2 = H_t + H_s + H_2 \quad (1)$$

where H_1 includes the kinetic effects in H_t as well as the interactions between the electrons and the crystal (organic core and anions) in H_s :

$$H_t = -\sqrt{2} \sum_n t_{n,n+1} ((n, n+1)^+ + (n+1, n)) \quad (2)$$

$$H_s = \sum_i \sum_{\sigma=\alpha,\beta}^N t_{ii} a_{i\sigma}^+ a_{i\sigma} \quad (3)$$

Expression (2) assumes that the calculation only involves the nearest-neighbor transfer integrals $t_{n,n+1}$. The t_{ii} integrals include the components of the crystal potential so that it is convenient to write :

$$t_{ii} = \alpha_i + \sum_{p \neq i}^N V_{pi} z_p + W_{\text{ext}} \quad (4)$$

where α_i is the site energy, V_{pi} is the interaction potential between the electron on the site i and the core of the site p , z_p is the effective charge of site p and W_{ext} is the external potential (anions in the organic conductors).

We have retained the extended Hubbard method to evaluate the correlation terms. Within this formalism, H_2 may be written as a sum of two terms H_U and H_V .

$$H_U = \frac{U}{2} \sum_{i=1}^N n_i (n_i - 1) \quad (5)$$

$$H_V = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N V_{ij} n_i n_j \quad (6)$$

where n_i is the number of electrons on site i . The evaluation of H_V distinguishes between the Hubbard ($H_V = 0$), extended Hubbard (the H_V values are given *a priori*), and Pariser-Parr-Pople (P.P.P.) [30] (the H_V values are calculated) models. The neglect of the tri- and tetracentric integrals in these formalisms results from the zero-differential overlap (ZDO) approximation. However, it may be noted that this approximation is well adapted to the study of polyenes, where the calculated overlap between two nearest neighbor $2p_z$ atomic orbitals is indeed large. On the contrary, in the organic conductors, as noted above, the overlap between two molecular orbitals is rather small compared to the transfer integral. Thus, there is no real need to invoke the ZDO approximation. In particular, this model might include the three and four center integrals without lack of consistency.

The wavefunctions $|\Psi\rangle$ are expanded on the non orthogonal VB diagrams $|k\rangle$:

$$|\Psi\rangle = \sum_k c_k |k\rangle \quad \text{represented by the vector } C. \quad (7)$$

Using the completeness of the VB basis, a convenient matrix representation h of the hamiltonian H is obtained from :

$$H|k\rangle = \sum_j h_{jk} |j\rangle. \quad (8)$$

This method does not require the evaluation of the overlap matrix and leads to the secular problem :

$$hC = EC. \quad (9)$$

Note : Although this diagonalization procedure does not require the overlap matrix, the wavefunction is analyzed through the calculation of the mean values of some operators which generally involve the overlaps. For large systems, this will represent the time consuming part of the calculation (see below).

Within the matrix representation of the hamiltonian (8), the H_s , H_U and H_V components, which do not modify the site occupation, are diagonal, while H_t is extradiagonal. In particular, if the sites are strictly equivalent, H_s acting on a VB diagram $|k\rangle$ gives :

$$H_s |k\rangle = N_e \cdot t_{ii} |k\rangle$$

and this term may be easily omitted in the matrix. If the sites have different neighborings, different $|k\rangle$ will lead to a different interaction with the lattice : only the site energy will give the same contribution $N_e \cdot \alpha_i$ for every $|k\rangle$, which is taken as the reference energy.

Model.

In the quasi 1D salts, the interchain interactions may act through the transfer integral or the electrostatic potential. The calculated interchain transfer integrals are around an order of magnitude smaller than the intrachain ones and may be conveniently neglected [6]. Concerning the interchain electrostatic terms, a decisive conclusion is not simple to establish, because the exact anisotropy of the potential is difficult to assert. For example, if one

considers the situation of two interacting chains represented in figure 1, the more favorable situation is intuitively described by the diagram *a*, which corresponds to a minimization of the interaction between the charges on each chain. But the evaluation of the terms V_{ij} in equation (6) is not easy, as shown below, and the importance of such interactions may not be ruled out. However, an « effective » 1D approach appears to be sufficient to account for the progressive localization which affects primarily the conductivity measured along the stacking axis.

Fig. 1. — Two VB diagrams built on 2 chains : diagram (b) is deduced from (a) by shifting the charges of the sites on one chain.

Cyclic boundary conditions are assumed in our calculations to ensure that the sites are all equivalent : the organic cores and anion potentials give the same contribution to every diagram and are omitted. As in the usual band calculation [2, 31, 32], each molecule is replaced by its highest occupied molecular orbital (HOMO) providing 3 conducting electrons per two sites (dimer). Note that this HOMO is not explicitly given within the DVB formalism. The evaluation of each multiplicity of the 12 electrons on 8 sites system is used for the magnetic susceptibility calculation and the singlet ground state of the 18 electrons on 12 sites cluster allows a better analysis of the electron distribution.

To discuss the possible implications of the chain dimerization on the electronic properties, two transfer integrals, t_{S1} and t_{S2} , sketched in figure 2, have been used. The S1 and S2 notation is also retained for the first neighbors V_{ij} interactions. The next nearest neighbor V_{ij} is denoted V_2 . As a convention, the dimer represents the pair of sites leading to the largest transfer integral t_{S1} .

Fig. 2. — Intradimer (S1) and interdimer (S2) integrals (a is the cell parameter).

Within the VB picture, the local description of the electronic localization is straightforward and may be related to the existence of particular areas where the number of charge carriers is decreasing. It is of course not possible to draw any conclusion on the existence of a gap in the energy spectrum of the infinite ring, but the fully correlated DVB wavefunction gives some insight on the effect of the correlations on the electrons in real space. The VB method, for which the site orbitals are not explicit, does not allow us to calculate any point property like the electron density. Nevertheless, the stabilization effect of the charge delocalization through distinct intermolecular spacings may be quantitatively calculated from the expectation value of the transfer operator on the ground state. Using expression (2) for H_t , one gets :

$$\langle \Psi | H_t | \Psi \rangle = -\sqrt{2} \sum_n^N t_{n,n+1} \langle \Psi | (n, n+1)^+ + (n+1, n) | \Psi \rangle. \quad (10)$$

The periodic conditions impose that the ring contains only intra, S1, and inter-dimer, S2, bonds to which correspond two bond orders, p_{S1} et p_{S2} .

$$2 \cdot p_{S1} = \sqrt{2} \langle \Psi | (2n-1, 2n)^+ + (2n, 2n-1) | \Psi \rangle \quad (11)$$

$$2 \cdot p_{S2} = \sqrt{2} \langle \Psi | (2n, 2n+1)^+ + (2n+1, 2n) | \Psi \rangle \quad (12)$$

so that :

$$\langle \Psi | H_t | \Psi \rangle = -\frac{N}{2} (2 \cdot p_{S1} t_{S1} + 2 \cdot p_{S2} t_{S2}) = -\frac{N}{2} (E_{S1} + E_{S2}). \quad (13)$$

The energy E_{S1} (E_{S2}) of the S1 (S2) bond gives the contribution of this bond to the total energy : it is expressed as a product of the monoelectronic transfer term multiplied by the bond order which includes the correlation effects of the exact DVB wavefunction. The following example deals with the Mott localization in a 4 sites/4 electron ring : the transfer term competes with the on-site correlation term U . The variation of the energy of a bond as a function of U is given in figure 3. This shows that very large U values are required to observe a noticeable effect : a decrease of $E(U=0)$ by a factor of 2 is only obtained for $U = 10$ eV.

Fig. 3.— Energy of a bond in a 4 electrons/4 sites ring as a function of U ($t = 1$ eV).

The analysis of the charge distribution is made through the correlation functions C_{pq}^{ij} which give the probabilities to find p electrons on site i and q electrons on site j . The charge distribution is evaluated from the contribution of H_V to the total energy, which is, for two sites i and j :

$$V_{ij} \langle \Psi | n_i n_j | \Psi \rangle,$$

so that the relation involving C_{pq}^{ij} is :

$$\langle \Psi | n_i n_j | \Psi \rangle = \sum_{p,q} p \cdot q \langle \Psi_{pq}^{ij} | \Psi_{pq}^{ij} \rangle = \sum_{p,q} p \cdot q \cdot C_{pq}^{ij} \quad (14)$$

where $|\Psi_{pq}^{ij}\rangle$ is the $|\Psi\rangle$ component collecting the diagrams in which there are p and q electrons on i and j respectively. We will discuss the correlation functions $C_{pq}^{i, i+1}$ between neighboring sites i and $i+1$, and the correlation functions $C_{pq}^{1, 1+n}$ between sites 1 and $1+n$. Using the boundary conditions, the intradimer (S1) distribution corresponds to

$C_{pq}^{1,2}$, while the interdimer one (S2) corresponds to $C_{pq}^{1,N}$. These functions are a very useful tool to analyze the wavefunction.

In the case of the 8 membered ring, the complete set of correlated states was obtained, allowing us to calculate the paramagnetic susceptibility of the π electrons. For each spin multiplicity, the partition function Z_S for the temperature T :

$$Z_S = \sum_i (2S + 1) \exp\left(-\frac{E}{kT}\right) \quad (15)$$

leads to the susceptibility per site:

$$\chi = g^2 \mu_B^2 \frac{\sum S(S+1) Z_S}{3 kTN \sum S Z_S} \quad (16)$$

where N is the number of sites, μ_B is the Bohr magneton. The g factor is taken as a temperature independent constant ($g = 2.0023$), in agreement with the experimental data.

Electronic parameters.

The method requires the one- and two-electron terms which involve the molecular orbitals of the organic cation. These parameters may be obtained from the modelling experiments, may be calculated by independent approaches, or evaluated through simple theoretical approximations (this is for example realized in the P.P.P. approach in order to calculate the two-electron repulsion terms).

It is possible, by simple models, to deduce the transfer integrals from infrared data in the plasmon range or thermoelectric power [33]. The results are roughly coherent and lead to intrachain transfer integrals between 150 and 200 meV for sulfur based salts and 250 to 300 meV for selenium based salts. The U and V values have been estimated from IR charge transfer spectra [33, 34]. The U values range from 1.2 to 1.5 eV while V (first neighbor) is around 0.4 eV. In a recent study of the reflectance spectra of BEDTTTF salts, Tajima *et al.* obtained: $U^* = 0.7$ eV (effective $U = U - V$) [35].

Theoretically, it has been proposed by Mazumdar and Soos [36] that the general tendency is $U > 2V > 4t$, in a 1D approach of the organic compounds. This is in rough agreement with the order deduced from the experiment and the regime might be qualified of intermediate strong coupling.

The calculation of the transfer integrals is feasible through band structure calculations. Quite currently, these band structures [31, 32] have been calculated within the tight binding approximation with the help of the extended Hückel Hamiltonian (EHT) [37]. Beyond this very simple approach, only two attempts have been made to obtain the self consistent field band structures [38, 39]. These two calculations, based on the same local density approximation, deal with the same salts (β -(BEDTTTF)₂X), but Kasowski and Whangbo [39] introduce some non-spherical potentials which allow a better representation of the intermolecular spacings. The general features of the band at the Fermi level and the shape of the Fermi surface appear to be quite similar in the latter calculation and for the EHT model. Moreover, the EHT transfer integrals lead to Fermi surface characteristics that well agree with those deduced in the Shubnikov-de Haas experiments in some representative salts of the β - and κ -phase families [40]. Thus, they have been retained in these calculations.

The evaluation of the U and V_{ij} terms is more complex. Following the P.P.P. scheme, it would be possible to obtain the V_{ij} terms from simple equations. However, this parametri-

zation has been initially realized only for the interactions between atomic orbitals [30] but no study deals with the corresponding formula in the intermolecular case. Then, a semi-empirical Hartree-Fock method, CNDO2 [41], has been used to obtain these parameters.

If one would think of choosing the HF orbitals for the calculation, we would have to evaluate the integral U :

$$U = \langle \chi_i(\mu) \chi_i(\nu) | 1/r_{\mu\nu} | \chi_i(\mu) \chi_i(\nu) \rangle$$

where χ_i is the highest occupied HF molecular orbital for a neutral molecule. It should be pointed out that the choice of the orbital is ambiguous in these mixed-valence compounds where the monomer orbital can carry 0, 1 or 2 electrons. The U values are collected in table I (calculation 1). The atomic coordinates were taken from crystallographic data obtained at different temperatures. The results on a charged monomer are also given for comparison, although this result is unphysical as U is related to a doubly occupied orbital. The values do not largely depend on the type of molecule and on the charge. They are around 6 eV, and slightly smaller for the Se compounds than for the S ones: the Se orbitals are more diffuse and lower U . The DIMET molecule is larger than the TMTTF one, so that U is smaller.

Table I. — Integrals U (CNDO2) in eV for neutral and charged monomers. The molecular geometries used in these calculations correspond to the crystal structures determined at the temperature shown.

Compound		calculation 1		calculation 2
		neutral	charged	
TMTTF ₂ PF ₆	300 K	6.33	6.45	1.94
TMTTF ₂ PF ₆	4 K	6.34	6.46	1.88
TMTTF ₂ SbF ₆	135 K	6.28	6.40	1.90
TMTTF ₂ Br	300 K	6.31	6.42	1.96
DIMET ₂ SbF ₆	300 K	6.09	6.26	1.72
TMTSF ₂ PF ₆	300 K	5.82	5.94	1.80
TMTSF ₂ PF ₆	4 K	5.71	5.80	1.84

The terms V_{ij} are:

$$V_{ij} = \langle \chi_i(\mu) \chi_j(\nu) | 1/r_{\mu\nu} | \chi_i(\mu) \chi_j(\nu) \rangle.$$

where χ_i et χ_j are the HOMO's of the neutral or charged molecules, i and j . These orbitals were obtained from a monomer calculation and injected in a dimer calculation. The results are listed in table II for different compounds.

The V_{ij} values are found to be around 3 eV, i.e. $U/2$. The intra-dimer (S1) and inter-dimer (S2) interactions are rather close, except for DIMET₂SbF₆, which exhibits a dimerized structure formed by isolated dimers [16].

Table II. — Nearest neighbor V_{ij} integrals in eV. For each compound, the results correspond to neutral monomers (first line), charged monomers (second line), one charge per dimer (third line (DIMET₂SbF₆)).

Compound		V_{S1}	V_{S2}
TMTTF ₂ PF ₆	300 K	3.13	3.02
		3.15	3.04
TMTTF ₂ PF ₆	4 K	3.16	3.12
		3.18	3.14
TMTTF ₂ Br	300 K	3.12	3.11
		3.14	3.13
DIMET ₂ SbF ₆	300 K	3.19	2.20
		3.23	2.21
		3.21	2.33
TMTSF ₂ PF ₆	300 K	3.02	2.98
		3.04	2.99
TMTSF ₂ PF ₆	4 K	3.02	3.01
		3.03	3.03

The dimerization ratios, V_{S1}/V_{S2} and t_{S1}/t_{S2} , are compared in table III. When the temperature is decreased, both ratios tend to decrease. The V_{ij} terms depend on the inverse of the intermolecular distance, R , but the transfer integrals vary exponentially with R . This leads to a smaller dimerization ratio in the first case. It is also expected that the second neighbor V_{ij} terms would be important, even if the corresponding transfer terms are close to 0.

Table III. — Dimerization ratios in some M_2X salts.

Compound		V_{S1}/V_{S2}	t_{S1}/t_{S2}
TMTTF ₂ PF ₆	300 K	1.04	1.47
TMTTF ₂ PF ₆	4 K	1.01	1.19
TMTTF ₂ Br	300 K	1.00	1.12
DIMET ₂ SbF ₆	300 K	1.45	1.98
TMTSF ₂ PF ₆	300 K	1.01	1.20
TMTSF ₂ PF ₆	4 K	1.00	1.10

The calculated values of the correlation terms are much larger, by a factor of 4, than the values which have been proposed in earlier studies [33-36]. The main reason for this discrepancy is due to the self-consistent Hartree-Fock process which minimizes all the molecular orbitals (MO) and their energies to obtain the better total energy. Symmetry considerations alone (the EHT MO are quite similar to the CNDO2 ones), explain the slight dependence of U and V on the molecular charge, although the iterative process modifies deeply the MO energies.

An alternative method to evaluate U is to relate this term to the difference between the ionization potential and the electroaffinity, following Pariser and Parr [30]. Using Koopmans' theorem [42], the U term is thus defined as the difference between the energy of the π site orbital filled by 2 electrons and the energy of the π site orbital filled by 1 electron. These MO orbitals are easily obtained from the CNDO2 calculation and the corresponding U values are given in table I (calculation 2). They are much smaller than those obtained above and close to the experimental values. Besides, they agree with the value, $U = 1.7$ eV, deduced from the ionization potential and the electroaffinity in TTF salt [43].

Concerning the V term, a similar approach leads to V (first neighbor) = 1.1 eV for $\text{TMTTF}_2\text{PF}_6$. This represents one third of the values of table II, but it is still larger than the experimental value around 0.3-0.4 eV [34, 35]. A possible explanation lies in the CNDO2 neglect of the penetration integrals, in order to compensate the neglect of the overlap integrals [41]. These integrals take into account the attractive effect of the atomic cores on the valence electrons of the neighboring site. The intermolecular distances are typically larger than 3.5 Å, and correspond to overlaps no larger than 10^{-2} and actually negligible, as already outlined. Consequently, such a compensation tends to unbalance the electrostatic potential experienced by the conduction electrons. Therefore, a more accurate method dealing with such an effect should lead to a decrease of V .

It is important to note that the DVB approach formally involves a strict core-peel separation. The explicit calculation of the parameters using Hartree-Fock molecular orbitals (calculation 1 of Tab. II) is not consistent with such a scheme. Besides, Klein and Soos [44] have shown that, in Hubbard's derivation of site representations, many kinds of intrasite electronic processes could be included in site energies, transfer integrals or correlation terms. It is also possible to include many-electron contributions by appropriately choosing the transfer integrals, as noted for example by Heeger [45] or Kondo [46]. In a similar manner, the Pariser and Parr approximation (calculation 2 of Tab. II) implicitly takes into account significant part of these many body effects, that is the core relaxation with the charge of the monomer; and our calculations clearly show that it is possible to obtain explicitly reliable values for the correlation terms, provided that the core-peel interaction is properly (although still approximately) handled. Further work is in progress to overcome the difficulties encountered in the calculation of the V term.

To bypass the problem of the exact values of the parameters, the present paper rather reports on the variation of the wavefunction characteristics on these parameters and on the changes in the electron distribution due to the variation of the electronic dimerization (represented by t_{S1}/t_{S2} and/or V_{S1}/S_{S2}).

Results.

The results are presented in two parts, depending on the degree of the electronic dimerization: large dimerization, met in dimerized compounds such as $\text{DIMET}_2\text{SbF}_6$ [16], or small dimerization, in regular and quasi regular systems, represented by the TMTTF_2X with octahedral anions [8]. The corresponding results have been presented in a condensed form elsewhere [47].

— **DIMERIZED SYSTEMS.** — The salts representative of this class are localized. They are semiconductors at room temperature : for example, the conductivity is only $10^{-3} (\Omega \cdot \text{cm})^{-1}$ at 300 K in $\text{DIMET}_2\text{SbF}_6$ [48], while it is around $50 (\Omega \cdot \text{cm})^{-1}$ in the TMTTF salts [8], which are more regular. The transfer integrals of $\text{DIMET}_2\text{SbF}_6$ have been used throughout the calculation : $t_{S1} = 0.17$ eV and $t_{S2} = 0.10$ eV [16]. In order to study the effect of the different correlation terms on the electronic properties, we use first the Hubbard model ($V = 0$) and then the extended Hubbard model, and we analyse the intersite terms successively : first neighbor, V_{S1} and V_{S2} , and second neighbor V_2 .

— *Hubbard model.* — In a $3/4$ filled system, the charge carrier may move without an increase of the number of doubly occupied sites. Consequently, the effect of U on localization is indirect, as demonstrated by the variation of the energies of the bonds with U (Fig. 4). The results are given for $N = 12$ sites, but are rather insensitive to the size of the system. Each energy decreases when U increases and reaches an asymptotic value for $U > 6$ eV. This effect is more pronounced for the interdimer bond : between $U = 0$ and $U = 1.4$ eV, the decrease of the bonding character is 36 % for S2, but 5 % only for S1. This is directly related to the difference in the transfer integrals t_{S1} and t_{S2} . In the Hückel limit, E_{S1}/E_{S2} is roughly equal to $t_{S1}/t_{S2} = 1.7$. This ratio increases to 2.85 for $U = 1.4$ eV. Thus, the apparent dimerization is increased by the onsite correlation.

Fig. 4. — Variation of E_{S1} and E_{S2} (eV) as a function of U (eV) in dimerized salts ($N = 12$ sites).

— *Hubbard model extended to first neighbors.* — The U value was chosen to be 1.3 eV according to spectroscopic data collected for $(\text{DIMET})_2\text{SbF}_6$ [34]. It has also been proposed that the difference between V_{S1} and V_{S2} would be 0.2 eV in the dimerized compounds. The results of table II qualitatively suggest that the structural dimerization indeed influences the intersite potential. In this section, we have evaluated the bond energies and the correlation functions as a function of the intersite averaged potential V_0 , and of its dimerization δ , by using the formulae :

$$V_{S1} = V_0 + \delta/2 \quad \text{and} \quad V_{S2} = V_0 - \delta/2.$$

In $3/4$ filled bands, the role of V_0 in localization is direct. It plays the same role as U in the half-filled band. The diagonal correlation energy is minimum for the diagrams which present an alternance of singly and doubly occupied sites. An electron transfer in a diagram of this type gives rise to a diagram whose diagonal energy is increased by V_{S1} (for an interdimer transfer) or V_{S2} (for an intradimer transfer). The latter stabilization is evidently enhanced by a larger δ .

The bond energies are given in figure 5. The effect of V_0 , which is larger on S1 than on S2, is only noticeable for sufficiently large values of this parameter. The non-zero value of U induces small values of E_{S2} . Therefore, the ratio E_{S1}/E_{S2} may be modified by even small variations of V_0 or δ , as evidenced by the results of table IV. Whatever the value of V_0 , the dimerization decreases E_{S2} more than E_{S1} , so that E_{S1}/E_{S2} is multiplied by 1.7 for δ varying from 0 to 0.4 eV. For the values of V_{S1} and V_{S2} close to the experimental suggestion ($V_0 = 0.4$ eV and $\delta = 0.2$ eV), one finds that the intradimer bond is 5 times stronger than the interdimer one. This ratio is only 1.9 in the uncorrelated case, while the S1 bond strength is similar in the two models. The inclusion of correlation within the extended Hubbard model thus leads to a very strong bond-order wave (BOW) picture. A dimerization of 5 means that the intersite S2 bond is virtually empty. For these compounds, the hole is localized in the unit cell, so that the short segments used in the DVB calculation do not represent a limitation for such a discussion.

Fig. 5. — Variation of E_{S1} and E_{S2} (eV) as a function of V_0 and δ in dimerized salts ($N = 12$; $U = 1.3$ eV).

Table IV. — E_{S1}/E_{S2} for different values of V_0 and δ in dimerized salts ($U = 1.3$ eV).

V_0	δ		
	0.0	0.2	0.4
0.2	3.46	4.85	6.00
0.4	3.74	5.10	6.31
0.6	3.56	4.96	6.08

This result is confirmed by the calculation of the charge correlation functions $C_{pq}^{i,i+1}$. They are given in figure 6 for the intradimer case (sites 1 and 2) and for the interdimer case (sites 1 and N). The ground state, which is mainly built on the diagrams exhibiting alternating singly and doubly occupied sites, corresponds to the larger values of $C_{12}^{i,i+1}$ and $C_{21}^{i,i+1}$ ($C_{12}^{i,i+1} = C_{21}^{i,i+1}$ by symmetry). For S1, the probability of having 3 electrons on the dimer ($C_{12}^{1,2} + C_{21}^{1,2}$) is 90 %, and does not depend on V_0 , as expected. This probability is still the largest for S2, but $C_{12}^{1,N}$ and $C_{21}^{1,N}$ are reduced. Their decrease is due to the delocalization in the S1 bond which tends to equalize $C_{12}^{1,N}$ (and $C_{21}^{1,N}$) to the probabilities $C_{11}^{1,N}$ or $C_{22}^{1,N}$ to have 2 or 4 electrons on S2. This is particularly true for $V_0 = 0.2$ eV, while the potential barrier through S1 is zero. For larger V_0 values, this effect decreases and the charge correlation propagates outside the dimer (S1) or the unit cell. This is illustrated by the charge correlation functions between sites 1 and the other sites ($1+n$) of the system : figure 7 (the case $n=1$ gives the intradimer correlation, while $n=11$ corresponds to the interdimer correlation). The very large correlation between sites 1 and 2 quickly decreases for $n > 2$. For $n=6$, the situation is almost completely uncorrelated with $C_{11}^{17} = C_{22}^{17} = C_{12}^{17} = C_{21}^{17}$.

a : S1

b : S2

Fig. 6. — Charge correlation functions $C_{pq}^{i,i+1}$ between neighbor sites for $(p, q) = (1, 2)$ as a function of V_0 in dimerized salts ($N = 12$; $U = 1.3$ eV; $\delta = 0.2$ eV). In the caption, these functions are denoted C_{pq} . (a) Intradimer case S1, (b) Interdimer case S2.

Fig. 7. — Charge correlation functions $C_{pq}^{1,1+n}$ between sites 1 and $1+n$ for $(p, q) = (1, 2)$ in dimerized salts ($N = 12$; $U = 1.3$ eV; $V_0 = 0.4$ eV; $\delta = 0.2$ eV). In the caption, these functions are denoted by C_{pq} .

— *Hubbard model extended to second neighbors.* — The effect of V_2 is quite interesting because it allows us to discriminate between the diagrams which present the same minimal number of doubly occupied sites (Fig. 8). The competition between these diagrams depends on the relative values of V_{S1} , V_{S2} and V_2 :

- if $2V_2 \ll V_{S2}$, type A is favored. The behavior will be close to those obtained with the preceding model;
- if V_{S2} is comparable to $2V_2$, the different electron distributions are almost equivalent and a singular behavior is expected;
- if $V_{S2} \ll 2V_2 < V_{S1}$, type Z is favored. The charge correlation would be different because these diagrams correspond to the same charge on the sites linked by $S2$.

We have shown in the preceding section that the localization is described by a strong BOW, so that it is expected that V_2 would have a small influence on the bond energies. The results show that, when V_2 increases from 0 to 0.15 eV, E_{S1} and E_{S2} increase by 5.5 % and 10 % respectively, so that the dimerization ratio E_{S1}/E_{S2} goes only from 5.1 to 4.9.

Fig. 8. — Representative diagrams with a large weight in the ground state and their corresponding potential energies (referenced to $4U$; $N = 8$).

On the contrary, the results on the charge correlation (Figs. 9 and 10) clearly show a strong influence of V_2 . Through S1, the correlation does not change : this is a direct consequence of the weakness of the S2 bond. The electrons are trapped on the dimer whatever the value of V_2 so that $C_{12}^{1,1+1} = C_{21}^{1,1+1} \approx 0.5$ invariably. The S2 correlation strongly depends on V_2 : around $V_2 = 0.15$ eV (in that case $V_{S2} - 2V_2 = 0$), a change in the regime occurs, as defined above. The charge between the dimers is almost fully uncorrelated as evidenced by the long distance correlation charge reported in figure 10. Thus, for the case where $V_{S2} = 2V_2$, the electronic system is made of isolated dimers : strong correlation inside the dimer contrasts with almost no correlation outside the dimer. These results complement the simple BOW picture given by the bond energies. For $V_2 > 0.2$ eV, $C_{11}^{1,1+n}$ and $C_{22}^{1,1+n}$ become larger than $C_{12}^{1,1+n}$ and $C_{21}^{1,1+n}$ for odd values of N . However, for this regime of large V_2 , it would be necessary to include the effect of the third-neighbor interaction which would be comparable to t_{S2} . Including these potentials would in turn favor the A against the Z diagrams, and the second regime would be recovered.

Finally, these results show that the correlation increases the apparent dimerization of these systems. They justify the previous conclusions of the effect of dimerization on the properties of triplet spin excitons [49], and extend them to the charge correlation.

Fig. 9. — Charge correlation functions $C_{pq}^{1,1+1}$ between neighbor sites for $(p, q) = (1, 2)$ as a function of V_2 in dimerized salts ($N = 12$; $U = 1.3$ eV; $V_0 = 0.4$ eV; $\delta = 0.2$ eV). In the caption, these functions are denoted by C_{pq} . (a) Intradimer case S1, (b) Interdimer case S2.

Fig. 10. — Charge correlation functions $C_{pq}^{1,1+n}$ between sites 1 and $1+n$ for $(p, q) = (1, 2)$ in dimerized salts ($N = 12$; $U = 1.3$ eV; $V_0 = 0.4$ eV; $\delta = 0.2$ eV; $V_2 = V_{s2}/2 = 0.15$ eV). In the caption, these functions are denoted by C_{pq} .

— *Consequences for the magnetic properties.* — The antiferromagnetic order observed at low T in $\text{DIMET}_2\text{SbF}_6$ [48] leads to a finite paramagnetic susceptibility at 0 K. This result has been modelled by a Heisenberg Hamiltonian on an infinite chain of $1/2$ spins [48]. In this model, the U term is not a molecular entity. For a finite ring, the ground state may be singlet or triplet depending on the number of sites (even or odd), or on the parameters. To be consistent with our results on the electronic distribution, the susceptibility calculations have been performed on a ring of 8 sites which gives a singlet ground state in the present case. The calculation of the T dependence of the static susceptibility has been performed for the ring of 8 sites only. The susceptibility per site is independent of the size N of the cluster at high T , in the Curie limit, and almost independent of N at the maximum (see for example [50]). The low T behavior is sensitive to various factors including the change of the dimerization, and therefore of the transfer integrals, upon lowering T , the difference between open and closed chains, the fact that the results corresponding to $N = 4n$ or $4n + 2$ might lead to different ground states, etc. This point will be discussed in more detail in the section reporting on regular systems. We then focuss on the shape of the plateau and of the maximum and on their

Fig. 11. — Variation of $\chi_{(T)}/\chi_{(300)}$ with T in dimerized salts : (a) calculated results for different values of V_2 ($N = 8$; $U = 1.3$ eV; $V_0 = 0.4$ eV; $\delta = 0.2$ eV); (b) ESR result for $\text{DIMET}_2\text{SbF}_6$ with spin $1/2$ Heisenberg fit [51].

dependences on the electronic parameters. The variation of $\chi(T)/\chi(300\text{ K})$ with the temperature T and for different values of V_2 are reported in figure 11a.

The maximum value of the susceptibility $\chi_{\max}$, and the temperature $T_{\max}$, at which it occurs, strongly depend on V_2 . These characteristics are collected in table V and compared to the experimental values. The calculations show that an increase of V_2 induces an increase of $T_{\max}$ and a decrease of $\chi_{\max}/\chi(300\text{ K})$. There is no experimental evidence for a relation between these numbers. The results obtained with $V_2 = 0$ disagree qualitatively with the experiment (see Fig. 11b): small $T_{\max}$ and sharp increase of $\chi(T)$ around $T_{\max}$. A better quantitative agreement is obtained when V_2 is taken into account. These results are quite comparable to the fit obtained by means of a spin-1/2 Heisenberg Hamiltonian [51]. These calculations on a cluster of small size and using molecular parameters in the range of an intermediate coupling justify the use of the DVB method on finite rings for the analysis of the magnetic properties.

Table V. — Calculated and experimental [51] magnetic susceptibilities in dimerized salts ($N = 8$; $U = 1.3\text{ eV}$; $V_0 = 0.4\text{ eV}$; $\delta = 0.2\text{ eV}$).

V_2 (eV)	$T_{\max}$ (K)	χ (300 K) (uem/mole)	$\chi_{\max}/\chi_{300\text{ K}}$
0.0	28	$1.0 \cdot 10^{-3}$	3.5
0.15	60	$9.4 \cdot 10^{-4}$	1.9
0.20	77	$7.9 \cdot 10^{-4}$	1.7
0.25	96	$8.9 \cdot 10^{-4}$	1.5
$\beta\text{-(ET)}_2\text{ICl}_2$	90	$8.5 \cdot 10^{-4}$	1.7
$\text{(ET)}_2\text{AuCl}_2$	80	$9.0 \cdot 10^{-4}$	1.6
$\text{DIMET}_2\text{SbF}_6$	80	$7.0 \cdot 10^{-4}$	1.5

— REGULAR SYSTEMS. — In the TMTTF_2X salts, the conductivity measurements show a metallic regime at room temperature and a semi-conductor behavior below the temperature of the resistivity minimum T_p [8]. For a rigid lattice, delocalization is assured in mean-field, and band theory is simpler than VB approaches. For systems showing an intermediate $T_p \approx 100\text{--}200\text{ K}$, the mean-field treatment leads to a size of the electron-hole pair of the order of the size of the cluster used in the DVB calculation. Consequently, it might be argued that localization is not well modelled by short segments and that its modelling is out of reach of the DVB formalism. This limitation would be well founded only if the size of the e-h pair evaluated by this mean-field treatment were an exact result. However, models like the g -ology formalisms [17, 18, 52, 53] are perturbative treatments, and the corresponding results are approximate, compared to the exact DVB modelization. Furthermore, in RG models, the choice of the cut-off energy is important and some guides should be extracted directly from the physical properties. On the contrary, the exact DVB data point to a small extension of the e-h pair. Moreover, this result is independent of the size of the ring (8 or 12 sites) and fully justifies the limited size of the cluster used in this study. Further comments can be made on the approach of localization by the g -ology model and on the g_i parameters. It is difficult to link the parameter g_3 to the microscopic nature of the salt. For example, some authors fix g_3 by fitting the experimental T_p at different pressures [17]. Besides, the g_3 parameter has been shown to depend on the g_1 parameter and on the stack dimerization [53]. However, our

calculation of the correlation terms U and V implies that g_1 would not depend strongly on the type of organic molecule. Thus, the g_3 parameter should be related only to the stack dimerization. But the comparison of the structural data on the stack dimerization (or of the calculated $t_{S1}-t_{S2}$) and of the T_p values in a large series of compounds shows that no simple relation can be established. The g_i parameters do not *a priori* allow us to discriminate between compounds.

The DVB approach appears to be a valuable tool for the study of the problem of localization, and may be viewed as an attempt to track back the effect of each hamiltonian term on this property, rather than a first principle evaluation of the continuous transition between the high T and the low T regimes. Keeping in mind this cautionary note, we now turn to the discussion of the electronic parameters.

The crystal structures of the TMTTF salts show a decrease in the stacking dimerization when the temperature is decreased [54]. This results from a larger contraction of the intermolecular (S2) spacing than of the intramolecular (S1) one. This leads to the calculated variations of the t_{S1}/t_{S2} ratios reported in table III. Then, the more localized (low T) system is related to the less dimerized structure. This is apparently contradictory to the previously discussed results, where the electronic localization has been shown to arise from the cumulative effect of the correlation and the dimerization.

The anions might possibly modify the electronic parameters. This effect is included phenomenologically in the g -ology model [17, 18]. A more local description has been proposed by Laversanne [51]. We present a model which supports this suggestion. The transfer integral between the site i and j is :

$$t_{ij} = \langle \chi_i(\mu) | T(\mu) + V(\mu) | \chi_j(\mu) \rangle$$

where $T(\mu)$ is the kinetic component and $V(\mu)$ the Coulomb term between a π electron of the organic stack and the potential due to the organic cores and the anions. In order to evaluate the possible influence of the last term on the transfer integral, and as the latter arises essentially because of the overlap between the sulfur $3p_z$ atomic orbitals, an *ab initio* calculation [55] has been performed on a model represented in figure 12 : two sulfur atoms, A and B, located at 3.5 Å apart on the z axis, represent the dimer and interact with a hydrogen atom H, located on the y axis at d Å from the z axis. The transfer integral between the two

Fig. 12. — Model of the change in the transfer integral due to the anion potential : (a) Model of two sulfur atoms S_A and S_B interacting with a hydrogen atom H ; (b) *ab initio* results : $D = t_0 - t$, where t_0 and t are the transfer integrals in absence and in presence respectively of H .

sulfur orbitals is given by the above equation, where $\chi_i(\mu)$ and $\chi_j(\mu)$ are the orbitals $3p_{zA}(\mu)$ and $3p_{zB}(\mu)$ respectively. This integral involves the potential of the hydrogen nucleus and can be extracted from the core Hamiltonian matrix. A negative charge would have an opposite effect on the integral. Therefore, the difference $D = t_0 - t$, where t_0 and t are the transfer integrals in absence and in presence respectively of H, gives the contribution of a negative charge on t and is given in figure 12b.

D is negative, this confirms that the transfer integrals decrease under an anion field. For $2 \text{ \AA} < d < 8 \text{ \AA}$, this curve follows a K/d law, and $K = -1.44 \text{ eV} \cdot \text{\AA}^{-1}$ (d in $\text{\AA}$). For $5 \text{ \AA}$, which is roughly the distance between the anion and the center of the dimer in the real material, this decrease is 0.29 eV , to be compared to a kinetic component of 0.066 eV . Although a straightforward extrapolation to the molecular species is not yet possible, it should be noted that the electrostatic effect of the anions may actually contribute strongly to the transfer integral.

This very simple approach thus confirms the hypothesis of a renormalization of the transfer integrals by the anion potential. However, a more accurate evolution of this effect is difficult. Inspection of the TMTTF_2X crystal structure shows that the intradimer S1 spacing might be more affected by the anion than the interdimer S2 one. Thus, if a decrease of 0.05 eV is assumed for S1 only, which seems reasonable, at high T , the transfer integrals [54] would evolve from $t_{S1} = 0.15 \text{ eV} > t_{S2} = 0.10 \text{ eV}$, to $t_{S1} = 0.15 \text{ eV} = t_{S2}$, while including the anion effect. This corresponds to a more delocalized situation. Similarly, the low T EHT result [54] $t_{S1} = 0.15 \text{ eV} = t_{S2}$ would change into $t_{S1} = 0.10 \text{ eV} < t_{S2} = 0.15 \text{ eV}$, which describes a more localized picture, in qualitative agreement with the conduction measurements. Two cases, corresponding to the equality or a slight difference of the transfer integrals, have been investigated.

— *Regular chain.* — From the equality between t_{S1} and t_{S2} , the DVB calculation requires the parameters : t , U , V (first neighbor), V_2 . The decrease of the bond energy with an increase of U in a Hubbard model is smaller than in the dimerized case : for U varying between 0 and 1.4 eV , this decrease is 16 % for a regular system ($t = 0.15 \text{ eV}$), to be compared to the 36 % decrease for S2 in the dimerized case. The effect of V is small : E_S decreases by only 7 % for V varying between 0 and 0.3 eV ($t = 0.15 \text{ eV}$; $U = 1.5 \text{ eV}$). The effect of V_2 is shown in figure 13. The correlation barrier against the charge transfer is $|V - 2V_2|$ and for $V = 0.3 \text{ eV}$, it will be minimum around $V_2 = 0.15 \text{ eV}$. For this set of parameters, the overall

Fig. 13. — Influence of V_2 on the energy of the bond in regular salts ($U = 1.5 \text{ eV}$; $V = 0.3 \text{ eV}$).

decrease in the bond energy is 16 % for $t = 0.15$ eV, with regard to the uncorrelated Hückel model. It was 60 % for E_{S2} in the dimerized systems. Thus, if we take into account the screening of V by the second neighbors, it appears that U gives the main contribution to the decrease of the bond energy.

The charge correlation along the ring is reported in figure 14. It is already negligible for the second neighbor, as found in the dimerized systems. A substantial difference lies in the value of the correlation between the first neighbor sites : while the probability to have 3 electrons in the dimer amounts to 95 % in the dimerized case, it is now only 70 %. Thus, there is a non-negligible probability to meet the situation with 2 or 4 electrons. This possibility of the charge variation may be related to the small decrease of the energy of the bond, which corresponds to the more delocalized nature of the electrons.

Fig. 14. — Charge correlation functions $C_{pq}^{1,1+n}$ between sites 1 and $1+n$ for $(p, q) = (1, 2)$ in the regular systems ($N = 12$; $t = 0.10$ eV; $U = 1.5$ eV; $V = 0.3$ eV; $V_2 = 0.15$ eV). In the caption, these functions are denoted by C_{pq} .

We have noted above that the multiplicity of the ground state might depend on various factors. For 3/4 filled systems, Hückel theory predicts that the ground state will be a triplet for $4n$ ring. Besides, Klein and Seitz [56] have shown that the electronic properties of a linear Hubbard chain might be modelled, in the atomic limit, by a Heisenberg model with antiferromagnetic exchange a function of band filling. For a regular cyclic system, we have checked that the ground state is indeed a triplet state, whatever the U value. The Klein and Seitz result does not appear to be valid for a ring whilst our result agrees with previous data of Mazumdar and Dixit [24] about the multiplicity of a ring with $N \neq N_c$. The different results obtained for the rings and the chains might be closely related to their different topologies.

For $N = 8$, we have calculated the ground state multiplicity as a function of the dimerization δ of the transfer integrals: $t_{S1} = 0.135 + \delta$ and $t_{S2} = 0.135 - \delta$, while fixing the correlation terms to: $U = 1.3$ eV; $V_{S1} = V_{S2} = 0.4$ eV; $V_2 = 0.2$ eV (with these parameters, the case $\delta = 0$ corresponds to the regular system studied here, and $\delta = 0.035$ eV corresponds to the dimerized case). It is found that the triplet is the ground state unless $\delta \geq 0.035$ eV (dimerized case). For this value, the singlet ground state is lower by only 0.0006 eV.

In the regular case, the triplet ground state leads to a divergence of the susceptibility at 0 K and forbids to reproduce the observed Pauli magnetism. The magnetic susceptibilities have been calculated only at 300 K and are given in table VI for two sets of correlation parameters

Table VI. — Room temperature magnetic susceptibilities χ (300 K) (uem.cgs/mole) in regular salts ($N = 8$; $V_2 = V/2$).

t (eV)	0.10	0.15	0.20
$U = 1.5$ eV; $V = 0.3$ eV	8.8×10^{-4}	7.5×10^{-4}	7.4×10^{-4}
$U = 1.1$ eV; $V = 0.4$ eV	8.1×10^{-4}	7.1×10^{-4}	7.0×10^{-4}

and for different values of the transfer integral. The calculated susceptibilities are somewhat larger than the experimental data (around 6×10^{-4} uemcgs/mole [51]). They increase when t decreases or U increases. The results are satisfactory with regard to the small size of the cluster. They account for the large susceptibility and justify the values of the correlation terms.

To summarize this part, the effect of the correlation on the localization is rather small and the intrasite term plays a leading role. If one assumes a complete screening of the first neighbor potential term by the second neighbor one, the decrease of the energy of the bond is only 20 % (for $t = 0.10$ eV). In this aspect, the correlated model gives results similar to the uncorrelated model. This may be related to the « bad » metallic character of these salts. However, the absence of a gap in this state cannot be checked by such calculations on finite systems.

— *Quasi-regular chain.* — The transfer integrals are dimerized and we have used: $t_{S1} = 0.15$ eV and $t_{S2} = 0.10$ eV, but the first neighbor V is not, since it is considered that the different electrostatic contributions of the molecules and the anions are additive. This set of parameters would correspond to a temperature less than T_p , that is for the semi-conducting regime.

The Hubbard model gives identical results to the case of dimerized salts which has been discussed previously (see for example Fig. 4). In particular, the E_{S2} decrease by U is reminiscent of the variation of the one-particle self-energy renormalization factor z_1^{-1} (in the notation of Solyom [52]) evaluated in the g -ology continuum model. This factor corresponds to a renormalization of the dispersion energy, and incorporates the local and long range Coulomb interactions, and the stack dimerization (see for example [53]). It is proportional to the single particle density of states at the Fermi level and it has been shown [18] to be significantly depressed due to the presence of a finite g_3 , as met in the (TMTTF)₂X compounds. The single transfer energies E_{S2} and z_1^{-1} are related, because both account for the effect of the dimerization mediated by the correlation on the localization. However, it is not possible to obtain an exact relationship between the two results, because the factor z_1^{-1} might also include the effect of the many-body effects on the energy of the bond E_{S1} . Thus, the DVB approach leads to a more accurate description of the electronic system, in terms of the distribution of the electron density on the various bonds of the system.

Figure 15 shows that the effect of V is larger on S2 than on S1 until V is larger than 0.4 eV, similarly to the dimerized case. The maximum of dimerization occurs for $0.3 \text{ eV} < V < 0.4 \text{ eV}$. This domain corresponds to the values of V deduced from the experiment. The effect of V_2 is less important: the ratio E_{S1}/E_{S2} decreases only by 3 % for $0 < V_2 < V/2 = 0.3 \text{ eV}$. In the Hückel model, E_{S1}/E_{S2} is 1.6 and increases by 80 % in the correlated regime: $U = 1.5 \text{ eV}$, $V = 0.3 \text{ eV}$, $V_2 = 0.15 \text{ eV}$. This results from a small decrease (2 %) of E_{S1} and a large decrease of E_{S2} (45 %). In the quasi-regular systems, the correlation is « selective », as in the dimerized salts.

Fig. 15. — Electronic dimerization as a function of V in the quasi-regular systems ($t_{S1} = 0.15$ eV ; $t_{S2} = 0.10$ eV ; $U = 1.5$ eV).

At low T , the susceptibility χ follows the behavior of a chain of spins with the temperature of the maximum of χ less than 20 K [8]. These data cannot be reproduced with a triplet ground state. The 300 K calculated χ are given in table VII. The increase of the mean transfer integral or a decrease of U lead to a decrease of χ . By comparison with the results of the preceding section, it appears that the dimerization of the transfer integrals changes only slightly the value of the susceptibility.

The smooth transition from a metallic to semi-conducting regime in these salts is modelled by a change in the dimerization of the transfer integrals due to the anion-cation interaction. The effect of the correlation differs in the 2 cases derived from this assumption: the t dimerization induces an appreciable weakening of the interdimer bond. The results are not extrapolable to the infinite limit, so that it is not possible to relate this increasing localization to the opening of a gap.

Table VII. — Room temperature susceptibilities χ (300 K) (uem.cgs/mole) in quasi-regular salts ($N = 8$; $V_2 = V/2$).

	t_{S1} (eV)	t_{S2} (eV)	χ (300 K)
$U = 1.5$ eV, $V = 0.3$ eV	0.15	0.10	$9.0 \cdot 10^{-4}$
	0.17	0.12	$8.1 \cdot 10^{-4}$
	0.20	0.15	$7.3 \cdot 10^{-4}$
$U = 1.1$ eV, $V = 0.4$ eV	0.15	0.10	$8.0 \cdot 10^{-4}$
	0.17	0.12	$7.2 \cdot 10^{-4}$
	0.20	0.15	$6.9 \cdot 10^{-4}$

Conclusion.

It has been shown that the DVB method may account for a strong localization effect of the electronic correlation within an extended Hubbard hamiltonian describing a $3/4$ filled band. This model is based on the molecular site and involves similar interactions in the cases of dimerized or regular structures. This allows a better understanding of the origin of the spin chain behavior of the localized salts when the correlation is in the intermediate range. This discriminates from the more phenomenological approaches for which the site is made of the dimer.

Providing that the electronic core is taken into account, the CNDO2 calculation of the intrasite correlation term leads to values less than 2 eV which agree with those deduced from the experiment. The intersite terms are larger than what is commonly retained, due to the inadequacy of the semi-empirical CNDO2 method for long range electrostatic interactions. A more sensible parametrization of this method should yield better results.

In the case of dimerized salts, the weaker (interdimer) bond is even weakened by the correlation, while the stronger bond is only slightly modified. Concerning the magnetic properties, a comparison of the theoretical and experimental results shows that the second neighbor intersite term is an important parameter. The value of the 300 K susceptibility, the maximum of $\chi(T)$ and the temperature at which it occurs, are fairly well reproduced by the DVB calculations. When the screening of the first neighbors' interaction by the second neighbors is taken into account, the electrostatic structure of these salts corresponds to isolated and uncorrelated dimers with 3 electrons on each, so that the localized regime could correspond to a BOW state. Through the charge correlation functions, the DVB method provides some additional information in terms of spatial correlation of the electrons.

In the case of the regular salts, the inclusion of the anion-cation interaction renormalizes the transfer integrals. Going from a regular to a quasi-regular model, where it is sufficient to consider only dimerized transfer integrals, allows us to simulate the localization observed when the temperature decreases. The behavior of the latter model is similar to the dimerized case, but to a smaller extent, due to the non-dimerization of the intersite potential term.

The DVB formalism shows the effect of the intermediate correlation which is sufficient to induce some large localization effects, depending on the structure of the stacks.

However, it may be noted that the size limitation of the complete basis of the DVB formalism is severe. The extrapolation of the results to the infinite system is hardly conceivable, and the prevision of a gap opening, related to the conductivity measurements, is not possible. The study of the optical properties of the 8- and 12-site rings would be quite useful in order to relate the absorption frequencies of the charge transfer spectra to the different correlation parameters. Finally the exact DVB results may constitute a reference for more approximate solutions of the model hamiltonian. This, in turn, would allow an evaluation of the properties of extended systems and, particularly, a study of the effect of the interchain interactions in the competition between the different ground states.

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