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ABSTRACT

The effect of the hopping on the magnetic and dielectric properties of the box model introduced by A. Zawadowski and M.H. Cohen [1] are considered.

By symmetry reasoning it is shown that the free energy is an even function of the hopping rate as well as of the external electric field.

It is proved that at finite temperature when the hopping is small enough the hopping processes in various boxed are uncorrelated. Based on this the magnetic and dielectric susceptibilities are calculated up to the second order of the hopping rate.

АННОТАЦИЯ

Исследовано влияние прыжка электронов /hopping/ на магнитные и диэлектрические свойства систем, описанных в рамках модели коробок /box model/, предложенной А. Завадовски и М.Г. Когеном.

На основе соображений симметрии показано, что свободная энергия является четной функцией как и внешнего поля так и амплитуды прыжка.

Доказано, что при конечных температурах в случае достаточно малой амплитуды прыжков, прыжки, происходящие в различных коробках являются независимыми. На этом основе рассчитаны магнитная и диэлектрическая восприимчивости во втором порядке по амплитудам прыжков.

KIVONAT

Megvizsgáljuk a hoppingnak az A. Zawadowski és M.H. Cohen által javasolt "box model" segitségével leirható rendszerek mágneses és dielektromos tulajdonságaira gyakorolt hatását.

Szimmetria érvek alapján megmutatjuk, hogy a szabadenergia mind a hopping-amplitudó, mind a külsõ tér páros függvénye.

Bebizonyitjuk, hogy véges hõmérsékleten elég kicsi hopping-amplitudó esetén a különbözõ boxokban végbemenõ elektronátugrások korrelálatlanok. Ennek alapján kiszámitjuk a mágneses és dielektromos szuszceptibilitást a hopping-amplitudóban másodrendig.

INTRODUCTION

During the last decade, the study of organic transfer salts has received a great deal of attention. Because of the richness of composition, and the possibility of replacing similarly functioning units by one another, these materials hold out the hope of eventually reaching the stage when materials can be tailormade for any desired purpose - assuming of course, that our wishes are in accord with nature's laws.

As the original excitement about the high a conductivity of TTF-TCNQ gradually died down, it gives place to systematic exploration of different properties of all kinds of TCNQ salts, which are proved to be almost as interesting as their never-realized superconductivity would have been. In particular, a class of compounds with the general composition $(DONOR)(TCNQ)_2$ was found to possess remarkable dielectric and magnetic properties. Recently A. Zawadowski and M.H. Cohen [1] introduced a simple model (the so- called box model) for their description.

The a structure described by the box model is schematically shown in Fig.1.

The main feature of this structure is that one electron is transfered per donor so that the acceptor chain is quarter field. Furthermore each acceptor chain can be devided into boxes with two acceptor sites as shown in Fig.2.

The Hamiltonian of the model is

$$H = \sum_i (I_i^z+1/2)(-I_{i+1}^z+1/2)(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})+2t\sum_i I_i^x$$

Where $\vec{\sigma}_i$ is the Pauli operator used to describe the spin state of the electron in the box i, I_i^z and I_i^x are the components of the isospin operator $\vec{I}_i$. The two eigenvalues of the operator I_i^z, namely, $I_i=-1/2$ and $I_i=+1/2$ correspond to the left and right hand sites in the box i. The operator I_i^x describes the hopping within the box i with rate t, U_1 and J are the effective Coulomb and exchange interactions between two electrons accupying adjacent acceptors in neighbouring boxes. The distance between two molecules in a box is assumed to be smaller than between two next molecules in neighbouring boxes and therefore the hopping between boxes is ignored compared to the hopping within a box.

In reference [1] the magnetic properties of the model were considered in two limiting cases, when the hopping rate $t=\infty$ and $t=0$. It was pointed out that in both cases the model can be solved exactly. In the first case it was shown that the model behaves like a 1-d Heisenberg chain,the ground state can be ferromagnetic or antiferromagnetic. In the second case it was found that depending on the signs and relative magnitude of the interactions the ground state can be singlet or paramagnetic (doublet or triplet). The ground state of the model in the intermediate case was discussed qualitatively.

In this paper we consider the effect of a weak hopping, on both, the magnetic and dielectric properties of the model. In Section I we consider the effect of the hopping on the magnetic properties after presenting briefly the solution obtained by Zawadowski and Cohen in the zero hopping case, and describing

the physical picture of the ground state in the intermediate case. In Section II. we consider the dielectric properties.

I. MAGNETIC PROPERTIES

1. Zero Hopping Case

Let us consider the box model in a static external magnetic field. The Hamiltonian of the system is

$$H = H_o + 2t\sum_i I_i^x \tag{1.1}$$

where

$$H_o = \sum_i (I_i^z + 1/2)(-I_{i+1}^z + 1/2)(U_1 - J\vec{\sigma}_i\vec{\sigma}_{i+1}) - \mu\mathcal{H}\sum_i \sigma_i^z \tag{1.2}$$

is the Hamiltonian of the zero hopping system in the field. Zawadowski and Cohen pointed out that the problem with the Hamiltonian H_o can be exactly solved. When t=O the eigenvalues of I_i^z are good quantum numbers and the system can be in configurations in which electrons form pairs or stand separately. The levels of the system can be classified following the spin states of single electrons and electron pairs and following isospin states of electrons. In particular, when $U_1 - J > O$ and $U_1 + 3J > O$ in the ground state every second site is occupied, the spins are decoupled and the chain is paramagnetic, when $U_1 - J < O$ and $J > O$ the ground state is built up of electron pairs in triplet state, the ground state is paramagnetic with spin S=1, when $U_1 + 3J < O$ and $J < O$ in the ground state electron pairs are in singlet state, the ground state is singlet. Since the levels of H_o can be classified by the eigenvalues of I_i^z and by spin states of single electrons and electron pairs, the partition function Z_o corresponding to H_o can be easily calculated. After taking the trace in the real spin space we get.

$$Z_o = e^{NA_1} \sum_{I_1 \ldots I_N} \exp\left(\sum_j B I_j I_{j+1}\right) \tag{1.3}$$

where

$$A_1 = \frac{1}{4}\ln Z_s + \frac{1}{2}\ln Z_p \qquad (1.4)$$

$$B = 2\ln Z_s - \ln Z_p$$

with

$$Z_s = 2\mathrm{ch}(\beta\mu\mathcal{H})$$

$$Z_p = (1+2\mathrm{ch}2\beta\mu\mathcal{H})e^{-\beta E_1} + e^{-\beta E_2} \qquad (1.5)$$

in which $E_1=U_1-J$ and $E_2=U_1+3J$ are the characteristic energies of an electron pair in triplet and singlet state, respectively.

The second factor in the right hand side of (1.3) is the partition function of a 1-d Ising model therefore it can be calculated by using the conventional transfer matrix method [2]. The result is

$$Z_o = [Z_s^{1/2}Z_p^{1/4}(Z_s^{1/2}Z_p^{-1/4}+Z_s^{-1/2}Z_p^{1/4})]^N \qquad (1.6)$$

The zero-field magnetic susceptibility can be obtained directly from (1.6)

$$\chi_{h_o} = N\beta\mu^2\{(\frac{1}{2} + \frac{2e^{-\beta E_1}}{3e^{-\beta E_1}+e^{-\beta E_2}}) + (\frac{1}{2} - \frac{2e^{-\beta E_1}}{3e^{-\beta E_1}+e^{-\beta E_2}})(\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}} + \frac{2}{2+\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}}})\} \qquad (1.7)$$

The low temperature susceptibility can be obtained by expanding.

(i) In the case $E_1>0$, $E_2>0$, when $J>0$ we get

$$\chi_{h_o} = N\beta\mu^2\{1+ \frac{1}{2\sqrt{3}} e^{-\frac{1}{2}\beta E_1}\} \qquad (1.8)$$

the second term in the right hand side of (1.8) can be associated with the forming of a triplet pair from two single electrons (Fig.3a). When $J<0$ we find

$$\chi_{h_o} = N\beta\mu^2\{1 - \frac{1}{2} e^{-\frac{1}{2}\beta E_2}\} \qquad (1.9)$$

Now the second term in the right hand side of (1.9) corresponds to the forming of a singlet pair. (Fig.3b)

(ii) In the case $E_1<0$ and $J<0$ we get

$$\chi_{h_o} = \frac{1}{3}N\beta\mu^2\{4-\frac{4}{3} e^{\beta(E_1-E_2)}- \frac{1}{\sqrt{3}} e^{\frac{1}{2}\beta E_2}\} \qquad (1.10)$$

The second term in the right hand side of (1.10) corresponds to the excitation of a triplet pair into a singlet pair (Fig.4a), the third term corresponds to the break of a triplet pair into two single electrons (Fig.4b)

(iii) In the case $E_2<0$ and $J<0$ we find

$$\chi_{h_o} = N\beta\mu^2\{4e^{\beta(E_2-E_1)}+2e^{\frac{1}{2}\beta E_2}\} \qquad (1.11)$$

The first term corresponds to the excitation of a singlet pair into a triplet pair (Fig.5a), the second term can be associated with the break of a singlet pair into two single electrons (Fig.5b).

2. Finite Hopping Case

a. Independent Hopping Approximation

When the hopping is finite the problem can not be solved exactly. Basing on physical arguments Zawadowski and Cohen [1] discussed the effect of the hopping on the ground state of the system. When the hopping is small the ground state can be constructed starting from the ground state of the zero hopping system and considering the effect of the hopping on these states. In the case when $U_1-J>0$ and $U_1+3J>0$ as it was

mentioned the ground state of the zero hopping system is paramagnetic, every second site is occupied. A small hopping makes, for example, the electron in the box i jump to the neighbouring site, then the exchange interaction acts between neighbours and finally the electron jumps back to the original position. In this way there is an effective interaction between spins in neighbouring boxes. This interaction causes the system to behave like a weak ferro- or antiferro-magnetic chain. In the case when $U_1-J<0$ and $J>0$ in the ground state of the zero hopping system electrons form triplet pairs. A small hopping makes electrons jump from one site to the other as above. Two separated triplet pairs can interact after two jumps in which two neighbouring pairs break up and temporarily form a new pair. In this way a weak exchange interaction is established between triplet pairs. Thus the triplet pairs will be ordered as in a Heisenberg chain. In the case when $U_1+3J<0$ and $J<0$ in the ground state of the zero hopping system electrons form singlet pairs. The weak singlet pair breaking results in a weak spin correlation existing between electrons separated by two unoccupied sites. Thus, in any ease, at low temperatures the hopping, though it is small gives rise to a correlation between electrons in the chain. This makes the problem difficult to solve.

When the temperature is raised the correlation between electrons is expected to become weaker, and in the limit when βt is small enough the effect of the hopping in various boxes must be independent and this makes the problem solvable. Mathematically this can be shown as follows. For the finite hopping system the partition function can be written in the following form

$$Z = Tr\{e^{-\beta(H_o+\sum_i 2t_i I_i^x)}\} \qquad (1.12)$$

where for the usefullness we have introduced the formal notation $t_i=t$. In order to calculate the trace in the right hand side of (1.12) let us choose the set of eigenstates of H_o and simultaneously of $I_i^z(i=1,...N)$ to be a basis. Let us suppose that $|m>$ is such a function. It is clear that

$$<m|I_i^x|m> = 0, \qquad <m|...I_i^x...I_j^x...|m> = \delta_{ij} \qquad (1.13)$$

By these relations the expansion of the right hand side of (1.12) in powers of βt_i contain only even powers of the latter. This is the consequence of the symmetry of the two sites in each box.

By making the use of (1.13) it is easy to prove that up to the second order of βt_i we have

$$Z = Z_o \prod_i \frac{Z_i}{Z_o} \qquad (1.14)$$

where

$$Z_i = \{T_r\, e^{-\beta(H_o+2t_i I_i^x)}\} \qquad (1.15)$$

is the partition function of a system in which hopping occurs in the box i only. The Hamiltonian of this system is

$$H_i = H_o+2t_i I_i^x \qquad (1.16)$$

Equality (1.14) enables us to reduce the solving of our problem with the Hamiltonian given by (1.1) to the solving of the problem with the Hamiltonian given by (1.16) and shows that indeed when βt_i small enough the hopping processes in various boxes are uncorrelated.

It should be noted that equality (1.14) requires the smallness not only of βt_i but also of $t_i/E_\alpha(\alpha=1,2)$ because in the case when $t_i \sim E_\alpha$ we have no right to ignore the

$(\beta t)^4$-terms while the $(\beta E_\alpha)^4$-terms are taken into account. Thus the restrictions imposed on our approximation which is based on (1.14) are the same as those imposed on the thermodynamic perturbation theory. (In fact (1.4) can be proved directly by using the pertubation expansion of the canonical statistical operator $\exp\{H_o+2t\Sigma_i I_i^x\}$ considering $2t\Sigma_i I_i^x$ as a small perturbation). Since equality (1.14) requires the smallness of βt_i the approximation is reasonable only when hopping is small and temperature is high enough. In particular it can not be used at $T=0^oK$ with $t\neq 0$. In other words the results, obtained by using (1.14) do not describe the effect of the hopping on the ground state.

b. Modified Transfer Matrix Method.

In order to calculate Z_i we separate the Hamiltonian H_i into two parts in such a way that one of them does not contain the dynamical variables of the electron in the box i. This can be easily done by using the following identity

$$(-I^z_{i-1}+1/2)(I^z_{i+1}+1/2)+(-I^z_{i-1}+1/2)(-I^z_{i+1}+1/2)+$$
$$+(I^z_{i-1}+1/2)(I^z_{i+1}+1/2)+(I^z_{i-1}+1/2)(-I^z_{i+1}+1/2)=1 \qquad (1.17)$$

The operator H_i then can be written in the following form

$$H_i=\sum_{j\neq i-1,i}\{(I^z_j+1/2)(-I^z_{j+1}+1/2)[(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})-\mu\mathcal{H}(\sigma^z_j+\sigma^z_{j+1})]$$
$$-\mu\mathcal{H}[(I^z_j+1/2)(I^z_{j+1}+1/2)\sigma^z_j+(-I^z_j+1/2)(-I^z_{j+1}+1/2)\sigma^z_{j+1}]\}+$$
$$+(-I^z_{i-1}+1/2)(I^z_{i+1}+1/2)H(i)+(I^z_{i-1}+1/2)(-I^z_{i+1}+1/2)H(i-1,i,i+1)+$$
$$+(I^z_{i-1}+1/2)(I^z_{i+1}+1/2)H(i-1,i)+(-I^z_{i-1}+1/2)(-I^z_{i+1}+1/2)\,H(i,i+1). \qquad (1.18)$$

where

$$H(i)=2t_i I_i^x-\mu\mathcal{H}\sigma_i^z$$

$$H(i-1,i)=(-I_i^z+1/2)(U_1-J\vec{\sigma}_{i-1}\vec{\sigma}_i)+2t_i I_i^x-\mu\mathcal{H}\,(\sigma_{i-1}^z+\sigma_i^z)$$

$$H(i,i+1)=(I_i^z+1/2)(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})+2t_i I_i^x-\mu\mathcal{H}(\sigma_i^z+\sigma_{i+1}^z)$$

$$H(i-1,i,i+1)=(-I_i^z+1/2)(U_1-J\vec{\sigma}_{i-1}\vec{\sigma}_i)+(I_i^z+1/2)(U_1 J\vec{\sigma}_i\vec{\sigma}_{i+1})+$$

$$+\ 2t_i I_i^x-\mu\mathcal{H}(\sigma_{i-1}^z+\sigma_i^z+\sigma_{i+1}^z) \qquad (1.19)$$

These operators correspond to the four configurations shown in Fig.6. where the electrons in the boxes i-1 and i+1 are situated at determined sites, the hopping takes place only in the box i. Each term in (1.18) commute with the others therefore they can be simultaneously diagonalized. Let us denote the partition function corresponding to H(i), H(i-1,i), H(i,i+1) and H(i-1,i,i+1) by Z_1, Z_{2-}, Z_{2+} and Z_3, respectively. By the symmetry it is clear that $Z_{2-}=Z_{2+}$ therefore there remain only three independent functions Z_1, $Z_2\equiv Z_{2-}=Z_{2+}$, and Z_3. From (1.18) it is easily seen that the partition function Z_i corresponding to H_i can be expressed in terms of Z_1, Z_2, and Z_3 as follows

$$Z_i=\sum_{I_1\cdots I_{i-1}I_{i+1}\cdots I_N} Z_s^{\sum_{j\neq i-1,i}(-I_j+1/2)(-I_{j+1}+1/2)+(I_j+1/2)(I_{j+1}+1/2)} \times$$

$$\times\ Z_p^{\sum_{j\neq i-1,i}(I_j+1/2)(-I_{j+1}+1/2)} \times Z_1^{(-I_{i-1}+1/2)(I_{i+1}+1/2)} \times$$

$$\times\ Z_2^{[(-I_{i-1}+1/2)(-I_{i+1}+1/2)+(I_{i-1}+1/2)(I_{i+1}+1/2)]} \times$$

$$\times\ Z_3^{(I_{i-1}+1/2)(-I_{i+1}+1/2)} \qquad (1.20)$$

Using identities $Z_s=\exp[\ln Z_s]$ etc. we get

$$Z_i=e^{(N-2)A_1+A_2}\sum_{I_1\ldots I_{i-1}I_{i+1}\ldots I_N} e^{\sum_{j\neq i-1,i} BI_jI_{j+1}+CI_{i-1}I_{i+1}+D(I_{i-1}-I_{i+1})} \tag{1.21}$$

where A_1 and B are given by (1.4) and

$$\begin{aligned} A_2&=\tfrac{1}{4}(\ln Z_1-2\ln Z_2+\ln Z_3)\\ C&=-\ln Z_1+2\ln Z_2-\ln Z_3\\ D&=\tfrac{1}{2}(\ln Z_3-\ln Z_1-\ln Z_p) \end{aligned} \tag{1.22}$$

The structure of Z_i in (1.21) is again somewhat similar to the partition function of a 1-d Ising model therefore it should be expected to be calculated in some way similar to the transfer matrix method. Let us introduce two matrices P_1 and P_2 defined as follows. P_1 is the matrix with elements

$$\langle I_j|P_1|I_{j+1}\rangle=e^{BI_jI_{j+1}} \tag{1.23}$$

with $j\neq i-1,i+1$; and P_2 is the matrix with elements

$$\langle I_{i-1}|P_2|I_{i+1}\rangle= e^{CI_{i-1}I_{i+1}+D(I_{i-1}-I_{i+1})} \tag{1.24}$$

The right hand side of (1.23) can be written in terms of the matrix elements of these matrices as follows

$$\begin{aligned} Z_i=e^{(N-2)A_1+A_2}\sum_{I_1\ldots I_{i-1}I_{i+1}\ldots I_N} &\langle I_i|P_1|I_2\rangle\ldots\langle I_{i-2}|P_1|I_{i-1}\rangle\ x\\ &x\langle I_{i-1}|P_2|I_{i+1}\rangle\langle I_{i+1}|P_1|I_{i+2}\rangle\ x\\ &x\ldots\langle I_N|P_1|I_1\rangle \end{aligned} \tag{1.25}$$

where N is the number of boxes in the chain.

$$Z_i=e^{(N-2)A_1+A_2}\cdot\ \mathrm{Tr}\{P_1{}^{N-2}P_2\} \tag{1.26}$$

The eigenvalues of P_1 can be easily found. They are

$$\lambda_{1\pm}=(Z_s^{1/2}Z_p^{-1/4}\ \pm\ Z_s^{-1/2}Z_p^{1/4}) \tag{1.27}$$

Denoting the matrix which diagonalizes P_1 by T, and the diagonal matrix elements of the matrix TP_2T^{-1} by $\lambda_{2\pm}$ from (1.26) we have

$$Z_i=e^{(N-2)A_1+A_2(\lambda_{1+}^{N-2}\lambda_{2+}+\lambda_{1-}^{N-2}\lambda_{2-})} \tag{1.28}$$

Since N is very large

$$Z_i=(e^{A_1}\lambda_{1+})^{N-2}e^{A_2\lambda_{2+}} \tag{1.29}$$

λ_{2+} can be easily found. It is

$$\lambda_{2+}=e^{c/4}+e^{-c/4}\ chD \tag{1.30}$$

Comparing (1.29) with (1.6) we see

$$Z_i=Z_o\Delta Z \tag{1.31}$$

where

$$\Delta Z=(e^{A_1}\lambda_{1+})^{-2}e^{A_2\lambda_{2+}} \tag{1.32}$$

Due to the equivalence of the boxes in fact Z_i is independent of the box index and therefore (1.14) gives us

$$Z=Z_o(\Delta Z)^N \tag{1.33}$$

Substituting (1.32) into (1.33) and using (1.4),(1.22), (1.27), and (1.30) we can express the partition function Z in terms of Z_1, Z_2, and Z_3.

c. Calculation of Z_1, Z_2, and Z_3

The Hamiltonian H(i) can be easily diagonalized and therefore the corresponding partition function Z_1 can be easily found

$$Z_1=2Z_s ch(\beta t) \tag{1.34}$$

Assuming that $\beta t<<1$ we have

$$Z_1=2Z_s+Z_s(\beta t)^2 \tag{1.35}$$

In order to calculate Z_2 we write the Hamiltonian $H(i-1,i,i+1)$ in the following form

$$H(i-1,i)=H_o(i-1,i)+2t_i I_i^x \tag{1.36}$$

where

$$H_o(i-1,i)=(-I_i^z+1/2)(U_1-J\vec{\sigma}_{i-1}\vec{\sigma}_i)-\mu\mathcal{H}(\sigma_{i-1}^z+\sigma_i^z) \tag{1.37}$$

The eigenstates of this operator can be easily found. They are

$$\begin{aligned}
\phi_{11}^{\pm}&=\varphi_i^{\pm}|1/2>_{i-1}|1/2>_i \\
\phi_{10}^{\pm}&=\frac{1}{\sqrt{2}}\varphi_i^{\pm}[\,|1/2>_{i-1}|1\bar{/}2>_i+|1\bar{/}2>_{i-1}|1/2>_i\,] \\
\phi_{1\bar{1}}^{\pm}&=\varphi_i^{\pm}|1\bar{/}2>_{i-1}|1\bar{/}2>_i \\
\phi_{00}&=\frac{1}{\sqrt{2}}\varphi_i^{\pm}[\,|1/2>_{i-1}|1\bar{/}2>_i-|1\bar{/}2>_{i-1}|1/2>_i\,]
\end{aligned} \tag{1.38}$$

Where φ_i^+ and φ_i^- are the eigenfunctions of the operator I_i^z with the eigenvalues $+1/2$ and $-1/2$, respectively, $|1/2>_i$ $|1\bar{/}2>_i$ are the eigenfunctions of the operator σ_i^z with the eigenvalues $+1/2$, and $-1/2$, respectively. The signs at ϕ indicate the site of the electron in the box i, the first index indicates the total spin of the pair formed by the electrons in the box i-1 and i, the second index indicates the z-component of the total spin.

The matrix corresponding to the operator $H(i-1,i)$ is denoted by the same symbol. In the basis formed by the system of functions in (1.38) it has the following form

$$H(i-1,i)=Q_{00}^{10}(-2)\oplus Q_{00}^{10}(0)\oplus Q_{00}^{10}(2)\oplus Q_{00}^{02}(0) \tag{1.39}$$

where

$$Q_{p'q'}^{pq}(s)=\begin{pmatrix} pE_1+qE_2+s\mu & t \\ t & p'E_1+q'E_2+s\mu \end{pmatrix} \tag{1.40}$$

The eigenvalues of the matrix H(i-1,i) can be easily found by solving the characteristic equations corresponding to the submatrices in the direct sum (1.39). In this way we obtain

$$Z_2=(1+2ch2\beta\mu\mathcal{H})\left(e^{-\beta(E_1+\frac{t^2}{E_1})}+e^{\beta\frac{t^2}{E_1}}\right)+ \\ +\left(e^{-\beta(E_2+\frac{t^2}{E_2})}+e^{\beta\frac{t^2}{E_2}}\right) \qquad (1.41)$$

The first term in the right hand side of (1.41) is the contribution of the states with S=1, the second term is the contribution of the states with S=0.

In getting this we used the condition $(t/E_\alpha)<<1$ $(\alpha=1,2)$. Assuming that $\beta t<<1$ we have

$$Z_2=(Z_s^2+Z_p)+\left[\frac{(1+2ch2\mu\beta\ )(1-e^{-\beta E_1})}{\beta E_1}+\frac{(1-e^{-\beta E_2})}{\beta E_2}\right](\beta t)^2 \qquad (1.42)$$

The partition function Z_3 can be found in a similar way. Let us write H(i-1,i,i+1) in the following form

$$H(i-1,i,i+1)=H_o(i-1,i,i+1)+2t_i I_i^x \qquad (1.43)$$

where

$$H_o(i-1,i,i+1)=(-I_i^z+1/2)(U_1-J\vec{\sigma}_{i-1}\vec{\sigma}_i)+(I_i^z+1/2)(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})- \\ -\mu\mathcal{H}(\sigma_{i-1}^z+\sigma_i^z+\sigma_{i+1}^z) \qquad (1.44)$$

This operator describes the zero hopping system of the three electrons in the boxes i-1, i and i+1 in which the electron in the box i-1 occupies the right hand site and the electron in the box i+1 occupies the left hand site. In this system the electron in the box i can form pair with the electron in the box i-1 or i+1 depending whether it is situated in the left or right site in its box. Paring with the electron in the box i-1 it leaves the electron in the

box i+1 alone and viceversa. Basing on this the eigenstates of $H_o(i-1,i,i+1)$ can be constructed in the following way. From the eigenfunctions of the operators σ^z_{i-1}, σ^z_i, and σ^z_{i+1} we can construct the following independent functions

$$\chi_1=|1/2>_{i-1}|1/2>_i|1/2>_{i+1}\ , \qquad \chi_5=|1\bar{/}2>_{i-1}|1/2>_i|1/2>_{i+1}$$

$$\chi_2=|1/2>_{i-1}|1\bar{/}2>_i|1/2>_{i+1}\ , \qquad \chi_6=|1\bar{/}2>_{i-1}|1\bar{/}2>_i|1/2>_{i+1} \tag{1.45}$$

$$\chi_3=|1/2>_{i-1}|1\bar{/}2>_i|1/2>_{i+1}\ , \qquad \chi_7=|1\bar{/}2>_{i-1}|1/2>_i|1\bar{/}2>_{i+1}$$

$$\chi_4=|1/2>_{i-1}|1\bar{/}2>_i|1\bar{/}2>_{i+1}\ , \qquad \chi_8=|1\bar{/}2>_{i-1}|1\bar{/}2>_i|1\bar{/}2>_{i+1}$$

The three electrons can be in states of total spin equals to 3/2 or 1/2. The spin functions corresponding to these states can be constructed from the functions in (1.45). For total spin S=3/2 we have four states

$$\chi_{3/2,3/2}=\chi_1\ , \qquad \chi_{3/2,1/2}=\chi_2+\chi_3+\chi_5 \tag{1.46}$$

$$\chi_{3/2,-3/2}=\chi_8\ , \qquad \chi_{3/2,-1/2}=\chi_4+\chi_6+\chi_7$$

For S=1/2 we have eight states

$$\chi^{(1)}_{1/2,1/2}=\frac{1}{\sqrt{2}}(\chi_5-\chi_2)\ , \qquad \chi^{(1)}_{1/2,-1/2}=\frac{1}{\sqrt{2}}(\chi_6-\chi_7)$$

$$\chi^{(2)}_{1/2,1/2}=\frac{1}{\sqrt{2}}(\chi_3-\chi_2)\ , \qquad \chi^{(2)}_{1/2,-1/2}=\frac{1}{\sqrt{2}}(\chi_4-\chi_7) \tag{1.47}$$

$$\chi^{(3)}_{1/2,1/2}=\frac{1}{\sqrt{6}}(\chi_5+\chi_2-2\chi_3)\ , \qquad \chi^{(3)}_{1/2,-1/2}=\frac{1}{\sqrt{6}}(\chi_6+\chi_7-2\chi_4)$$

$$\chi^{(4)}_{1/2,1/2}=\frac{1}{\sqrt{6}}(\chi_3+\chi_2-2\chi_5)\ , \qquad \chi^{(4)}_{1/2,-1/2}=\frac{1}{\sqrt{6}}(\chi_4+\chi_7-2\chi_6)$$

The eigenstates of $H_o(i-1,i,i+1)$ now can be constructed from these spin functions and the isospin functions $\varphi^{\pm}_2$. There are

16 functions of them. For S=3/2 we have

$$\phi^{-}_{3/2,\pm 3/2}=\varphi^{-}_{i}\chi_{3/2,\pm 3/2}\ , \qquad \phi^{+}_{3/2,\pm 3/2}=\varphi^{+}_{i}\chi_{3/2,\pm 3/2}$$
$$\phi^{-}_{3/2,\pm 1/2}=\varphi^{-}_{i}\chi_{3/2,\pm 1/2}\ , \qquad \phi^{+}_{3/2,\pm 1/2}=\varphi^{+}_{i}\chi_{3/2,\pm 1/2} \tag{1.48}$$

For S=1/2 we hawe

$$\phi^{-}_{1/2,\pm 1/2}=\varphi^{-}_{i}\chi^{(1)}_{1/2,\pm 1/2}\ , \qquad \varphi^{+}_{1/2,\pm 1/2}=\varphi^{+}_{i}\chi^{(2)}_{1/2,\pm 1/2}$$
$$\phi'^{-}_{1/2,\pm 1/2}=\varphi^{-}_{i}\chi^{(3)}_{1/2,\pm 1/2}\ , \qquad \varphi'^{+}_{1/2,\pm 1/2}=\varphi^{+}_{i}\chi^{(4)}_{1/2,\pm 1/2} \tag{1.49}$$

where the signs at ϕ indicate the isospin state of the electron in the box i, the first index indicates the total spin of the three electrons, the second index indicates the z-component of the total spin.

From the functions in (1.49) we construct the following symmetric and antisymmetric functions

$$\phi^{S}_{1/2,\pm 1/2}=\frac{1}{2}(\phi^{-}_{1/2,\pm 1/2}+\phi^{+}_{1/2,\pm 1/2}),$$
$$\phi^{a}_{1/2,\pm 1/2}=\frac{1}{2}(\phi^{-}_{1/2,\pm 1/2}-\phi^{+}_{1/2,\pm 1/2})$$
$$\phi'^{,S}_{1/2,\pm 1/2}=\frac{1}{2}(\phi'^{,-}_{1/2,\pm 1/2}+\phi'^{,+}_{1/2,\pm 1/2}),$$
$$\phi'^{,a}_{1/2,\pm 1/2}=\frac{1}{2}(\phi'^{,-}_{1/2,\pm 1/2}-\phi^{+}_{1/2,\pm 1/2}) \tag{1.50}$$

The matrix corresponding to H(i-1,i,i+1) in the basis formed by the system of functions in (1.48) and (1.50) (denoted by the same symbol) has the following form

$$H(i-1,i,i+1)=Q^{10}_{10}(-1)\oplus Q^{10}_{10}(1)\oplus Q^{10}_{10}(-3)\oplus Q^{10}_{10}(3)\oplus$$
$$\oplus\ R^{+}(-1)\oplus R^{-}(1)\oplus R^{+}(1)\oplus R^{-}(-1)\ . \tag{1.51}$$

where $Q^{pq}_{p'q'}(s)$ is given by (1.40) and

$$R^{\pm}(s)=\begin{pmatrix} E_2\pm\frac{t}{2}+s\mu\mathcal{H} & \mp\frac{\sqrt{3}t}{2} \\ \mp\frac{\sqrt{3}t}{2} & E_1\mp\frac{t}{2}+s\mu\mathcal{H} \end{pmatrix} \tag{1.52}$$

The eigenvalues of the matrix H(i-1,i,i+1) can be easily found. The corresponding partition function is

$$Z_3=2Z_s\{e^{-\beta E_1}ch(\beta t)+\left[e^{-\beta E_1+\frac{3(\beta t)^2}{4\beta(E_2-E_1)}}+e^{-\beta E_2-\frac{3(\beta t)^2}{4\beta(E_2-E_1)}}\right]ch(\frac{\beta t}{2})\} \tag{1.53}$$

In getting (1.53) we used the condition $(t/E_\alpha)<<1$ $(\alpha=1,2)$.

The first term in the right hand side of (1.53) is the contribution of the states with S=3/2, the second term is that of the states with S=1/2.

Assuming that $\beta t<<1$ we have

$$Z_3=2Z_sZ_p+Z_s\{[2ch2\beta\mu\mathcal{H}+\frac{1}{4}+\frac{3}{2\beta(E_2-E_1)}]e^{-\beta E_1}+ \\ +[\frac{1}{4}-\frac{3}{2\beta(E_2-E_1)}]e^{-\beta E_2}\}(\beta t)^2 \tag{1.54}$$

d. Free Energy and Magnetic Susceptibility

Making use of (1.33),(1.35),(1.42), and (1.54) we can calculate the partition function Z and therefore the free energy. The result is

$$F=F_o+\Delta F_1+\Delta F_2+\Delta F_3 \tag{1.55}$$

where F_o is the free energy of the zero hopping system, ΔF_γ $(\gamma=1,2,3)$ are the contributions of the hopping corresponding to the configurations shown in Figs. 6a, 6b and 6c, and 6d, respectively.

$$\Delta F_1=\frac{(\beta t)^2}{2\beta(Z_s+Z_p^{1/2})^2}\,Z_p^{1/2}Z_s$$

$$\Delta F_2=\frac{(\beta t)^2}{\beta(Z_s+Z_p)^2}\,\frac{(1+2ch2\beta\mu\mathcal{H})(1-e^{-\beta E_1})}{\beta E_1}+\frac{1-e^{-\beta E_2}}{\beta E_2}$$

$$\Delta F_3=-\frac{(\beta t)^2}{2\beta(Z_s+Z_p^{1/2})^2}\,Z_p^{-1/2}Z_s\{[2ch2\beta\mu\mathcal{H}+\frac{1}{4}+\frac{3}{2\beta(E_2-E_1)}]e^{-\beta E_1}+ \\ +[\frac{1}{4}+\frac{3}{2\beta(E_2-E_1)}]e^{-\beta E_2}\} \tag{1.56}$$

(1.55) is nothing but the perturbational expansion of the free energy in powers of (βt) up to the second order.

In principle, this result can be obtained by using the conventional thermodynamical perturbation theory, in practice, however, we can not do it because of the high degeneracy of our system. By (1.13) the free energy is an even function of t. Its expansion in powers of (βt) contains only even powers. This is the consequence of the equivalence of the two sites in each box.

The magnetic susceptibility can be obtained directly by using (1.55) and (1.56). The result is

$$\chi_h=\chi_{h_o}+\Delta\chi_{h_1}+\Delta\chi_{h_2}+\Delta\chi_{h_3} \tag{1.57}$$

where χ_{h_o} is the magnetic susceptibility of the zero hopping system given by (1.7) and $\Delta\chi_{h_\gamma}$ $(\gamma=1,2,3)$ are the contributions of the hopping corresponding to the configurations shown in Fig. 6.

$$\Delta\chi_{h_1}=(\beta t)^2\,\frac{N\beta\mu^2}{(2+\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}})^3\sqrt{3e^{-\beta E_1}+\beta E_2}}\quad x$$

$$x\ (2-\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}})(e^{-\beta E_1}-e^{-\beta E_2})$$

$$\Delta\chi_{h_2}=(\beta t)^2\,\frac{4N\beta\mu^2}{(2+\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}})^3\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}}}\quad x$$

$$x\ \Big[\ \frac{(1-e^{-\beta E_1})(\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}}+2e^{-\beta E_2})}{\beta E_1}\quad -$$

$$-\ \frac{(1-e^{-\beta E_2})(\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}}+2e^{-\beta E_1})}{\beta E_2}\ \Big]$$

$$\Delta\chi_{h_3}=(\beta t)^2\frac{N\beta\mu^2}{(2+\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}})^3\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}}}\ x$$

$$x\ \{(2-\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}})(e^{-\beta E_1}-e^{-\beta E_2})\ -$$

$$-\frac{3[(14+9\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}})e^{-\beta E_1}+(2-\sqrt{3e^{-\beta E_1}+e^{-\beta E_2}})e^{-\beta E_2}]}{2\beta(3e^{-\beta E_1}+e^{-\beta E_2})}\ x$$

$$x[(\frac{1}{E_2-E_1}-\frac{1}{2}\beta)e^{-\beta E_1}-(\frac{1}{E_2-E_1}+\frac{1}{2}\beta)e^{-\beta E_2}]\}\qquad(1.58)$$

For hopping small enough we can find its contribution at low temperatures by expanding (1.58).

(i) In the case $E_1>0$ and $E_2>0$ we find $\Delta\chi_{h_1}=\Delta\chi_{h_3}=0$ and

$$\Delta\chi_{h_2}=\frac{1}{2}(\beta t)^2N\beta\mu^2(\frac{1}{\beta E_1}-\frac{1}{\beta E_2})\qquad(1.59)$$

If $J>0$ we have approximately

$$\Delta\chi_{h_2}=\frac{N\mu^2}{2E_1}(\beta t)^2\qquad(1.60)$$

It is the contribution of the hopping corresponding to the configuration shown in Fig.6b (or Fig.6c) in state with S=1 (Fig.7a). If $J<0$ we have approximately

$$\Delta\chi_{h_2}=-\frac{N\mu^2}{2E_2}\qquad(1.61)$$

This is the contribution of the hopping corresponding to the configuration shown in Fig.6b (or Fig.6c) in state with S=0 (Fig.7b).

(ii) In the case $E_1<0$ and $J>0$ we find $\Delta\chi_{h_2}=0$ and

$$\Delta\chi_{h_1}=-\frac{1}{3\sqrt{3}}(\beta t)^2N\beta\mu^2e^{\frac{1}{2}\beta E_1}\qquad(1.62)$$

$$\Delta\chi_{h_3} = \frac{1}{3\sqrt{3}}(\beta t)^2 N\beta\mu^2 [2e^{\frac{1}{2}\beta E_1} - \frac{3}{4}e^{\frac{1}{2}\beta E_1}] \qquad (1.63)$$

$\Delta\chi_{h_1}$ can be associated with the break of a triplet pair to form the configuration shown in Fig.6a (Fig.8a). The first term in (1.63) corresponds to the break of a triplet pair to form the configuration shown in Fig.6d in state with S=3/2 (Fig.8b), the second term corresponds to the break of a triplet pair to form the configuration shown in Fig.6d in state with S=1/2 (Fig.8c)

(iii) In the case $E_2<0$ and $J<0$ we find $\Delta\chi_{h_2}=0$ and

$$\Delta\chi_{h_1} = (\beta t)^2 N\beta\mu^2 e^{\frac{1}{2}\beta E_2} \qquad (1.64)$$

$$\Delta\chi_{h_3} = \frac{1}{4}(\beta t)^2 N\beta\mu^2 e^{\frac{1}{2}\beta E_2} \qquad (1.65)$$

$\Delta\chi_{h_1}$ corresponds to the break of a singlet pair to from the configuration shown in Fig.6a (Fig.9a), $\Delta\chi_{h_3}$ can be associated with the break of a singlet pair to form the configuration shown in Fig.6d, in state with S=1/2 (Fig.9b). From (1.54) it is clear that at low temperature the configuration shown in Fig.6d in state with S=3/2 gives no contribution.

II. DIELECTRIC PROPERTIES

1. Zero Hopping Case

The box model contains not only spin but also coordinate variables therefore it can also be used to describe the dielectric properties of corresponding systems.

Let us consider the model in a static electric field . The Hamiltonian of the system is

$$H'=H'_o+2t\Sigma_i I_i^x \tag{2.1}$$

where

$$H'_o=\Sigma_i(I_i^z+1/2)(I_{i+1}^z)(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})+e\mathcal{E}\Sigma_i I_i^z \tag{2.2}$$

is the Hamiltonian of the zero hopping system in the field.

The problem with H'_o can also be solved exactly in the same way as when solving the problem with H_o in Section I. The partition function Z'_o corresponding to H'_o can be found by taking the trace in the real spin space first. After doing this we get

$$Z'_o=e^{NA_1}\sum_{I_1\cdots I_N} e^{\Sigma_i[B'I_iI_{i+1}-\beta e\mathcal{E}I_i]} \tag{2.3}$$

where

$$A'_1=\frac{1}{4}\ln Z'_p+\frac{1}{2}\ln Z'_s$$
$$B'=2\ln Z'_s-\ln Z'_p \tag{2.4}$$

with

$$Z'_s=2, \quad Z'_p=3e^{-\beta E_1}+e^{-\beta E_2} \tag{2.5}$$

The second factor in the right hand side of (2.3) again is the partition function of a 1-d Ising model in an external field therefore it can be calculated by using the conventional transfer matrix method. The result is

$$Z'_o=(Z'_s ch\tfrac{1}{2}\beta e\mathcal{E}+\sqrt{Z'^2_s sh^2\tfrac{1}{2}\beta e\mathcal{E}+Z'_p})^N \qquad (2.6)$$

The dielectric susceptibility can be obtained directly from (2.6)

$$\chi_{eo}=\frac{N\beta e^2}{2\sqrt{3e^{\beta E_1}+e^{-\beta E_2}}} \qquad (2.7)$$

This quantity is always positive. Thus the zero hopping system is paraelectric. At $T=0^oK$ $\Delta\chi_{eo}$ diverges when $U_1-J>0$ and $U_1+3J>0$, and becomes zero when $U_1-J<0$ and $J>0$ as well as when $U_1+3J<0$ and $J<0$. This indicates some charge ordering in the ground state. Namely, as it can be easily seen, the ground state is ferroelectric in the first case and antiferroelectric in the second and third cases, and at high temperatures when even $\beta E_\alpha \ll 1$ $(\alpha=1,2)$ we have

$$\chi_{eo}=\frac{N\beta e^2}{4}(1+\tfrac{1}{2}\beta U_1) \qquad (2.8)$$

The first term has the form of the Curie law describing the free dipol- moment system. The second term describes the effect of the Coulomb interaction. The latter supports or prevents the polarization depending whether it is repulsion or attraction thereby $\chi_{eo}(U_1>0)>\chi_{eo}(U_1<0)$ as it can be seen from (2.8).

2. Finite Hopping Case

a. Independent Hopping Approximation

The problem with Hamiltonian H' can not be solved exactly. It can, however, be solved approximately if βt is small.

Since the eigenstates of H'_o have the same structure as that of H_o the same reasoning as in Section I. can be used here to get

$$Z'=Z'_{oi}\prod\frac{Z'_i}{Z'_o} \qquad (2.9)$$

where Z' is the partition function corresponding to H', Z'_i is the partition function of the single hopping system described by the following Hamiltonian

$$H'_i=H'_o+2t_iI_i^x \tag{2.10}$$

b. Modified Transfer Matrix Method

The function Z'_i can be calculated in similar way as when calculating Z_i in Section I. By using identity (1.17) we can write H'_i in the following form

$$H'_i=\sum_{j\neq i-1,i}(I_j^i+1/2)(-I_{j+1}^z+1/2)(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})+e\mathcal{E}\sum_{j\neq i}I_i^z +$$

$$+(-I_{i-1}^z+1/2)(I_{i+1}^z+1/2)H'(i)+(I_{i-1}^z+1/2)(-I_{i+1}^z+1/2)H'(i-1,i,i+1)+$$

$$+(I_{i-1}^z+1/2)(I_{i+1}^z+1/2)H'(i-1,i)+(-I_{i-1}^z+1/2)(-I_{i+1}^z+1/2)H'(i,i+1) \tag{2.11}$$

where

$$H'(i)=2t_iI_i^x+e\mathcal{E}I_i^z \tag{2.12}$$

$$H'(i-1,i)=(-I_i^z+1/2)(U_1-J\vec{\sigma}_{i-1}\vec{\sigma}_i)+2t_iI_i^x+e\mathcal{E}I_i^z \tag{2.13}$$

$$H'(i,i+1)=(I_i^z+1/2)(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})+2t_iI_i^x+e\mathcal{E}I_i^z \tag{2.14}$$

$$H'(i-1,i,i+1)=(-I_i^z+1/2)(U_1-J\vec{\sigma}_{i-1}\vec{\sigma}_i)+(I_i^z+1/2)(U_1-J\vec{\sigma}_i\vec{\sigma}_{i+1})$$
$$+2t_iI_i^x+e\mathcal{E}I_i^z \tag{2.15}$$

The structure of (2.11) is the same as (1.18) therefore the same arguments as in Section I. can be used here. By using the identity

$$\sum_{j\neq i}I_j=\frac{1}{2}\sum_{j\neq i-1,i}(I_j+I_{j+1})+\frac{1}{2}(I_{i-1}+I_{i+1}) \tag{2.16}$$

which can be easily proved by using the cyclic boundary condition

$$I_{N+1}=I_1 \tag{2.17}$$

we can write Z'_i in the following form

$$Z'_i = e^{(N-2)A'_1+A'_2} \sum_{I_1 \cdots I_{i-1} I_{i+1} \cdots I_N} e^{\sum_{j \neq i-1,i} B' I_j I_{j+1} - \frac{1}{2}(I_j + I_{j+1})} \times e^{C' I_{i-1} I_{i+1} + D^- I_{i-1} - D^+ I_{i+1}} \tag{2.18}$$

where A'_1 and B' are given by (2.4) and

$$\begin{aligned} A'_2 &= \tfrac{1}{4}(\ln Z'_1 + \ln Z'_2 + \ln Z'_2 + \ln Z'_3) \\ C' &= -\ln Z'_1 + \ln Z'_{2-} + \ln Z'_{2+} - \ln Z'_3 \\ D^{\pm} &= \tfrac{1}{2}(\ln Z'_3 - \ln Z'_1 \mp \ln Z'_{2-} \pm \ln Z'_{2+} \pm \beta e \mathcal{E} - \ln Z'_p) \end{aligned} \tag{2.19}$$

where Z'_1, Z'_{2-}, Z'_{2+}, and Z'_3 are the partition functions corresponding to $H'(i)$, $H'(i-1,i)$, $H'(i,i+1)$, and $H'(i-1,i,i+1)$ respectively. In order to calculate the right hand side of (2.18) let us indtroduce the matrices P_1 and P_2 with matrix elements

$$\langle I_j | P_1 | I_{j+1} \rangle = e^{B' I_j I_{j+1} - \frac{1}{2}\beta e \mathcal{E}(I_j + I_{j+1})} \tag{2.20}$$

with $j \neq i-1, i+1$ and

$$\langle I_{i-1} | P'_2 | I_{i+1} \rangle = e^{C' I_{i-1} I_{i+1} + D^- I_{i-1} - D^+ I_{i+1}} \tag{2.21}$$

Relation (2.18) then can be written as

$$Z'_i = e^{(N-2)A'_1+A'_2} \operatorname{Tr}\{P'^{N-2}_1 P'_2\} \tag{2.22}$$

The eigenvalues of P'_1 can be easily found. They are

$$\lambda_{1\pm} = Z'^{-1/2}_s Z'^{-1/4}_p \left(Z'_s \operatorname{ch} \tfrac{1}{2}\beta e \mathcal{E} \pm \sqrt{Z'^2_s \operatorname{sh}^2 \tfrac{1}{2}\beta e \mathcal{E} + Z'_p}\right) \tag{2.23}$$

Denoting the matrix which diagonalizes P'_1 by T' and the diagonal matrix elements of the matrix $T' P'_2 T'^{-1}$ by $\lambda'_{2\pm}$ from (2.22) we have

$$Z'_i=e^{(N-2)A'_1+A'_2}(\lambda_{1+}{}^{N-2}\lambda'_{2+}+\lambda'_{1-}{}^{N-2}\lambda'_{2-}) \tag{2.24}$$

For large N we have approximately

$$Z'_i=(e^{A'_1}\lambda'_{1+})^{N-2}e^{A'_2}\lambda'_{2+} \tag{2.25}$$

λ'_{2+} can be easily found. A simple calculation gives us

$$\lambda'_{2+}=\frac{[\sqrt{sh^2\frac{1}{2}\beta e\mathcal{E}+e^{-B'}}\,ch(D_-/2)+sh(\frac{1}{2}\beta e\mathcal{E})sh(D_-/2)]e^{\frac{C'}{4}}+e^{\frac{B'}{2}-\frac{C'}{4}}ch(D_+/2)}{\sqrt{e^{B'}Sh^2\frac{1}{2}\beta e\mathcal{E}+1}} \tag{2.26}$$

where

$$D_\pm=D^+\pm D^- \tag{2.27}$$

Comparing (2.25) with (2.6) we see

$$Z'_i=Z'_o\Delta Z' \tag{2.28}$$

where

$$\Delta Z'=(e^{A'_1}\lambda'_{1+})^{-2}e^{A'_2}\lambda'_{2+} \tag{2.29}$$

Due to the equivalence of the boxes Z'_i in fact is independent of the box index therefore from (2.9) and (2.28) we have

$$Z'=Z'_o(\Delta Z')^N \tag{2.30}$$

c. Calculation of Z'_1, $Z'_{2\pm}$, and Z'_3

The Hamiltonian H'(i), H'(i-1,i), and H'(i,i+1)can be exactly diagonalized in the same way as when treating with H(i), H(i-1,i), and H(i,i+1) in Section I. The Hamiltonian H'(i-1,i,i+1) can not be diagonalized exactly. Its spectrum can be found approximately by treating the last term in (2.15) as a small perturbation and using the perturbation theory. In this way we find

$$z_1' = 4\mathrm{ch}\left(\beta t + \frac{\beta e^2 \mathcal{E}^2}{8t}\right)$$

$$z_{2\pm}' = 3\{\exp[-\beta(E_1 + \frac{t^2}{E_1} \pm M_1 e\mathcal{E} + N_1 e^2\mathcal{E}^2)] +$$

$$+\exp[\beta(\frac{t^2}{E_1} \pm M_1 e\mathcal{E} + N_1 e^2\mathcal{E}^2)]\} +$$

$$+ \exp[-\beta(E_2 + \frac{t^2}{E_2} \pm M_2 e\mathcal{E} + N_2 e^2\mathcal{E}^2)] +$$

$$+\exp[\beta(\frac{t^2}{E_2} \pm M_2 e\mathcal{E} + N_2 e^2\mathcal{E}^2)]\} .$$

$$z_3' = 4[e^{-\beta(E_1 + t + \frac{e^2\mathcal{E}^2}{8t})} + e^{-\beta(E_1 - t - \frac{e^2\mathcal{E}^2}{8t})}] +$$

$$+ 2[e^{-\beta(E_1 - \frac{t}{2} - \frac{3t^2}{4(E_2 - E_1)} - \frac{e^2\mathcal{E}^2}{4t})} + e^{-\beta(E_1 + \frac{t}{2} - \frac{3t^2}{4(E_2 - E_1)} + \frac{e^2\mathcal{E}^2}{4t})}] +$$

$$+ 2[e^{-\beta(E_2 + \frac{t}{2} + \frac{3t^2}{4(E_2 - E_1)} - \frac{15e^2\mathcal{E}^2}{336(E_2 - E_1)})} +$$

$$+ e^{-\beta(E_2 - \frac{t}{2} + \frac{3t^2}{4(E_2 - E_1)} + \frac{15e^2\mathcal{E}^2}{336(E_2 - E_1)})}] \qquad (2.31)$$

where

$$M_\alpha = \frac{1}{2} \frac{E_\alpha}{(E_\alpha^2 + 4t^2)^{1/2}} \quad ; \quad N_\alpha = \frac{t^2}{(E_\alpha^2 + 4t^2)^{3/2}}$$

$$(\alpha = 1, 2) \qquad (2.32)$$

In getting (2.31) we assumed that $t \gg \mathcal{E}$ therefore the results obtained in the following are true only for $t \neq 0$.

d. Free Energy and Dielectric Susceptibility

By making the use of (2.29), (2.30), and (2.31) it can be easily seen that the free energy of the system is an even function of the electric field. This is quite general result and independent of the approximations used. It is the consequence

of the left-right symmetry of the system under consideration. Since for our system there is no difference between the left and right the free energy is of course independent of the direction of the field.

For the dielectric susceptibility we find

$$\chi_e = \chi_{eo} + \Delta\chi_e \tag{2.33}$$

where χ_{eo} is the dielectric susceptibility of the zero hopping system, $\Delta\chi_e$ is the contribution of the hopping.

$$\Delta\chi_e = \frac{1}{2}N\beta e^2\{-2Z_p'^{-1/2} - \frac{1}{2}e^{B'/4} +$$

$$+S_1+S_2+S_3+ \frac{1}{e^{C'/4}+e^{-C'/4}\,chD'}\{e^{C'/4}[S_2-S_1+$$

$$+ S_3+\frac{1}{2}(2S\, e^{B'/4}+e^{3B'/4})^2]+e^{-C'/4}\,[2(S_3-S_1)\,x$$

$$x\ shD'-(S_2-S_1+S_3)chD'\}\} \tag{2.34}$$

where

$$S_1 = \frac{1}{Z_1'}\,\frac{sh(\beta t/2)ch(\beta t/2)}{\beta t}$$

$$S_2 = -\frac{1}{Z_2'}\,\frac{2}{\beta}[3N_1(e^{-\beta(E_1+\frac{t^2}{E_1})} - e^{\beta\frac{t^2}{E_1}}) +$$

$$+ N_2(e^{-\beta(E_2+\frac{t^2}{E_2})} - e^{\beta\frac{t^2}{E_2}})]$$

$$S_3 = -\frac{1}{Z_3'}\,e^{-\beta E_1}\frac{sh(\beta t/2)}{\beta t}[e^{\frac{\beta t^2}{4(E_2-E_1)}} - 2ch(\frac{\beta t}{2})]$$

$$S = \frac{1}{2} - \frac{1}{Z_2'}\{3M_1[e^{-\beta(E_1+\frac{t^2}{E_1})} - e^{\beta\frac{t^2}{E_1}}] +$$

$$M_2[e^{-\beta(E_2+\frac{t^2}{E_2})} - e^{\beta\frac{t^2}{E_2}}]\} \tag{2.35}$$

in which Z_1', Z_2', Z_3', and C' and D' are determined by (1.34), (1.41),(1.54), and (1.22), respectively with $\mathcal{H}$=0.

At high temperature when even $\beta E_\alpha << 1$ (α=1,2) we have approximately

$$\chi_e = \frac{N\beta e^2}{2}\{\frac{1}{6} + \frac{3}{8}\beta U_1 - \frac{1}{36}\beta(U_1-J)\} \qquad (2.36)$$

Comparing (2.36) with (2.7) we see that at the same temperature the dielectric susceptibility of the finite hopping system is smaller than that of the zero hopping one. This is the direct consequence of the fact that the hopping breaks the order which has been established by the field.

CONCLUDING REMARKS

The method used here can clearly be generalized to consider the effect of the hopping on the behaviour of the 3-d box model coupled by the Coulomb interaction [3].

Since the method is based on the uncorrelated hopping processes, which take place only at finite temperature, it can not be used to consider the effect of the hopping on the ground state. This problem is hoped to be solved by using the variational method [4].

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FIGURE CAPTIONS

Fig.1. Schematic representation of ordered salts of (DONOR) $(TCNQ)_2$ with alternating donor-ion dipole moments. The donor sites are represented by arrows and the dimerised acceptor sites by open circuits.

Fig.2. The structure of an acceptor chain ($d_1 < d_2$)

Fig.3. The processes giving contributions to the magnetic susceptibility at low temperatures in the case $E_1 > 0$ and $E_2 > 0$

Fig.4. The processes giving contributions to the magnetic susceptibility at low temperatures in the case $E_1 < 0$ and $J > 0$.

Fig.5. The processes giving contributions to the magnetic susceptibility at low temperatures in the case $E_2 < 0$ $J < 0$

Fig.6. The configurations corresponding to the four Hamiltonian in (1.19).

Fig.7. The processes corresponding to the contribution of the hopping to the magnetic susceptibility at low temperatures in the case $E_1 > 0$ $E_2 > 0$.

Fig.8. The processes corresponding to the contribution of the hopping to the magnetic susceptibility at low temperatures in the case $E_1 < 0$ and $J > 0$.

Fig.9. The processes corresponding to the contribution of the hopping to the magnetic susceptibility at low temperatures in the case $E_2 < 0$ and $J < 0$.

Fig. 1.

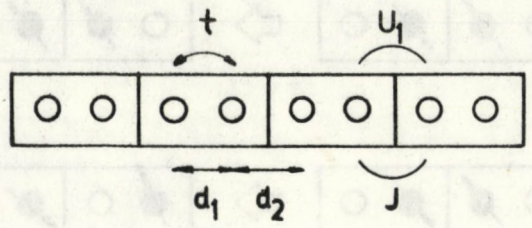


Fig. 2.

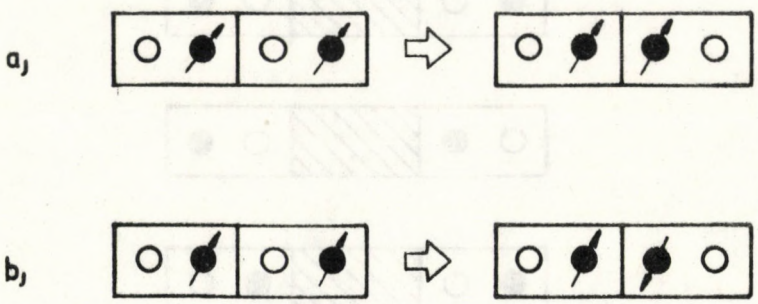
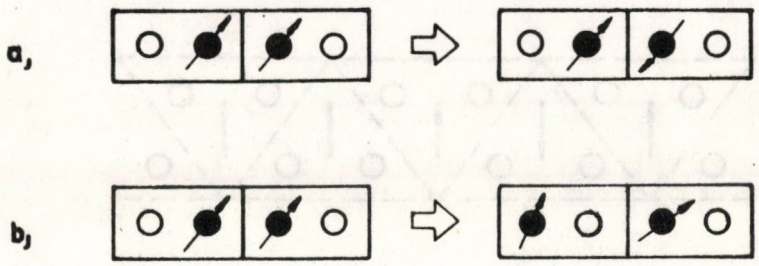


Fig. 3.



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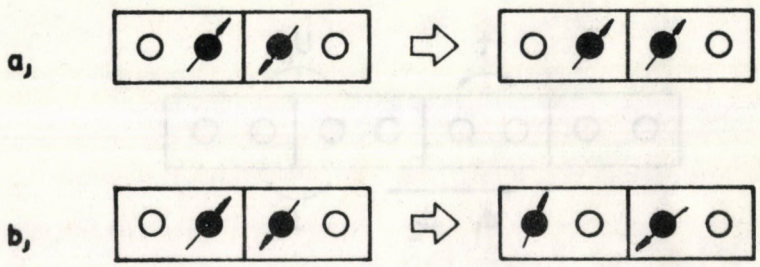

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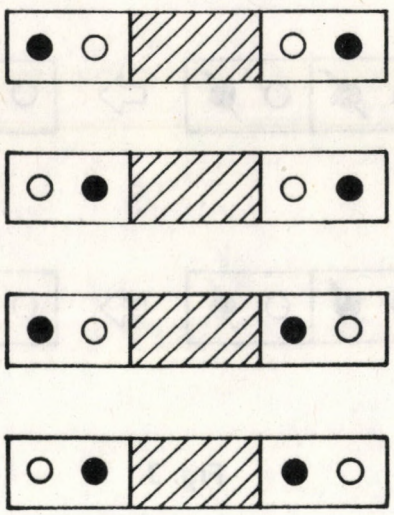

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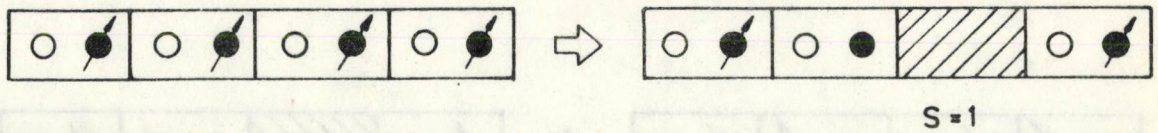

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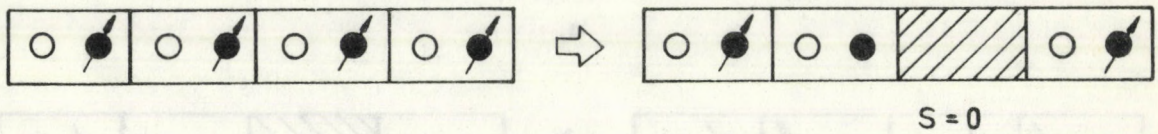
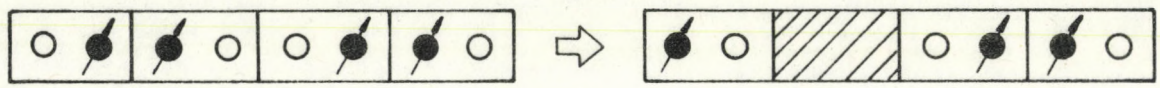


b)

Fig. 7.



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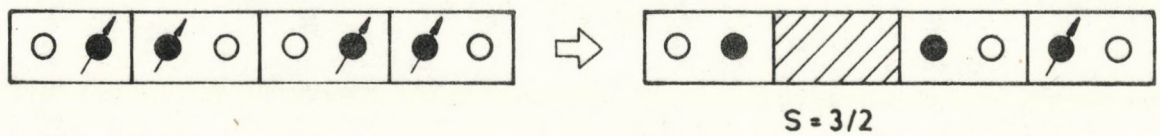

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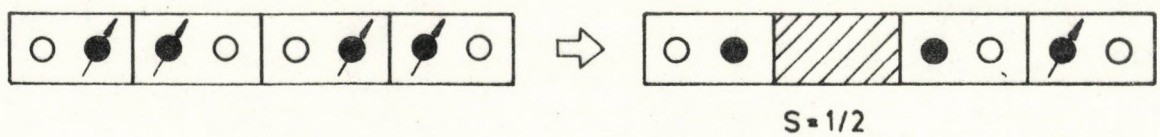

c)

Fig. 8.

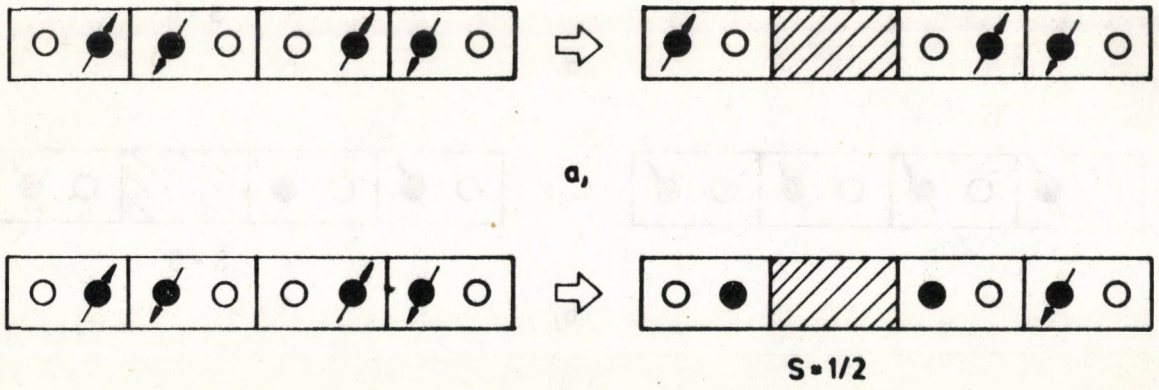

Fig. 9.

Kiadja a Központi Fizikai Kutató Intézet
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Szakmai lektor: Zawadowski Alfréd
Nyelvi lektor Woynarovich Ferenc
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