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# A MODIFIED FORM OF THE POLAR MODEL OF CRYSTALS*

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A modified form of the polar model of crystals is proposed. A peculiarity of the model is the dependence of the hopping integral on the site occupation. In the cases of weak and strong interactions the effective model Hamiltonian, which generalises the known forms of the effective Hamiltonian, is derived. It is shown that the model has the electron-hole asymmetry, in contrast to the Hubbard model. The metal-insulator transition within the model is also studied. The obtained results are compared with experimental data for narrow-band materials. Some specific narrow-band effects are discussed.

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## 1. Introduction

**1.** The fact that unique properties of narrow-band systems (for example oxides, sulphides and selenides of transition metals) are caused by electron-electron interactions is generally accepted in our time. But, in spite of the great number of the papers concerning this problem, it is still an actual problem of condensed matter physics to construct the consistent theory of narrow-band systems. During the recent years the range of problems connected with the correlation problem and an importance of investigating the narrow band systems have intensified with the discovery of high-$T_{\rm c}$ superconductors.

Important problems can be separated into three groups:

(1) a construction of the narrow-band-system models using adequate Hamiltonians;

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(2) an elaboration of effective mathematical methods to study those model Hamiltonians;

(3) a construction of the consistent theory of correlation effects and an explanation of peculiarities of physical properties in the narrow-band systems.

Problems (1) and (2) had been considered and partially solved by Shubin and Vonsovsky within their famous polar model [1]. In this a model Hamiltonian and its "configurational" representation had been proposed. The polar model proves to be very meaningful due to the heuristic value of "configurational" description idea (basic for model treatment of $3d$-compounds [2].) In the frame of the polar model a criterion of metal-insulator transition (MIT) was formulated for the first time; an explanation of fractional atom momentum in transition $3d$-metals, a hypothesis of the possibility of charge ordering were also proposed; a possibility of having a gapeless semiconductor and superexchange interaction were predicted. Commonly used Hubbard model is a partial case of the polar model [3].

However, a direct use of the polar model (in the traditional form [1]) to solve the problems had been proved to be not effective in many cases.

Firstly, the transition from the second quantisation Hamiltonian in terms of electron operators to its representation in terms of Shubin–Vonsovsky operators had been realized by the substitution of some combination of electron operators through the combination of Shubin–Vonsovsky operators with the same action on the wave function. Such transition is cumbersome and difficult even for the $s$-band situation (see for example [4]).

Secondly, the approximations underlying the mathematical treatment of the polar model are uncontrollable (first of all, the postulation of Bose-type commutation rules for the operators of current excitation).

**2.** The polar model theory was developed in two ways. The first one is connected with developing the methods of effective mathematical treatment of initial polar model Hamiltonian in the electron representation. The fundamental results in this way belong to Bogolubov [5]. He proposed the effective Hamiltonian method which took into account high energy electron states with the help of special form of the perturbation theory. This method is one of the most consistent approaches to study of the exchange interactions in magnetic insulators [6]. A use of the configurational representation of the polar model (polar and homeopolar states) proved to be helpful for interpretation of the obtained results, and control of the performed calculations (sometimes very bulky).

The second way is based on a direct use of the configurational representations. This approach is effective for investigation of peculiarities of narrow-band systems, insulators and semiconductors, on one hand, metals and materials in which MIT is caused by external influences, on the other.

Important achievement in this way was obtained in the works of Lviv branch in theory of solids. Here the works [7, 8, 9] of Glauberman, Vladimirov, Stasyuk were precursory. In this way, the important problems of the polar model of non-metallic crystals (the problem of constructing model Hamiltonians in the terms of site elementary excitations and the problem of commutation rules for operators of site elementary excitations) were solved.

**3.** The wide use of the configurational forms of model Hamiltonians to consider physical properties of narrow-band materials is associated with paper of Hubbard [10] in which $X_i^{kl}$-operators had been introduced and papers [11, 12] where the relation between electron- and transition-operators had been first established, an effective form of perturbation theory had been proposed. It had been shown that the proper identification of the Shubin–Vonsovsky operators and transition-operators (the Hubbard operators) leads to formal equivalence of the traditional form of the polar model and its modern representations in terms of transition-operators. It also had been shown that

$$X_i^{kl} = \alpha_{ik}^{\dagger}\alpha_{il},$$

where $\alpha_{ik}^{\dagger}$, $\alpha_{il}$ — Shubin–Vonsovsky operators of creation and destruction of $|k\rangle$-state and $|l\rangle$-state respectively on $i$-site.

An expediency of using $X_i^{kl}$- or $\alpha_{i\nu}^{\dagger}\alpha_{i\mu}$-representation is predicted by requirements of considered problem. In calculations using diagrammatic Green functions technique or perturbation theory it is convenient to use $X_i^{kl}$-representation of Hamiltonian [13], in problems using approximate second quantisation method (*e.g.* to study MIT using the mean-field approximation (MFA) in generalised Hartree–Fock approximation [14]) $\alpha_{i\nu}^{\dagger}\alpha_{i\mu}$-representation is more convenient. The $b$-$c$-representation (see Ref. [14]) can also be useful.

**4.** The representation of a narrow-band Hamiltonian in the terms of $X_i^{kl}$, $b$-$c$- or $\alpha_{i\nu}^{\dagger}\alpha_{i\mu}$-operators are helpful for understanding the correlation effects, to explain physical properties of narrow-band materials. This representation is convenient from the point of view of mathematical treatment of models.

Below a consistent form of the polar model of narrow-band materials is proposed and the consequences derived from this model are discussed.

## 2. The Hamiltonian

Hamiltonian of the system of $s$-electrons in the Wannier-representation is written as

$$\begin{aligned} H \; = \; & -\mu\sum_{i\sigma} a^{\dagger}_{i\sigma}a_{i\sigma} + {\sum}'_{ij\sigma} t(ij)a^{\dagger}_{i\sigma}a_{j\sigma} \\ & +\frac{1}{2}\sum_{\substack{ijkl\\ \sigma,\sigma'}} J(ijkl)a^{\dagger}_{i\sigma}a_{j\sigma'}a_{l\sigma'}a_{k\sigma}\,, \end{aligned} \tag{2.1}$$

where $a^{\dagger}_{i\sigma}$, $a_{i\sigma}$ — creation and destruction operators of electron on site $i$, $\sigma =\uparrow,\downarrow$, $\mu$ — chemical potential, $n_{i\sigma} = a^{\dagger}_{i\sigma}a_{i\sigma}$, and

$$t(ij) \; = \; \int \phi^*(\boldsymbol{r}-\boldsymbol{R}_i)\sum_n V(\boldsymbol{r}-\boldsymbol{R}_n)\phi(\boldsymbol{r}-\boldsymbol{R}_j)d\boldsymbol{r}\,, \tag{2.2}$$

$$\begin{aligned} J(ijkl) \; = \; & \int\int \phi^*(\boldsymbol{r}-\boldsymbol{R}_i)\phi(\boldsymbol{r}-\boldsymbol{R}_k)\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \\ & \times\phi^*(\boldsymbol{r}'-\boldsymbol{R}_j)\phi(\boldsymbol{r}'-\boldsymbol{R}_l)d\boldsymbol{r}d\boldsymbol{r}'\,, \end{aligned} \tag{2.3}$$

are respectively the matrix elements which describe hoppings of electrons between nearest-neighbour sites of lattice ($V(\boldsymbol{r}-\boldsymbol{R}_i)$ is the potential energy of electron interacting with an ion on $i$-site), and the electron–electron interactions. The prime by the second sum in Eq. (2.1) means that $i \neq j$.

Narrow energy bands allow to simplify Hamiltonian (2.1). Here wave functions closely resemble atomic 3$d$-functions (their overlapping decrease quickly with increase of the inter-atomic spacing), so matrix elements $t(ij)$ and $J(ijkl)$ can be estimated from degree of overlapping. Thus quantities $J(iiii)$ and $J(ikik)$ will be of zero order, $J(iiij)$, $J(ijkj)$ — of first order (as $t(ij)$), $J(ijkl)$ at $i\neq k$, $j\neq l$ — of second order (immediate estimation of $J(ijkl)$ is given in the paper [3]). In accordance with this we limit ourselves to accounting in Hamiltonian (2.1) matrix elements $J(iiii) = U$, $J(ijij) = V(ij)$ ($i$ and $j$ are nearest neighbours), $J(iiij) = T(ij)$, $J(ijkj)$ ($k\neq i$, $k\neq j$), $J(ijji) = J(ij)$; taking into account quantity of second order $J(ij)$ is on principle necessary to describe ferromagnetism in this model in Mott–Hubbard insulator state. Then

$$\begin{aligned} H = \; - \; & \mu\sum_{i\sigma} a^{\dagger}_{i\sigma}a_{i\sigma} + {\sum}'_{ij\sigma} a^{\dagger}_{i\sigma}(t(ij) + \sum_k J(ikjk)n_k)a_{j\sigma} + U\sum_i n_{i\uparrow}n_{i\downarrow} \\ + \; & \frac{1}{2}{\sum}'_{ij\sigma\sigma'} J(ij)a^{\dagger}_{i\sigma}a^{\dagger}_{j\sigma'}a_{i\sigma'}a_{j\sigma} + \frac{1}{2}{\sum}'_{ij\sigma\sigma'} V(ij)n_{i\sigma}n_{j\sigma'}\,, \end{aligned} \tag{2.4}$$

where $n_i = n_{i\uparrow} + n_{i\downarrow}$.

In Hamiltonian (2.4) we rewrite the sum $\sum'_{ij\sigma k} J(ikjk)a^{\dagger}_{i\sigma}n_k a_{j\sigma}$ in the form

$$\sum_{ij\sigma}{}' \sum_{\substack{k\neq i\\ k\neq j}} J(ikjk)a^{\dagger}_{i\sigma}n_k a_{j\sigma} + \sum_{ij\sigma}{}' \left(J(iiij)a^{\dagger}_{i\sigma}a_{j\sigma}n_{i\bar{\sigma}} + \text{h.c.}\right) \tag{2.5}$$

($\bar{\sigma}$ denotes spin projection which is opposite to $\sigma$). We suppose (as in papers [14, 15]) that

$$\sum_{ij\sigma}{}' \sum_{\substack{k\neq i\\ k\neq j}} J(ikjk)a^{\dagger}_{i\sigma}n_k a_{j\sigma} = n \sum_{\substack{k\neq i\\ k\neq j}} J(ikjk) \sum_{ij\sigma}{}' a^{\dagger}_{i\sigma}a_{j\sigma}$$

with $n = \langle n_{i\uparrow} + n_{i\downarrow}\rangle$ (sites $i$ and $j$ are nearest neighbours). It should be noted that this supposition is exact in the homeopolar limit ($n_i = 1$).

Thus Hamiltonian (2.4) takes the following form

$$\begin{aligned} H = &- \mu \sum_{i\sigma} a^{\dagger}_{i\sigma}a_{i\sigma} + \sum{}'_{ij\sigma} t_{ij}(n)a^{\dagger}_{i\sigma}a_{j\sigma} \\ &+ \sum{}'_{ij\sigma} \left(T(ij)a^{\dagger}_{i\sigma}a_{j\sigma}n_{i\bar{\sigma}} + \text{h.c.}\right) + U\sum_i n_{i\uparrow}n_{i\downarrow} \\ &+ \frac{1}{2}\sum{}'_{ij\sigma\sigma'} J(ij)a^{\dagger}_{i\sigma}a^{\dagger}_{j\sigma'}a_{i\sigma'}a_{j\sigma} + \frac{1}{2}\sum{}'_{ij\sigma\sigma'} V(ij)n_{i\sigma}n_{j\sigma'}\,, \end{aligned} \tag{2.6}$$

where

$$t_{ij}(n) = t(ij) + n\sum_{\substack{k\neq i\\ k\neq j}} J(ikjk) \tag{2.7}$$

is the effective hopping integral between nearest neighbours.

Neglecting all matrix elements in (2.6) except $t(ij)$ and $J(iiii)$ we obtain the Hubbard Hamiltonian.

The transition from the general form of Hamiltonian (2.6) to the Hubbard Hamiltonian, *i.e.* taking into account only the intra atomic Coulomb repulsion, it is often argued that the quantities $J(iiij)$, $J(ikjk)$, $J(ijji)$ and $J(ijij)$ are small in comparison with $J(iiii)$. However, taking inclusion of these matrix elements can be in principle important from the point of view of both the construction of correlation effects theory in materials with narrow energy bands and the interpretation of physical properties of these materials [13, 15–17].

Neglecting inter-atomic exchange interaction is justified by a smallness of $J(ij)$ in comparison with $U$ and hopping integral $t(ij)$, on the one hand, a possibility of ferromagnetic ordering stabilisation in narrow energy band (NEB) as a consequence of “translational” mechanism of exchange, on the other hand. Without consideration of a possibility of ferromagnetism realization in the one-band Hubbard model it should be noted that in NEB a contribution of translational part of energy in total system energy can be smaller then a contribution of energy of inter-atomic exchange interaction (in spite of the fact that $|t(ij)| \gg J(ij)$). Really, in partially filled NEB (for $U \gg |t(ij)|$) the contribution of translational part of ground state energy $\sim n\delta w$ ($\delta$ — degree of deviation from half-filling, $n$ is the average number of electrons per site, $2w$ is the bandwidth) [16], and the contribution of exchange interaction in ground state energy $\sim zn^2J$ ($J$ is the exchange integral between the nearest neighbours, $z$ is the number of the nearest neighbours to a site). It is clearly, that in NEB close to half-filling ($\delta \to 0$) the contribution of energy of inter-atomic exchange interaction in total system energy will be the largest. In particular, in non-doped Mott–Hubbard ferromagnets magnetic ordering is stabilised by inter-atomic exchange interaction only.

Taking into account inter-atomic Coulomb interaction is also important to understand a character of charge ordering in materials with NEB.

Finally, we can neglect the correlated hopping term (2.5); this is justified by estimating the matrix elements [3]. However, matrix elements $J(ikjk)$ are the hopping integrals. Thus taking into account (2.5) leads to the renormalisation of those processes describing the band part of Hamiltonian (2.6). In effect, $t(ij)$, $T(ij)$, $J(ikjk)$ are the quantities of the same order of magnitude.

If direct exchange interaction and inter-atomic Coulomb repulsion can be taken into account by respective renormalisation of chemical potential (ferromagnetic and charge orderings are absent) then Hamiltonian (2.6) takes the form

$$\begin{aligned} H = & -\mu\sum_{i\sigma} n_{i\sigma} + {\sum}'_{ij\sigma} t_{ij}(n) a^{\dagger}_{i\sigma} a_{j\sigma} \\ & + {\sum}'_{ij\sigma}\left(T(ij) a^{\dagger}_{i\sigma} a_{j\sigma} n_{i\bar{\sigma}} + \text{h.c.}\right) + U\sum_{i} n_{i\uparrow} n_{i\downarrow}. \end{aligned} \tag{2.8}$$

The peculiarity of the model of NEB material described by Hamiltonian (2.8) relies on taking into account inter-site hopping of electrons which are caused by electron–electron interaction. In this connection the following fact should be noted. Formally, correlated hopping has been introduced in the papers beginning from the pioneering work of Shubin and Vonsovsky [1]; the possible renormalisation of “band” hopping as a consequence of taking into account correlated hopping had been noted in the papers [5, 18, 19]. The important role of the correlated hopping in NEB in generalizing the concept of the Hubbard subbands had been pointed out in [20]. In that work, in particular, it had been shown that NEB had electron-hole asymmetry and essentially renormalised bandwidths connected by hopping in “hole and doublon subbands”. This approach has been developed in the papers [21, 22], where it has been shown that some properties of narrow-band materials can be interpreted using the idea of correlated hopping and caused by it electron-hole asymmetry in NEB.

The fact that the correlated hopping is necessary, was pointed out also in the papers [23]. In recent years models with correlated hopping have been studied intensively [24–28].

## 3. Particular cases of the polar model

### *3.1. Weak intra atomic interaction*

To simplify the considerations we use model Hamiltonian (2.8). If intra atomic Coulomb interaction is weak ($U < |t_{ij}(n)|$) then we can take into account the electron–electron interaction in the Hartree-Fock approximation:

$$\begin{aligned} n_{i\uparrow}n_{i\downarrow} &= n_{\uparrow}n_{i\downarrow} + n_{\downarrow}n_{i\uparrow}, \\ a^{\dagger}_{i\sigma}n_{i\bar{\sigma}}a_{j\sigma} &= n_{\bar{\sigma}}a^{\dagger}_{i\sigma}a_{j\sigma} + \langle a^{\dagger}_{i\sigma}a_{j\sigma}\rangle n_{i\bar{\sigma}}, \end{aligned} \tag{3.1}$$

where the average value $\langle n_{i\sigma}\rangle = n_{\sigma}$ is independent of the site index (if assumed that distributions of electron charge and magnetic momentum are homogenous). Taking into account (3.1) we can write Hamiltonian (2.8) in the following form:

$$H = \sum\nolimits'_{ij\sigma} \epsilon_{\sigma}(ij) a^{\dagger}_{i\sigma}a_{j\sigma}\,, \tag{3.2}$$

where

$$\epsilon_{\sigma}(ij) = -\mu + \beta_{\sigma} + n_{\bar{\sigma}}U + t_{ij}(n\sigma)\,; \tag{3.3}$$

$$\beta_{\sigma} = \frac{2}{N}\sum_{ij} T(ij)\langle a^{\dagger}_{i\bar{\sigma}}a_{j\bar{\sigma}}\rangle\,, \tag{3.4}$$

$$t_{ij}(n\sigma) = t_{ij}(n) + 2n_{\bar{\sigma}}T(ij)\,. \tag{3.5}$$

The use of (3.2) allows us to explain the peculiarities of the dependence of binding energy on atomic number in transition metals and also to modify the theory of ferromagnetism in a collective electron model.

### *3.2. Strong intra atomic interaction*

For typical narrow-band materials the conditions of strong $U \gg t(ij)$ or moderate $U \sim t(ij)$ intra atomic Coulomb repulsion are met. In this case Hamiltonian (2.6), using the “configurational ideology” of the polar model proposed in [12], can be written in the form suitable for a detailed treatment. For that purpose let us rewrite Hamiltonian (2.6) in “configurational” representations

[11, 12]. The relations to the $\alpha$ operators are provided by the formulae:

$$a^\dagger_{i\sigma} = \alpha^\dagger_{i\sigma}\alpha_{i0} - \eta_\sigma\alpha^\dagger_{i2}\alpha_{i\bar\sigma}, \quad a_{i\sigma} = \alpha^\dagger_{i0}\alpha_{i\sigma} - \eta_\sigma\alpha^\dagger_{i\bar\sigma}\alpha_{i2},$$

where $\eta_\sigma = +1$ when $\sigma =\uparrow$, $\eta_\sigma = -1$ when $\sigma =\downarrow$, site $i$ can be unoccupied with electron ($|0\rangle$), singly occupied ($|\sigma\rangle$) or doubly occupied ($|2\rangle$). The relations to the $X$ operators are given by:

$$a^\dagger_{i\sigma} = X_i^{\sigma 0} - \eta_\sigma X_i^{2\bar\sigma}, \quad a_{i\sigma} = X_i^{0\sigma} - \eta_\sigma X_i^{\bar\sigma 2}, \tag{3.6}$$

where $X_i^{kl}$ — operators of site $i$ transition from state $|l\rangle$ to state $|k\rangle$, [1]

The Hamiltonian can be written then in the form:

$$H = H_0 + H_1 + H_1' + H_{\mathrm{ex}}, \tag{3.7}$$

where

$$\begin{aligned} H_0 &= -\mu\sum_i \left(X_i^\uparrow + X_i^\downarrow + 2X_i^2\right) + U\sum_i X_i^2 \\ &\quad + \frac{1}{2}\sum_{ij} V(ij)\left(1 - X_i^0 + X_i^2\right)\left(1 - X_j^0 + X_j^2\right), && (3.8) \\ H_1 &= {\sum}'_{ij\sigma} t_{ij}(n) X_i^{\sigma 0} X_j^{0\sigma} + \sum_{ij\sigma} \tilde t_{ij}(n) X_i^{2\sigma} X_j^{\sigma 2}, && (3.9) \\ H_1' &= {\sum}'_{ij\sigma}\left(t'_{ij}(n)\left(X_i^{\downarrow 0}X_j^{\uparrow 2} - X_i^{\uparrow 0}X_j^{\downarrow 2}\right) + \mathrm{h.c.}\right), && (3.10) \\ H_{\mathrm{ex}} &= -\frac{1}{2}{\sum_{ij\sigma}}' J(ij)\left(\left(X_i^\sigma + X_i^2\right)\left(X_j^\sigma + X_j^2\right) + X_i^{\sigma\bar\sigma}X_j^{\sigma\bar\sigma}\right), && (3.11) \end{aligned}$$

where $X_i^k$ is the number operator of $|k\rangle$-states on site $i$, and

$$\begin{aligned} \tilde t_{ij}(n) &= t_{ij}(n) + 2T(ij), && (3.12) \\ t'_{ij}(n) &= t_{ij}(n) + T(ij). && (3.13) \end{aligned}$$

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[1] In the papers [11, 12] notations of site transition-operators $B^i_{kl}$ was introduced. In the present paper we use the modern notations $X_i^{kl}$, and more convenient notations of state $|ik\rangle$.

The essence of configurational representation is proved by the fact that the intra atomic interaction takes the diagonal form. Besides, effects of intra atomic Coulomb interactions correlating electron translations are described by Hamiltonians $H_1$ and $H_1'$.

$H_1$ describes transitions of $|j\sigma\rangle$-configurations to $|i0\rangle$-configurations and $|j\uparrow\downarrow\rangle$-configurations to $|j\sigma\rangle$-configurations of neighbouring sites, which forms $\sigma$-0-subband —"hole" subband and 2-$\sigma$-subband —"doublon" subband, respectively (they are analog of "lower" and "upper" Hubbard subbands).

$H_1'$ describes transitions between $\sigma - 0$- and $\uparrow\downarrow -\sigma$-subbands ( processes of paired creation and destruction of holes and doublons). These processes are "translational" in the distinction from "activational "processes described by $H_1$.

If we neglect inter atomic Coulomb and exchange interaction in Hamiltonian (3.7) then the Hamiltonian takes the operator structure equivalent to the Hubbard Hamiltonian. However, in this model hopping integrals in $\sigma$-0 and $\uparrow\downarrow$ $\sigma$-subbands and "interband" hopping integrals are dependent on concentration and different, in distinction from the Hubbard model (see Fig. 1). Properties of this "asymmetrical Hubbard model" can be essentially different.

### 3.3. Generalised t–J model

Configurational representation is especially useful in an investigation of narrow-band system, in which the condition $U \gg t(ij)$ is satisfied. In this case system can be both Mott–Hubbard insulator at $n = 1$ and doped Mott–Hubbard insulator at $n \neq 1$. Then general Hamiltonian using suitable form of the perturbation theory [12] generalising Bogolubov perturbation theory [5] for metallic systems can be written in the form of effective Hamiltonian, which is convenient to the mathematical treatment. Thus, transition to the well-known $t$–$J$ model is obtained (see the review [29] and also the papers [12, 16] where modern form of $t$–$J$-model was formulated first). Let us use the approach proposed in [12] for generalised narrow-band Hamiltonian (3.7). Namely, we perform the canonical transformation

$$\tilde{H} = e^s H e^{-s}, \tag{3.14}$$

where

$$S = \sum_{ij} \left( L(ij) \left( X_i^{\uparrow 0} X_j^{\downarrow 2} - X_j^{\downarrow 0} X_i^{\uparrow 2} \right) - \text{h.c.} \right). \tag{3.15}$$

If we limit ourselves to quantities of second order of smallness in Eq. (3.14) ($S$ is of first order), then

$$\begin{aligned}\tilde{H} &= H_0 + H_1 + H_1' + [SH_0] \\ &\quad + [SH_1] + [SH_1'] + \tfrac{1}{2}\,[S[SH_0]]\ . \end{aligned} \tag{3.16}$$

Use the condition of an elimination of "activational" processes

$$H_1' + [SH_0] = 0. \tag{3.17}$$

Taking into account inter-atomic Coulomb interaction in the mean-field approximation we obtain that

$$L(ij) = t_{ij}'(n)/\mathit{\Delta}, \tag{3.18}$$

where

$$\mathit{\Delta} = U - V + zV\left(\langle X_i^0\rangle + \langle X_i^2\rangle\right) \tag{3.19}$$

is the activation energy of hole-doublon pair ($V$ is the strength of Coulomb repulsion between nearest neighbours ).

The components of commutator $[S;H_1]$ have operator structures similar to structure of $H'$, but with "hopping integrals" of second order; in the considered approximation they do not contribute to $\tilde{H}$. Thus for the case of $\sigma$-0- and $\uparrow\downarrow$-$\sigma$-subbands are separated by energy gap and $t_i'j(n) \ll \mathit{\Delta}$ the initial Hamiltonian (2.6) has the form

$$\begin{aligned}\tilde{H} &= H_0 + {\sum_{ij}}' t_{ij}(n) X_i^{\sigma 0} X_j^{0\sigma} \\ &\quad + {\sum_{ij\sigma}}' \tilde{t}_{ij}(n) X_i^{2\sigma} X_j^{\sigma 2} + H_{\mathrm{ex}} + \tilde{H}_{\mathrm{ex}} + \tilde{H}_t\,, \end{aligned} \tag{3.20}$$

where

$$\begin{aligned}\tilde{H}_{\mathrm{ex}} &= -\frac{1}{2}{\sum_{ij\sigma}}' \tilde{J}(ij)(X_i^{\sigma} X_j^{\bar{\sigma}} \\ &\quad - X_i^{\sigma\bar{\sigma}} X_j^{\bar{\sigma}\sigma} - X_i^2 X_j^0), \end{aligned} \tag{3.21}$$

$$\begin{aligned}\tilde{H}_t &= -\frac{1}{2}{\sum_{ijk\sigma}}' J(ijk)\left(X_i^{\sigma 0} X_j^{\bar{\sigma}} X_k^{0\sigma} - X_i^{\sigma 0} X_j^{\bar{\sigma}\sigma} X_k^{0\bar{\sigma}}\right) \\ &\quad -\frac{1}{2}{\sum_{ijk\sigma}}' J(ijk)\left(X_i^{2\sigma} X_j^{\sigma\bar{\sigma}} X_k^{\bar{\sigma}2} - X_i^{2\sigma} X_j^{\bar{\sigma}} X_k^{\sigma 2}\right)\ . \end{aligned} \tag{3.22}$$

Here

$$\tilde{J}(ij) = 2t_{ij}'(n) t_{ij}'(n)/\mathit{\Delta} \tag{3.23}$$

— integral of indirect exchange (through polar states),

$$J(ijk) = 2t'_{ij}(n)t'_{jk}(n)/\Delta \tag{3.24}$$

— integral of indirect charge transfer in $\sigma$-0- and $\uparrow\downarrow$-$\sigma$-subbands; in sum (3.22) sites $i$ and $k$ are nearest neighbours to $j$.

An elimination of the processes of paired creation and destruction of holes and doublons (in first order on hopping integral $t'_{ij}(n)$) leads to a rise of two terms $\tilde{H}_{\text{ex}}$ and $\tilde{H}_t$ in EH (3.20). $\tilde{H}_{\text{ex}}$ describes indirect exchange interaction (superexchange), $\tilde{H}_t$ describes indirect hopping of electrons (superhopping). EH (3.20) generalises the EH obtained in [12] for the Hubbard model. The distinctions of EH (3.20) from the forms of $t$-$J$-models ([30, 31]) are caused by the concentration-dependence of hopping integrals in $\sigma$-0- and 2-$\sigma$-subbands, firstly, the difference of the noted hopping integrals (the absence of electron-hole symmetry), secondly, unusual form of the superexchange and superhopping integrals (the being of the concentration-dependence in hopping integrals, formula (3.19) for $\Delta$), thirdly.

In the modified in this way $t$-$J$-model, in particular, the conditions of a realization of high-$T_c$ are more favourable than in the similar Spałek model [32]. A number of peculiarities of the model EH are useful to interpret physical properties of narrow-band materials.

## 4. New two-pole approximations

### *4.1. Approximation I*

#### 4.1.1. Single-particle energy spectrum. Metal–insulator transition

Beyond the frameworks of approximations considered in Sect. 3 the region of parameters remains, in which the width of unperturbed band $2z|t(ij)|$ and a strength of Coulomb repulsion are close to each other. From general physical considerations in this region we have to expect the metal-insulator transition (for $n = 1$). Although a great number of papers are devoted to the determining the energy gap, the question of a correct description of metal-insulator transition attracts the attention of researchers (see, for example [34, 35]).

The most significant defect of the approximation "Hubbard-I" is the inability to describe of the metal-insulator transition (MIT) because of the presence of an energy gap in a spectrum at all values of $U/w > 0$. Other approximations are free from this defect, but have their own defects [34, 35].

We propose a new approach to calculating the single-particle energy spectrum of narrow-band materials which leads to correct description of metal-insulator transition. The approach is based on a variant of the approximate second quantisation representation method [36] within a generalised Hartree–Fock approximation (GHFA) [37].

We start from the Hamiltonian (3.7) without the $H_{\mathrm{ex}}$ term. Suppose that electron ordering is absent (taking into account the inter-atomic interaction in the mean-field approximation leads to chemical potential renormalisation).

The single-particle Green function

$$G^{\sigma}_{pp'}(E) = \left\langle\left\langle a_{p\sigma} | a^{\dagger}_{p'\sigma} \right\rangle\right\rangle \tag{4.1}$$

in terms of Hubbard operators is written as

$$\begin{aligned} G^{\sigma}_{pp'}(E) = & \left\langle\left\langle X^{0\sigma}_{p} \middle| X^{\sigma 0}_{p'} \right\rangle\right\rangle + \eta_\sigma \left\langle\left\langle X^{0\sigma}_{p} \middle| X^{2\bar{\sigma}}_{p'} \right\rangle\right\rangle + \eta_\sigma \left\langle\left\langle X^{\bar{\sigma}2}_{p} \middle| X^{\sigma 0}_{p'} \right\rangle\right\rangle \\ & + \left\langle\left\langle X^{\bar{\sigma}2}_{p} \middle| X^{2\bar{\sigma}}_{p'} \right\rangle\right\rangle . \end{aligned} \tag{4.2}$$

The Green function $\left\langle\left\langle X^{0\sigma}_{p} \middle| X^{\sigma 0}_{p'} \right\rangle\right\rangle$ is given by the equation

$$\begin{aligned} (E+\mu) \left\langle\left\langle X^{0\sigma}_{p} \middle| X^{\sigma 0}_{p'} \right\rangle\right\rangle = & \frac{\delta_{pp'}}{2\pi} \langle X^{\sigma}_{p} + X^{0}_{p} \rangle + \left\langle\left\langle [X^{0\sigma}_{p}, H_1] \middle| X^{\sigma 0}_{p'} \right\rangle\right\rangle \\ & + \left\langle\left\langle [X^{0\sigma}_{p}, H'_1] \middle| X^{\sigma 0}_{p'} \right\rangle\right\rangle , \end{aligned} \tag{4.3}$$

with $[A,B] = AB - BA$, and

$$[X^{0\sigma}_{p}, H_1] = t \sum_{j} \left( (X^{\sigma}_{p} + X^{0}_{p}) X^{0\sigma}_{j} + X^{\bar{\sigma}\sigma}_{p} X^{0\bar{\sigma}}_{j} \right) - \tilde{t} \sum_{j} X^{02}_{p} X^{2\sigma}_{j}, \tag{4.4}$$

$$\begin{aligned} [X^{0\sigma}_{p}, H'_1] = & -t' \sum_{j} X^{02}_{p} X^{\bar{\sigma}0}_{j} + t' \sum_{j} X^{\bar{\sigma}\sigma}_{p} X^{\sigma 2}_{j} \\ & -t' \sum_{j} (X^{\sigma}_{p} + X^{0}_{p}) X^{\bar{\sigma}2}_{j} . \end{aligned} \tag{4.5}$$

To terminate the sequence of Green-function equations according to the generalised Hartree–Fock approximation [37] we suppose that

$$[X^{0\sigma}_{p}, H_1] = \sum_{j} \epsilon(pj) X^{0\sigma}_{j}, \;\; [X^{0\sigma}_{p}, H'_1] = \sum_{j} \epsilon_1(pj) X^{\bar{\sigma}2}_{j}, \tag{4.6}$$

where $\epsilon(pj)$ and $\epsilon_1(pj)$ are the non-operator expressions. The choice of the commutators in form (4.2) and (4.3) is prompted by the operator structure of these commutators, which maps the energy non-equivalence of the hopping processes prescribed by $H_1$ and $H_1'$. Taking into account (4.4) we rewrite Eq. (4.1) in the form

$$\begin{aligned}(E+\mu)\left\langle\left\langle X_p^{0\sigma}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle = \; & \frac{\delta_{pp'}}{2\pi}\langle X_p^{\sigma}+X_p^{0}\rangle + \sum_j \epsilon(pj)\left\langle\left\langle X_j^{0\sigma}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle \\ & + \sum_j \epsilon_1(pj)\left\langle\left\langle X_j^{\bar\sigma 2}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle . \qquad (4.7)\end{aligned}$$

After anticommutating both sides of (4.4) with $X_k^{\sigma 0}$ and with $X_k^{2\bar\sigma}$, we obtain, respectively

$$\begin{aligned}\epsilon(pk)(X_k^{\sigma}+X_k^{0}) = \; & t(X_p^{\sigma}+X_p^{0})(X_k^{\sigma}+X_k^{0}) + tX_k^{\sigma\bar\sigma}X_p^{\bar\sigma\sigma} \\ & -\delta_{pk}t\sum_j X_k^{\bar\sigma 0}X_j^{0\bar\sigma} + \delta_{pk}\tilde{t}\sum_j X_j^{2\sigma}X_k^{\sigma 2} \\ & -\tilde{t}X_k^{20}X_p^{02}, \qquad (4.8)\end{aligned}$$

$$\begin{aligned}\epsilon_1(pk)(X_k^{\bar\sigma}+X_k^{2}) = \; & -t'(X_p^{\sigma}+X_p^{0})(X_k^{\bar\sigma}+X_k^{2}) + t'X_p^{\bar\sigma\sigma}X_k^{\sigma\bar\sigma} \\ & -\delta_{pk}t'\sum_j X_j^{\bar\sigma 0}X_k^{0\bar\sigma} + \delta_{pk}t'\sum_j X_k^{2\sigma}X_j^{\sigma 2} \\ & -t'X_k^{20}X_p^{02}. \qquad (4.9)\end{aligned}$$

Similarly, for the Green function $\left\langle\left\langle X_p^{\bar\sigma 2}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle$ we can write the equation

$$\begin{aligned}(E+\mu-U)\left\langle\left\langle X_p^{\bar\sigma 2}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle = \; & \sum_j \tilde{\epsilon}(pj)\left\langle\left\langle X_j^{\bar\sigma 2}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle \\ & + \sum_j \epsilon_2(pj)\left\langle\left\langle X_j^{0\sigma}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle , \qquad (4.10)\end{aligned}$$

where $\tilde{\epsilon}(pj)$ and $\epsilon_2(pj)$ are determined through the expressions which are analogous to (4.6) and (4.7). Thus we obtain the closed system of equations for the Green functions $\left\langle\left\langle X_p^{0\sigma}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle$ and $\left\langle\left\langle X_p^{\bar\sigma 2}\middle|X_{p'}^{\sigma 0}\right\rangle\right\rangle$.

By neglecting correlated hopping and by averaging expressions (4.6) and (4.7) we obtain the approximations [3, 38]; the defects of these approximations are well-known (see, for example Ref. [39]). Here we use the approach which has been proposed in the papers [14, 40].

To determine $\epsilon(pj)$, $\epsilon_1(pj)$ we rewrite $X_i^{kl}$-operator in Eqs. (4.8) and (4.9) in the form [41] $X_i^{kl} = \alpha_{ik}^{\dagger}\alpha_{il}$, where $\alpha_{ik}^{\dagger}$, $\alpha_{il}$ are the operators of creation and destruction for $|k\rangle$- and $|l\rangle$-states on $i$-site respectively (the Shubin–Vonsovsky operators [1]); thus $X_i^0 = \alpha_{i0}^\dagger\alpha_{i0}$, $X_i^2 = \alpha_{i2}^\dagger\alpha_{i2}$, $X_i^\sigma = \alpha_{i\sigma}^\dagger\alpha_{i\sigma}$. Let us substitute $\alpha$-operators by $c$-numbers in Eqs. (4.6) and (4.7) (here there is a partial equivalence with slave boson method [42])

$$\alpha_{i\sigma}^\dagger = \alpha_{i\sigma} = \left(\frac{1-2d}{2}\right)^{1/2}, \qquad \alpha_{i0}^\dagger = \alpha_{i0} = \alpha_{i2}^\dagger = \alpha_{i2} = d^{1/2} \tag{4.11}$$

(we consider a paramagnetic case, electron concentration on site $n = 1$); $d$ is the concentration of polar states (holes or doublons).

The proposed approximation is based on the following physical idea. Let us consider a paramagnetic Mott–Hubbard insulator at temperature $T \neq 0$. In the temperature interval ($k_BT \ll U$) the concentration of polar states is small ($d \ll 1$). An analogous consideration is valid for a paramagnetic Mott–Hubbard semimetal (hole and doublon subbands overlap weakly, $d \ll 1$). So, the change of states and polar excitations influences on $|\sigma\rangle$-states weakly. Thus we may consider $|\sigma\rangle$-states as the quasiclassical system and substitute the operators $\alpha_{i\sigma}^\dagger$, $\alpha_{i\sigma}$ by $c$-numbers. In addition, when we find $\epsilon(pj)$, $\epsilon_1(pj)$ we substitute the creation and destruction operators of $|0\rangle$- and $|2\rangle$-states through the respective quasiclassical expressions. Actually the proposed approximation is equivalent to a separation of the charge and spin degrees of freedom. Note that the present approach is justifiable when $d \to 0$.

Thus in $\boldsymbol{k}$-representation we obtain [43]

$$\epsilon(\boldsymbol{k}) = (1-d)^2 t_{\boldsymbol{k}} - 2d^2\tilde{t}_{\boldsymbol{k}}, \quad \epsilon_1(\boldsymbol{k}) = -2dt'_{\boldsymbol{k}}, \tag{4.12}$$

where $t_{\boldsymbol{k}}$, $\tilde{t}_{\boldsymbol{k}}$, $t'_{\boldsymbol{k}}$ are the Fourier transforms of the hopping integral $t$, $\tilde{t}$, $t'$ respectively. Similarly, we find that

$$\tilde{\epsilon}(\boldsymbol{k}) = (1-d)^2 \tilde{t}_{\boldsymbol{k}} - 2d^2 t_{\boldsymbol{k}}, \quad \epsilon_2(\boldsymbol{k}) = -2dt'_{\boldsymbol{k}}. \tag{4.13}$$

The Fourier transform of the Green function $\left\langle\left\langle X_p^{0\sigma} \middle| X_{p'}^{\sigma 0}\right\rangle\right\rangle$ is found from the system of equations (4.5) and (4.8)

$$\left\langle\left\langle X_p^{0\sigma} \middle| X_{p'}^{\sigma 0}\right\rangle\right\rangle_{\boldsymbol{k}} = \frac{1}{4\pi}\,\frac{E+\mu-U-(1-2d+2d^2)\tilde{t}_{\boldsymbol{k}}+2d^2t_{\boldsymbol{k}}}{(E-E_1(\boldsymbol{k}))(E-E_2(\boldsymbol{k}))}, \tag{4.14}$$

with

$$E_{1,2}(\boldsymbol{k}) = -\mu + \frac{(1-2d)(t_{\boldsymbol{k}}+\tilde{t}_{\boldsymbol{k}})+U}{2} \mp \frac{1}{2}F_{\boldsymbol{k}}, \tag{4.15}$$

$$F_{\boldsymbol{k}} = \sqrt{\left[B(t_{\boldsymbol{k}}-\tilde{t}_{\boldsymbol{k}})-U\right]^2 + (4dt'_{\boldsymbol{k}})^2}, \; B = 1-2d+4d^2. \tag{4.16}$$

An analogous procedure is realized also in the equations for the other Green functions in Eq. (4.2).

Finally, in $\boldsymbol{k}$-representation the single-particle Green function is

$$G_{\boldsymbol{k}}(E) = \frac{1}{2\pi}\left(\frac{A_{\boldsymbol{k}}}{E-E_1(\boldsymbol{k})}+\frac{B_{\boldsymbol{k}}}{E-E_2(\boldsymbol{k})}\right), \tag{4.17}$$

$$A_{\boldsymbol{k}} = \frac{1}{2}-\frac{2dt'_{\boldsymbol{k}}}{F_{\boldsymbol{k}}}, \quad B_{\boldsymbol{k}}=\frac{1}{2}+\frac{2dt'_{\boldsymbol{k}}}{F_{\boldsymbol{k}}}. \tag{4.18}$$

Single-particle Green function (4.17) gives the exact atomic and band limits: if $U=0$ and $t_{\boldsymbol{k}}=\tilde{t}_{\boldsymbol{k}}=t'_{\boldsymbol{k}}=t_0(\boldsymbol{k})$ (it means neglecting correlated hopping) then $G_{\boldsymbol{k}}(E)$ takes the band form ($d=1/4$ when $U=0$), if $t_{\boldsymbol{k}}=\tilde{t}_{\boldsymbol{k}}=t'_{\boldsymbol{k}}\to 0$ then we obtain the exact atomic limit.

The peculiarities of obtained quasiparticle energy spectrum (4.15) of narrow-band system which is described by Hamiltonian (2.5) are the dependence on the concentration of polar states and the non-equivalence of the lower and upper Hubbard bands. This non-equivalence is caused by the difference of the hopping integrals $t$, $\tilde{t}$, $t'$.

Quasiparticle energy spectrum (4.15) allows to study MIT in the proposed model which has been investigated in the paper [43].

With the help of energy spectrum of electrons (4.15) we find the expression for the energy gap width (difference of energies between bottom of the upper and top of the lower Hubbard bands):

$$\begin{aligned}\Delta E &= -(1-2d)(w+\tilde{w})+\frac{1}{2}(Q_1+Q_2),\\ Q_1 &= \sqrt{[B(w-\tilde{w})-U]^2+(4dzt')^2},\\ Q_2 &= \sqrt{[B(w-\tilde{w})+U]^2+(4dzt')^2},\end{aligned} \tag{4.19}$$

where $w$ and $\tilde{w}$ are the half-widths of the lower (hole) and upper (doublon) Hubbard bands respectively: $w=z|t|$, $\tilde{w}=z|\tilde{t}|$ ($z$ is the number of nearest neighbours to a site).

The peculiarities of the expression for energy gap (4.19) are dependences on the concentration of polar states, on the widths of hole and doublon bands, on the hopping integral $t'$ (thus on external pressure). At given $U$, $t$, $\tilde{t}$, $t'$ (constant external pressure) the concentration dependence of $\Delta E$ allows to study MIT under the action of external influences: temperature change, photoeffect and magnetic field. In particular, $\Delta E(T)$-dependence can lead to the transition from a metallic state to an insulating state with the increase of temperature (in this connection the transition from the state of a paramagnetic metal to the paramagnetic insulator state in the

$(V_{1-x}Cr_x)_2O_3$ compound [44,45], in $NiS_2$ [46] and in the $NiS_{2-x}Se_x$ system [46,47] should be noted). Under the action of light or magnetic field the concentration of polar states can be changed; it leads to the fact that the energy gap width is changed also and MIT can occur.

Distinction of formulae (4.15) and (4.19) from earlier obtained results (*e.g.*, see reviews [34,35]) is the dependence on concentration of polar states. Let us find the expression for its calculation.

The concentration of polar states is given by the equation

$$\begin{aligned} d = \langle X_i^2 \rangle &= \frac{1}{N}\sum_{\boldsymbol{k}} \int\limits_{-\infty}^{+\infty} J_{\boldsymbol{k}}(E)dE \\ &= \frac{1}{2N}\sum_{\boldsymbol{k}} \left( \frac{C_{\boldsymbol{k}}}{\exp\frac{E_1(\boldsymbol{k})}{\theta}+1} + \frac{D_{\boldsymbol{k}}}{\exp\frac{E_2(\boldsymbol{k})}{\theta}+1} \right), \qquad (4.20) \end{aligned}$$

where

$$C_{\boldsymbol{k}} = \frac{1}{2} - \frac{B(\tilde{t}_{\boldsymbol{k}} - t_{\boldsymbol{k}})}{2F_{\boldsymbol{k}}} - \frac{U}{2F_{\boldsymbol{k}}},$$
$$D_{\boldsymbol{k}} = \frac{1}{2} + \frac{B(\tilde{t}_{\boldsymbol{k}} - t_{\boldsymbol{k}})}{2F_{\boldsymbol{k}}} + \frac{U}{2F_{\boldsymbol{k}}},$$

$\theta = k_{\rm B}T$, $k_{\rm B}$ is the Boltzmann's constant, $N$ is the number of sites, $J_{\boldsymbol{k}}(E)$ is the spectral intensity of the Green function

$$\left\langle\left\langle X_p^{\bar{\sigma}2} \middle| X_{p'}^{2\bar{\sigma}} \right\rangle\right\rangle_{\boldsymbol{k}} = \frac{1}{4\pi}\left( \frac{C_{\boldsymbol{k}}}{E - E_1(\boldsymbol{k})} + \frac{D_{\boldsymbol{k}}}{E - E_2(\boldsymbol{k})} \right). \qquad (4.21)$$

At $T = 0$ and the rectangular density of states

$$\frac{1}{N}\sum_{\boldsymbol{k}} \delta(E - t_{\boldsymbol{k}}) = \frac{1}{2w}\theta(w^2 - E^2)$$

($\theta(x) = 1$ if $x > 0$, $= 0$ otherwise) from Eq. (4.20) we obtain that

$$\begin{aligned} &-\frac{B}{z}\frac{\tilde{t}-t}{\lambda}\left[\varphi(\epsilon_0) - \varphi(-\epsilon_0)\right] + \frac{U}{z\sqrt{\lambda}}\left(1 - \frac{B^2(\tilde{t}-t)^2}{\lambda}\right) \\ &\times \ln\left| \frac{\sqrt{\lambda}\varphi(\epsilon_0) - \lambda\epsilon_0 - BU(\tilde{t}-t)}{\sqrt{\lambda}\varphi(-\epsilon_0) + \lambda\epsilon_0 - BU(\tilde{t}-t)} \right| = 8d - 2 \quad (U < w + \tilde{w}) \ (4.22) \end{aligned}$$

with

$$\epsilon_0 = 2\sqrt{\frac{\mu U - \mu^2}{(1-2d)^2(t+\tilde{t})^2 - \lambda}}, \quad \mu = \frac{(1-2d+2d^2)w - 2d^2\tilde{w}}{(1-2d)(w+\tilde{w})}U,$$

$$\varphi(\epsilon) = \left\{\lambda\epsilon^2 - 2BU(\tilde{t}-t)\epsilon + U^2\right\}^{\frac{1}{2}}, \quad \lambda = B^2(\tilde{t}-t)^2 + (4dt')^2.$$

For narrow-band semimetal ($d \ll 1$) Eq. (4.22) takes the following form:

$$d = \frac{1}{4}\left(1 - \frac{U}{w+\tilde{w}}\right). \tag{4.23}$$

Figure 1 shows the dependence of $d$ on $U/w$ which is obtained from Eq. (4.22). The parameters $\tau_1 = T_1/|t_0|$, $\tau_2 = T_2/|t_0|$ characterise the value of correlated hopping. One can see that a value of $d$ depends on the parameters of correlated hopping $\tau_1$, $\tau_2$ (thus on $\tilde{w}/w$) weakly when $U/w$ is close to zero. But with the increase of $U/w$ the concentration of polar states becomes strongly dependent on the parameters $\tau_1$, $\tau_2$. It testifies on the fact that taking into account the correlated hopping is important to consider the metal-insulator transition problem.

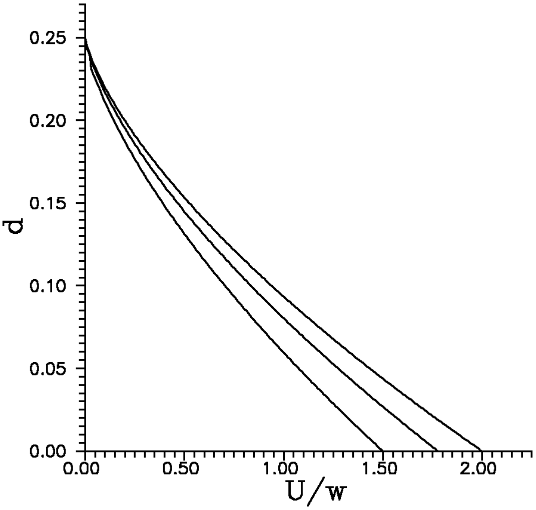

Fig. 1. Concentration of polar states $d$ as a function of $U/w$: the upper curve corresponds to $\tau_1 = \tau_2 = 0$; the middle curve — $\tau_1 = \tau_2 = 0.1$; the lower curve — $\tau_1 = \tau_2 = 0.2$.

Fig. 1 shows also that if $U \geq w + \tilde{w}$ then the concentration of polar states $d = 0$. In the special case $t + \tilde{t} = t' = 0$ this consequence is in accordance with the results of Refs. [48–50].

At $T = 0$ the energy gap width $\varDelta E \leq 0$ (*i.e.* MIT occurs) when the condition

$$U \leq w + \tilde{w} \tag{4.24}$$

is satisfied (in agreement with general physical ideas [45]). For the special case $t' = 0$ condition (4.24) covers the exact results of Refs. [48–50].

Fig. 2 which is obtained from formula (4.19) using Eq. (4.24) shows that in a metallic state the overlapping of energy subbands decreases and in an insulating state the energy gap width increases with decrease of the parameter $\tilde{w}/w$ (at given $U/w$).

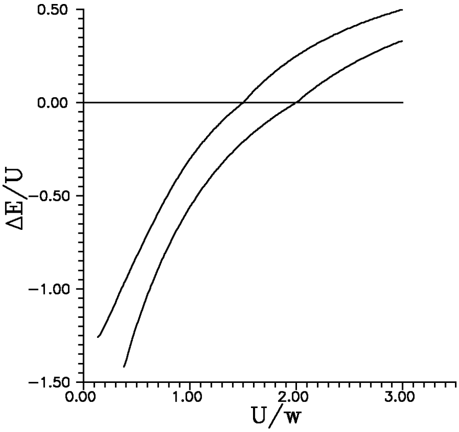

Fig. 2. Energy gap width $\varDelta E$ as a function of $U/w$: the upper curve corresponds to $\tau_1 = \tau_2 = 0.2$; the lower curve — $\tau_1 = \tau_2 = 0$.

In the Hubbard model energy gap width (4.19) takes the following form:

$$\varDelta E = -2w(1 - 2d) + \sqrt{U^2 + (4dw)^2}, \tag{4.25}$$

and the concentration of polar states (4.22) is

$$d = \left(\frac{1}{4} + \frac{U}{32dw}\ln(1 - 4d)\right)\theta(2w - U). \tag{4.26}$$

In the region of metal-insulator transition $d = 1/4 - U/(8w)$; this dependence is in qualitative accordance with the result of Brinkman and Rice [51] obtained by use of Gutzwiller variational method [52], those of the general Gutzwiller-correlated wave functions in infinite dimensions [53] and the Kotliar-Ruckenstein slave bosons [42]. For $U/2w \to 0$ we obtain $d = 1/4 + U/(8w)\ln(U/2w)$ (if we consider Coulomb repulsion as perturbation then $d(U \to 0) = 1/4 - \mathcal{O}(U)$); in order to compare the obtained dependence (4.26) $d$ on $U/w$ in the Hubbard model with other approximate theories see *e.g.* [54]). $\varDelta E \leq 0$ when the condition $2w \geq U$ is satisfied.

#### 4.1.2. Temperature-induced metal-insulator transition

At given $U$, $w$, $\tilde{w}$, $t'$ (constant exterior pressure) concentration of polar states (4.20) increases with the increase of temperature. It leads to the fact that system can undergo transition from the state with $\varDelta E \leq 0$ to the state with $\varDelta E > 0$, *i.e.* metal-to-insulator transition can occur. In this case the results obtained in the Hubbard model and those obtained in non-symmetric Hubbard model can be essentially different (Fig. 3 illustrates it) [55]. Let us take for example $U/w = 0.9$. One can see that at $T = 0$ K the energy gap width in both models is $\varDelta E < 0$ (a metallic state). With the increase of temperature metal-to-insulator transition does not occur in the Hubbard model, in non-symmetric model the values of parameters $\tau_1$, $\tau_2$ exist at which metal-to-insulator transition occurs.

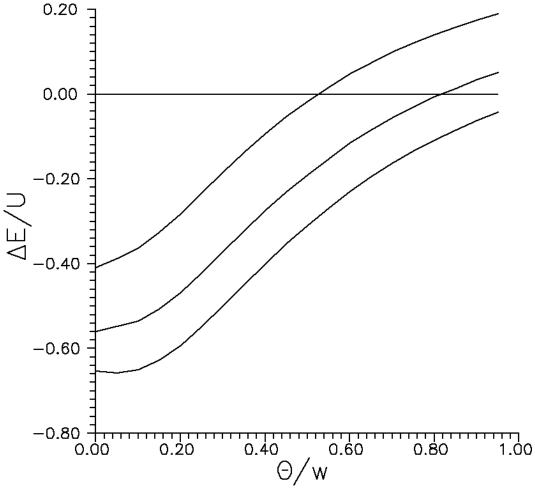

Fig. 3. The dependence of energy gap on temperature at $U/w = 0.9$. The upper curve corresponds to $\tau_1 = \tau_2 = 0.2$, the middle curve — $\tau_1 = \tau_2 = 0.1$, the lower curve — $\tau_1 = \tau_2 = 0$ (the Hubbard model).

In case metal-to-insulator transition occurs in both models from Fig. 3 one can see that at given values of $U/w$ in model with non-equivalent Hubbard subbands metal-to-insulator transition occurs at smaller temperature than in the Hubbard model. So, for example, for $w_0 = z|t_0| \approx 1.05$ eV (such bandwidth of $NiS_2$ was estimated in paper [56]) in considered model in a paramagnetic state metal-to-insulator transition occurs at $T \approx 280$ K for $U/w_0 = 1.94$ and $\tau_1 = \tau_2 = 0.01$ (the observable transitions temperature of $NiS_2$ is $T \sim 280$ K at $p \sim 3$ MPa [46]). For the same value of $U/w_0$ metal-to-insulator transition occurs at $T \approx 940$ K when $\tau_1 = \tau_2 = 0$ (neglecting of correlated hopping, the Hubbard model) and at $T = 0$ K when

$\tau_1 = \tau_2 = 0.015$. If $U/w_0 = 1.98$ then transition from a metallic state to an insulating state is realized at $T \approx 290$ K for $\tau_1 = \tau_2 = 0$; at $T = 0$ K when $\tau_1 = \tau_2 = 0.005$. Note that at $U \sim 2w$ the temperatures of metal-to-insulator transition found in both models are essentially different; with a deviation from this ratio the difference decreases.

The obtained temperature dependence of energy gap can explain observable transition from the state of a paramagnetic metal to the paramagnetic Mott–Hubbard insulator state in the $(V_{1-x}Cr_x)_2O_3$ compound [44, 45] in $NiS_2$ [46] and in the $NiS_{2-x}Se_x$ system [46, 47] with the increase of temperature.

## *4.2. Approximation II*

### **4.2.1. Single-particle Green function and energy spectrum**

In the present Section recently proposed two-pole approximation [57] is used to study effects of electron correlations in the Hubbard model.

The single-particle Green function is written in $X_i^{kl}$-operators as

$$\begin{aligned}\left\langle\left\langle a_{p\uparrow}\middle|a^{\dagger}_{s\uparrow}\right\rangle\right\rangle &= \left\langle\left\langle X_p^{\downarrow 2}\middle|X_s^{2\downarrow}\right\rangle\right\rangle - \left\langle\left\langle X_p^{0\uparrow}\middle|X_s^{2\downarrow}\right\rangle\right\rangle - \left\langle\left\langle X_p^{\downarrow 2}\middle|X_s^{\uparrow 0}\right\rangle\right\rangle \\ &\quad + \left\langle\left\langle X_p^{0\uparrow}\middle|X_s^{\uparrow 0}\right\rangle\right\rangle . \end{aligned} \tag{4.27}$$

The functions $\left\langle\left\langle X_p^{\downarrow 2}\middle|X_s^{2\downarrow}\right\rangle\right\rangle$ and $\left\langle\left\langle X_p^{0\uparrow}\middle|X_s^{2\downarrow}\right\rangle\right\rangle$ satisfy the equations

$$\begin{aligned}(E+\mu-U)\left\langle\left\langle X_p^{\downarrow 2}\middle|X_s^{2\downarrow}\right\rangle\right\rangle &= \frac{\delta_{ps}}{2\pi}\left\langle X_p^{\downarrow} + X_p^{2}\right\rangle + \left\langle\left\langle \left[X_p^{\downarrow 2}, H_1\right]_-\middle|X_s^{2\downarrow}\right\rangle\right\rangle \\ &\quad + \left\langle\left\langle \left[X_p^{\downarrow 2}, H_1'\right]_-\middle|X_s^{2\downarrow}\right\rangle\right\rangle , \\ (E+\mu)\left\langle\left\langle X_p^{0\uparrow}\middle|X_s^{2\downarrow}\right\rangle\right\rangle &= \left\langle\left\langle \left[X_p^{0\uparrow}, H_1\right]_-\middle|X_s^{2\downarrow}\right\rangle\right\rangle \\ &\quad + \left\langle\left\langle \left[X_p^{0\uparrow}, H_1'\right]_-\middle|X_s^{2\downarrow}\right\rangle\right\rangle , \end{aligned} \tag{4.28}$$

with $[A,B]_- = AB - BA$. To obtain the closed system of equations we apply new two-pole approximation, proposed in work [57]. Suppose in Eq. (4.28) that

$$\left[X_p^{0\uparrow}, H_1\right]_- = \sum_j \epsilon(pj) X_j^{0\uparrow}, \quad \left[X_p^{\downarrow 2}, H_1\right]_- = \sum_j \tilde{\epsilon}(pj) X_j^{\downarrow 2}, \tag{4.29}$$

where $\epsilon(pj)$ and $\tilde{\epsilon}(pj)$ are non-operator expressions which we calculate using the method of work [36]. At electron concentration $n$=1 in a paramagnetic state we have

$$\epsilon(pj) = (1-2d)t_{pj}\,,\ \ \tilde{\epsilon}(pj) = (1-2d)t_{pj}\,, \tag{4.30}$$

with $d = \langle X_p^2 \rangle$ being the concentration of doublons.

Let us take into account the functions $\left\langle\left\langle \left[X_p^{\downarrow 2}, H_1'\right]_- \middle| X_s^{2\downarrow} \right\rangle\right\rangle$ and $\left\langle\left\langle \left[X_p^{0\uparrow}, H_1'\right]_- \middle| X_s^{2\downarrow} \right\rangle\right\rangle$ in the mean-field approximation:

$$\begin{aligned}
&\left\langle\left\langle \left[X_p^{\downarrow 2}, H_1'\right]_- \middle| X_s^{2\downarrow} \right\rangle\right\rangle \\
&= -\sum_{i,i\neq p} t_{ip}\left[\left\langle\left\langle (X_p^{\downarrow} + X_p^2)X_i^{0\uparrow} \middle| X_s^{2\downarrow} \right\rangle\right\rangle + \left\langle\left\langle X_p^{02}X_i^{2\uparrow} \middle| X_s^{2\downarrow} \right\rangle\right\rangle\right. \\
&\left.-\left\langle\left\langle X_p^{\downarrow\uparrow}X_i^{0\downarrow} \middle| X_s^{2\downarrow} \right\rangle\right\rangle\right] \simeq -\sum_{i,i\neq p} t_{ip}\langle X_p^{\downarrow} + X_p^2 \rangle \left\langle\left\langle X_i^{0\uparrow} \middle| X_s^{2\downarrow} \right\rangle\right\rangle\,, \\
&\left\langle\left\langle \left[X_p^{0\uparrow}, H_1'\right]_- \middle| X_s^{2\downarrow} \right\rangle\right\rangle \\
&= -\sum_{i,i\neq p} t_{ip}\left[\left\langle\left\langle (X_p^{0} + X_p^{\uparrow})X_i^{\downarrow 2} \middle| X_s^{2\downarrow} \right\rangle\right\rangle + \left\langle\left\langle X_p^{02}X_i^{\downarrow 0} \middle| X_s^{2\downarrow} \right\rangle\right\rangle\right. \\
&\left.-\left\langle\left\langle X_p^{\downarrow\uparrow}X_i^{\uparrow 2} \middle| X_s^{2\downarrow} \right\rangle\right\rangle\right] \simeq -\sum_{i,i\neq p} t_{ip}\left\langle X_p^{0} + X_p^{\uparrow} \right\rangle \left\langle\left\langle X_i^{\downarrow 2} \middle| X_s^{2\downarrow} \right\rangle\right\rangle\,,
\end{aligned} \tag{4.31}$$

in this way we neglect the processes describing the "inter-band" hoppings of electrons which are connected with spin turning over and "inter-band" hoppings with creation or annihilation of two electrons on the same site.

So we obtain the closed system of equations

$$\begin{aligned}
&(E-\mu\ +\ U)\left\langle\left\langle X_p^{\downarrow 2} \middle| X_s^{2\downarrow} \right\rangle\right\rangle - \sum_i \tilde{\epsilon}(pi)\left\langle\left\langle X_i^{\downarrow 2} \middle| X_s^{2\downarrow} \right\rangle\right\rangle \\
&\quad + \left\langle X_p^{\downarrow} + X_p^2 \right\rangle \sum_{i,i\neq p} t_{ip}\left\langle\left\langle X_i^{\downarrow 2} \middle| X_s^{2\downarrow} \right\rangle\right\rangle = \frac{\left\langle X_p^2 + X_p^{\downarrow} \right\rangle}{2\pi}\delta_{ps}\,, \\
&(E\ -\ \mu)\left\langle\left\langle X_p^{0\uparrow} \middle| X_s^{2\downarrow} \right\rangle\right\rangle - \sum_i \epsilon(pi)\left\langle\left\langle X_i^{0\uparrow} \middle| X_s^{2\downarrow} \right\rangle\right\rangle \\
&\quad + \left\langle X_p^{0} + X_p^{\uparrow} \right\rangle \sum_{i,i\neq p} t_{ip}\left\langle\left\langle X_i^{\downarrow 2} \middle| X_s^{2\downarrow} \right\rangle\right\rangle = 0\,.
\end{aligned} \tag{4.32}$$

After the Fourier transformation we obtain solutions of system of Eqs. (4.32):

$$\begin{aligned}\left\langle\left\langle X_p^{\downarrow 2}\middle| X_s^{2\downarrow}\right\rangle\right\rangle_{\boldsymbol{k}} &= \frac{\left\langle X_p^2+X_p^{\downarrow}\right\rangle}{2\pi}\left(\frac{A^1_{\boldsymbol{k}}}{E-E_h(\boldsymbol{k})}+\frac{B^1_{\boldsymbol{k}}}{E-E_d(\boldsymbol{k})}\right), \qquad (4.33)\\ A^1_{\boldsymbol{k}} &= \frac{1}{2}\left(1-\frac{U-\epsilon(\boldsymbol{k})+\tilde{\epsilon}(\boldsymbol{k})}{E_d(\boldsymbol{k})-E_h(\boldsymbol{k})}\right), \quad B^1_{\boldsymbol{k}}=1-A^1_{\boldsymbol{k}},\\ \left\langle\left\langle X_p^{0\uparrow}\middle| X_s^{2\downarrow}\right\rangle\right\rangle_{\boldsymbol{k}} &= \frac{\langle X_p^2+X_p^{\downarrow}\rangle\langle X_p^0+X_p^{\uparrow}\rangle}{2\pi}\\ &\times\frac{t(\boldsymbol{k})}{E_d(\boldsymbol{k})-E_h(\boldsymbol{k})}\left(\frac{1}{E-E_h(\boldsymbol{k})}-\frac{1}{E-E_d(\boldsymbol{k})}\right). \qquad (4.34)\end{aligned}$$

Here $t(\boldsymbol{k})$ is the hopping integral in $\boldsymbol{k}$−representation and

$$\begin{aligned}E_h(\boldsymbol{k}) &= -\mu+\frac{U}{2}+\frac{\epsilon(\boldsymbol{k})+\tilde{\epsilon}(\boldsymbol{k})}{2}\\ &- \frac{1}{2}\sqrt{[U-\epsilon(\boldsymbol{k})+\tilde{\epsilon}(\boldsymbol{k})]^2+\langle X_p^0+X_p^{\uparrow}\rangle\langle X_p^{\downarrow}+X_p^2\rangle(t(\boldsymbol{k}))^2}\,, \qquad (4.35)\\ E_d(\boldsymbol{k}) &= -\mu+\frac{U}{2}+\frac{\epsilon(\boldsymbol{k})+\tilde{\epsilon}(\boldsymbol{k})}{2}\\ &+ \frac{1}{2}\sqrt{[U-\epsilon(\boldsymbol{k})+\tilde{\epsilon}(\boldsymbol{k})]^2+\langle X_p^0+X_p^{\uparrow}\rangle\langle X_p^{\downarrow}+X_p^2\rangle(t(\boldsymbol{k}))^2} \qquad (4.36)\end{aligned}$$

are the energies of electron in lower (“hole”) and upper (“doublon”) subbands, respectively; $\epsilon(\boldsymbol{k})$ and $\tilde{\epsilon}(\boldsymbol{k})$ are the Fourier components of $\epsilon(pj)$ and $\tilde{\epsilon}(pj)$.

Analogous procedure gives for functions $\left\langle\left\langle X_p^{\downarrow 2}\middle| X_s^{\uparrow 0}\right\rangle\right\rangle$ and $\left\langle\left\langle X_p^{0\uparrow}\middle| X_s^{\uparrow 0}\right\rangle\right\rangle$ the following expressions:

$$\begin{aligned}\left\langle\left\langle X_p^{\downarrow 2}\middle| X_s^{\uparrow 0}\right\rangle\right\rangle_{\boldsymbol{k}} &= \left\langle\left\langle X_p^{0\uparrow}\middle| X_s^{2\downarrow}\right\rangle\right\rangle_{\boldsymbol{k}},\\ \left\langle\left\langle X_p^{0\uparrow}\middle| X_s^{\uparrow 0}\right\rangle\right\rangle_{\boldsymbol{k}} &= \frac{\left\langle X_p^0+X_p^{\uparrow}\right\rangle}{2\pi}\left(\frac{A^2_{\boldsymbol{k}}}{E-E_h(\boldsymbol{k})}-\frac{B^2_{\boldsymbol{k}}}{E-E_d(\boldsymbol{k})}\right),\\ A^2_{\boldsymbol{k}} &= B^1_{\boldsymbol{k}}, \quad B^2_{\boldsymbol{k}}=A^1_{\boldsymbol{k}}\,. \qquad (4.37)\end{aligned}$$

Finally, in $\boldsymbol{k}$-representation the single-particle Green function (4.27) we obtain

$$\left\langle\left\langle a_{p\uparrow}\middle| a^{\dagger}_{s\uparrow}\right\rangle\right\rangle_{\boldsymbol{k}} = \frac{1}{2\pi}\left(\frac{A_{\boldsymbol{k}}}{E-E_h(\boldsymbol{k})}+\frac{B_{\boldsymbol{k}}}{E-E_d(\boldsymbol{k})}\right),$$

$$\begin{aligned} A_{\boldsymbol{k}} &= \frac{1}{2}\left(1-\frac{(C_1-C_2)(U-\epsilon(\boldsymbol{k})+\tilde{\epsilon}(\boldsymbol{k}))+4t(\boldsymbol{k})C_1C_2}{E_d(\boldsymbol{k})-E_h(\boldsymbol{k})}\right), \\ B_{\boldsymbol{k}} &= 1-A_{\boldsymbol{k}}, \end{aligned} \tag{4.38}$$

where $C_1=\left\langle X_p^0+X_p^{\uparrow}\right\rangle$, $C_2=\left\langle X_p^2+X_p^{\downarrow}\right\rangle$.

In the important for an investigation of metal-insulator transition case $n=1$ in a paramagnetic state $\left(\left\langle X_p^{\uparrow}\right\rangle=\left\langle X_p^{\downarrow}\right\rangle\right)$ single-particle Green function (4.38) has the form

$$\begin{aligned} \left\langle\left\langle a_{p\uparrow}\middle| a_{s\uparrow}^{\dagger}\right\rangle\right\rangle_{\boldsymbol{k}} &= \frac{1}{2\pi}\left(\frac{A_{\boldsymbol{k}}}{E-E_h(\boldsymbol{k})}+\frac{B_{\boldsymbol{k}}}{E-E_d(\boldsymbol{k})}\right), \\ A_{\boldsymbol{k}} &= \frac{1}{2}\left(1-\frac{t(\boldsymbol{k})}{\sqrt{U^2+(t(\boldsymbol{k}))^2}}\right), \\ B_{\boldsymbol{k}} &= 1-A_{\boldsymbol{k}}, \end{aligned} \tag{4.39}$$

where single-particle energy spectrum is

$$\begin{aligned} E_h(\boldsymbol{k}) &= (1-2d)t(\boldsymbol{k})-\frac{1}{2}\sqrt{U^2+(t(\boldsymbol{k}))^2}, \\ E_d(\boldsymbol{k}) &= (1-2d)t(\boldsymbol{k})+\frac{1}{2}\sqrt{U^2+(t(\boldsymbol{k}))^2}, \end{aligned} \tag{4.40}$$

(here we took into account that $\mu=\frac{U}{2}$ for $n=1$).

Single-particle Green function (4.39) and energy spectrum (4.40) are exact in the band and atomic limits. It is worthwhile to note, that in distinction from the results of two-pole approximations of Hubbard [3] and Ikeda, Larsen, Mattuck [63] the energy spectrum (4.40) depends on polar states concentration (thus on temperature). In distinction from approximations based on ideology of Roth [37] (in this connection see also Refs. [30, 67]) the energy spectrum (4.40) describes metal-insulator transition. Energy spectrum which describes metal-insulator transition was earlier obtained in work [36]. Expressions (4.40) differ from the respective expressions in work [36] by presence of term $\sqrt{U^2+t^2(\boldsymbol{k})}$ instead of $\sqrt{U^2+4d^2t^2(\boldsymbol{k})}$. This leads to the series of distinctions between results of this work and results of work [36] ($d(U/w)$–dependence, the condition of metal-insulator transition, *etc*); at the same time expression (4.40) depends on polar state concentration similarly to respective expression in work [36].

### 4.2.2. Energy gap and polar states concentration

The energy gap (difference of energies between bottom of the upper and top of the lower Hubbard bands) is given by

$$\varDelta E=E_d(-w)-E_h(w)=-2w(1-2d)+\sqrt{U^2+w^2}\,. \tag{4.41}$$

Expression (4.41) describes the vanishing of the energy gap in the spectrum of paramagnetic insulator at critical value $\left(\frac{U}{w}\right)_c$ when the halfbandwidth $w$ increase (under pressure). Dependence of $\Delta E$ on temperature can lead to the transition from metallic to insulator state with increase of temperature.

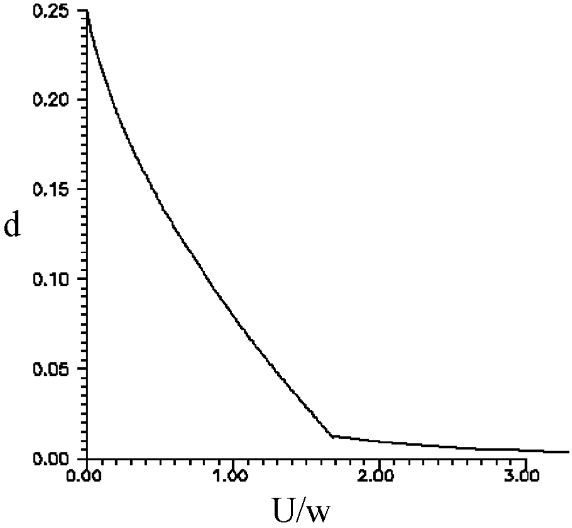

Fig. 4. The dependence of doublon concentration $d$ on $U/w$ at zero temperature.

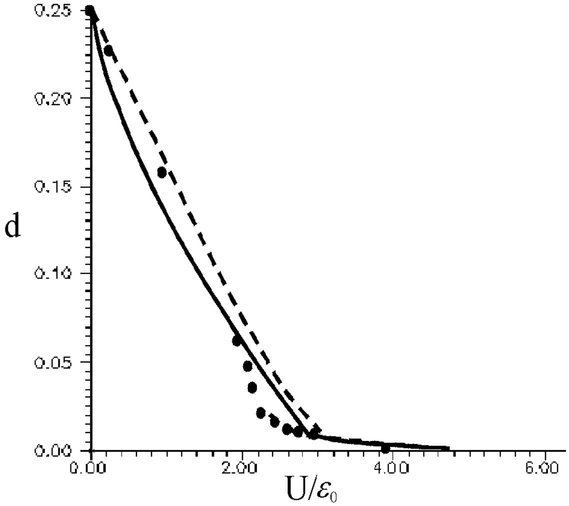

Fig. 5. The comparison of $d(U/w)$ dependences: solid line — our result, dashed line — iterative-perturbative theory [62, 69], circles — QMC method [69].

For the calculation of polar states concentration we use function (4.33). At $T = 0$ and rectangular density of states the concentration of polar states is

$$d = \frac{1}{4} + \frac{U}{8w} \ln\left(\frac{1-4d}{3-4d}\right) \tag{4.42}$$

if $\left(\frac{U}{w}\right) \leq \left(\frac{U}{w}\right)_c$ and

$$d = \frac{1}{4} + \frac{U}{8w} \ln\left(\frac{\sqrt{1+\frac{U}{w}^2}+1}{\sqrt{1+\frac{U}{w}^2}-1}\right) \tag{4.43}$$

if $\left(\frac{U}{w}\right) > \left(\frac{U}{w}\right)_c$. At $T = 0$ we have $\left(\frac{U}{w}\right)_c = 1.672$.

The dependence $d\left(\frac{U}{w}\right)$ given by Eqs.(4.42)–(4.43) is plotted on Fig. 4. One can see that in the point $\left(\frac{U}{w}\right)_c$ the slope of $d\left(\frac{U}{w}\right)$ –dependence changes; the concentration of doublons vanishes at $\frac{U}{w} \to \infty$. Our result for $d\left(\frac{U}{w}\right)$ in region of MIT is in good agreement with result of papers [62, 69] obtained in the limit of infinite dimensions (Fig. 5). The parameter $U$ is normalised by averaged band energy in absence of correlation $\varepsilon_0$.

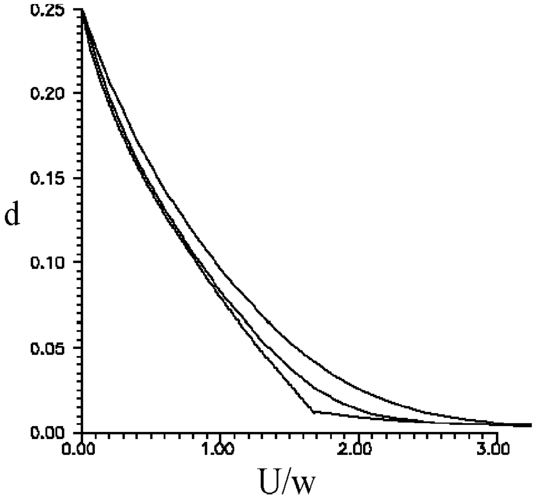

Fig. 6. The dependences of doublon concentration $d$ on $U/w$ at different temperatures: the upper curve corresponds to $kT/w = 0.16$, the middle curve corresponds to $kT/w = 0.08$, the lower curve corresponds to $kT/w = 0$.

In Fig. 6 the dependences of polar states concentration on parameter $\frac{U}{w}$ at different temperatures are presented. Note the important difference (see

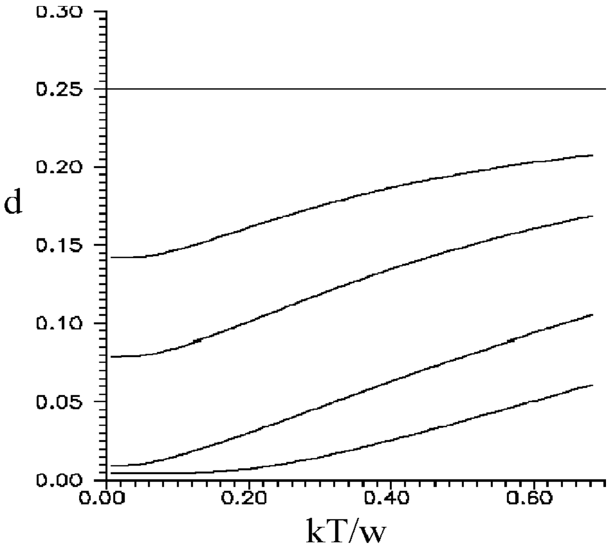

Fig. 7. The dependences of doublon concentration $d$ on temperature at different $U/w$: values of $U/w$ from down to up are 3, 2, 1.5, 1, 0.5, 0

Fig. 7) of the dependence of $d$ on temperature from result of papers [62, 69]: we found that at any temperature polar states concentration increases monotonically with increasing temperature at the fixed value of $\frac{U}{w}$ when respective dependence in [62,69] has a minimum.

The dependence of $\frac{\Delta E}{U}$ on parameter $\frac{U}{w}$ at zero temperature is plotted in Fig. 8. It is important to note that in the point of gap disappearance $d \neq 0$ in contrast to the previously obtained result [36]. At increasing $\frac{U}{w}$ the energy gap width increases (the negative values of $\Delta E$ correspond to the overlapping of the subbands). For comparison on Fig. 8 results of approximation "Hubbard-I" [3] is also plotted. In the point of energy gap vanishing $\left(\frac{U}{w}\right)_c = 1.672$ what is very close to result of "Hubbard-III" approximation [68].

At increase of temperature in metallic state the overlapping of subbands decreases and temperature induced transition from metallic to insulating state can occur at some values of parameter $\frac{U}{w}$ (Fig. 9). The obtained results allows us to draw the $(w/U, T)$ phase diagram of the model (Fig. 10). This phase diagram can explain the experimentally observed transitions from metallic to insulating state with increase of temperature and from insulating to metallic state with increase of bandwidth (under external pressure) in paramagnetic state.

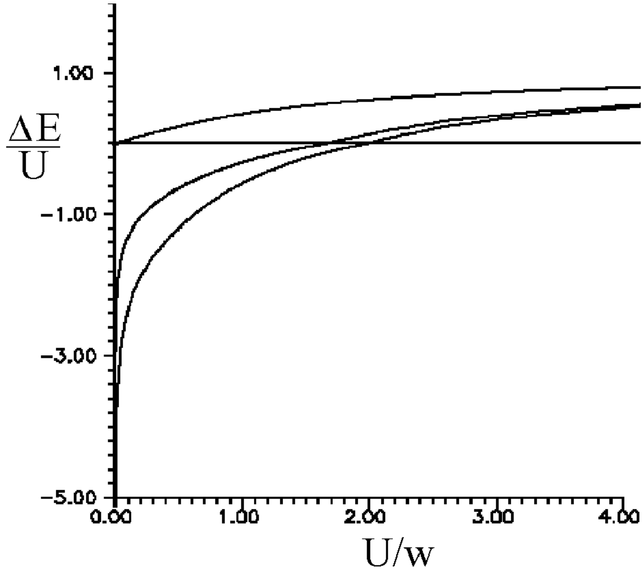

Fig. 8. The dependences of energy gap width on $U/w$: "Hubbard-I" approximation (upper curve), our result (middle curve), approximation [36] (lower curve).

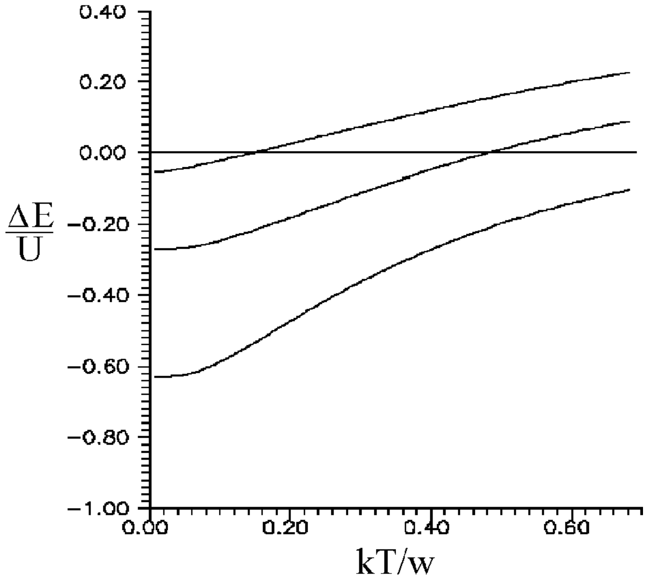

Fig. 9. The dependences of energy gap width on temperature at different $U/w$: values of $U/w$ from down to up are 0.5, 1.2, 1.5.

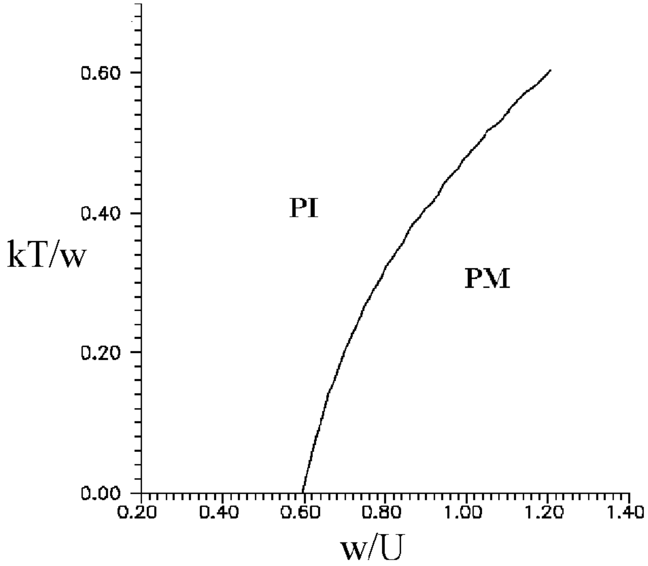

Fig. 10. The obtained $(kT, w/U)$-phase diagram of the model.

### 4.2.3. Ground state energy

The ground state energy of the model

$$\frac{E_0}{N} = \frac{1}{N}\left\langle \sum_{ij\sigma} t_{ij} a^{\dagger}_{i\sigma} a_{j\sigma} \right\rangle + Ud, \tag{4.44}$$

calculated using single particle Green function (4.39) and expressions (4.42)-(4.43) for the concentration of polar states has the form:

$$\frac{E_0}{N} = -\frac{w}{2} + \frac{U}{4}(1+3d) - \frac{U^2}{2w}\frac{(1-4d)}{4(1-2d)^2-1} \tag{4.45}$$

if $\left(\frac{U}{w}\right) \leq \left(\frac{U}{w}\right)_c$ and

$$\frac{E_0}{N} = -\frac{1}{2}\sqrt{U^2+w^2} + 2U\left(\frac{1}{4} - d\right) \tag{4.46}$$

if $\left(\frac{U}{w}\right) > \left(\frac{U}{w}\right)_c$. In Fig. 11 the dependence of the ground state energy on parameter $\frac{U}{w}$ given by Eqs.(4.45)–(4.46) is compared with the exact result, found in one-dimensional case [70]. The upper and lower bounds on ground state energy in one-dimensional case found in paper [71] are also shown. Our result for the ground state energy in metallic state lies slightly lower than exact one and in insulator state fits the exact ground state energy very well.

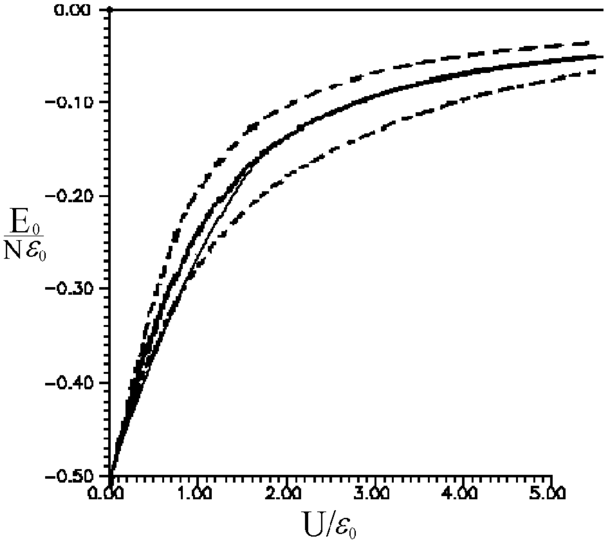

Fig. 11. The comparison of ground state energies in one-dimensional case: dashed curves correspond to upper and lower bounds given by Langer and Mattis, upper solid curve corresponds to exact ground state (Lieb and Wu [70]), lower solid curve corresponds to result of this paper.

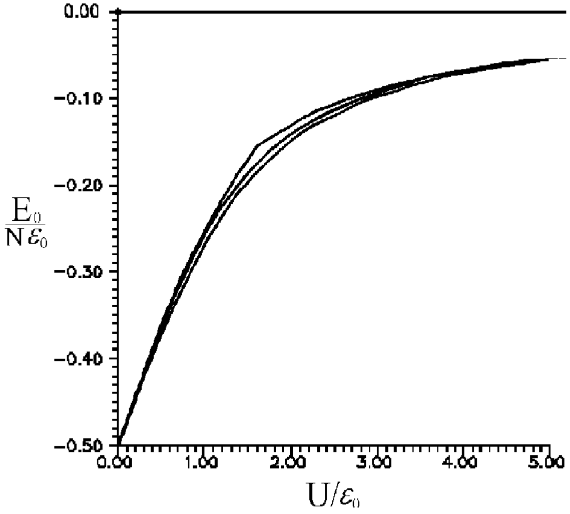

Fig. 12. The ground state energy found in this paper (upper curve), best upper (middle curve) and lower (lower curve) bounds on ground state energy in infinite-dimensional case [72].

In Fig. 12 our plot of the ground state energy is compared with the best upper and lower bounds on in infinite-dimensional case [72]. In Fig. 13 we have the comparison with bounds on ground state energy for three-dimensional simple cubic lattice obtained in paper [71]. In Figs. 11-13 the ground state energy per electron is normalised by averaged band energy in absence of correlation $\varepsilon_0$; in considered case and rectangular density of states $\varepsilon_0 = -\frac{w}{2}$. Figs. 11–13 show that our result present a good approximation for the ground state energy of the system. In Fig. 14 we plot our result for the kinetic part of ground state energy. This plot describes the same behaviour of kinetic energy of electrons with change of correlation strength in paramagnetic state as respective result of work [69]: in metallic state absolute value of kinetic energy decreases rapidly due to rapid decreases of doublon (hole) concentration. In insulating state absolute value of kinetic energy decrease slowly what in the approximation of effective Hamiltonian (obtained for the case $\frac{t_{ij}}{U} \ll 1$) is equivalent to the interaction of local magnetic moments.

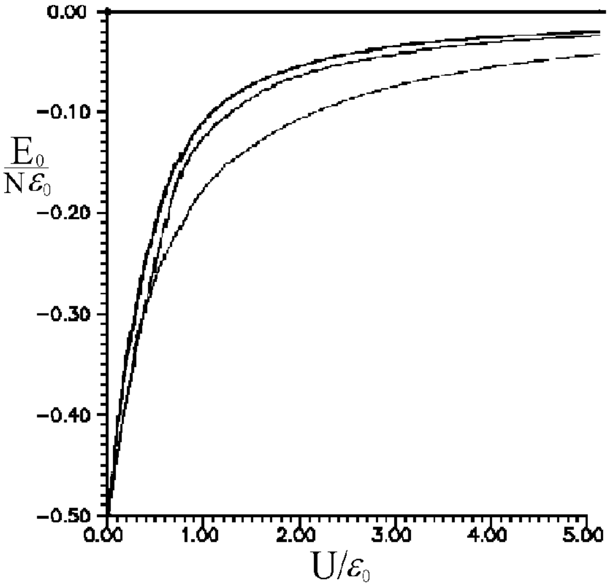

Fig. 13. The upper (upper curve) and lower (lower curve) bounds on ground state energy in three-dimensional case and the ground state energy found in this paper (middle curve).

The comparison of calculated ground state energy with results of other approximations and the exact result found in one-dimensional case shows that the used method is a good approximation for the model under consideration. The obtained phase diagram of the model can explain the transitions from paramagnetic metal state to paramagnetic insulator state at

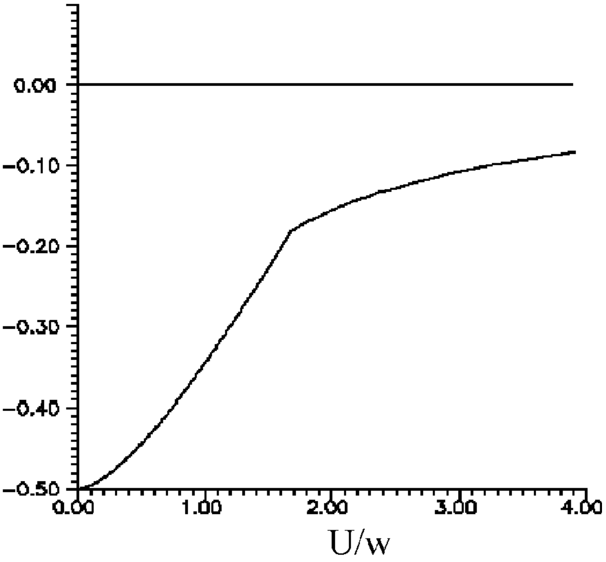

Fig. 14. The kinetic part of ground state energy as a function of $U/w$.

increase of temperature and the paramagnetic insulator — paramagnetic metal transitions under external pressure observed in the systems $\mathrm{NiS}_{2-x}\mathrm{Se}_x$, $(\mathrm{V}_{1-x}\mathrm{Cr}_x)_2\mathrm{O}_3$ and $\mathrm{Y}_{1-x}\mathrm{Ca}_x\mathrm{TiO}_3$.

## 5. Specific narrow-band effects

### *5.1. Absence of electron-hole asymmetry in NEB*

Let us consider narrow-band system in which the electron concentration $n < 1$ and the energy subbands $\sigma$-0 and $\uparrow\downarrow$-$\sigma$ are separated by gap $\Delta E$. Thus at temperature $kT \ll \Delta E$ we can limit ourselves by a consideration of the lower $\sigma - 0$-subband. State of such system (doped Mott–Hubbard insulator — DMHI) will be described by EH (3.20) in which we take that the expressions corresponding to hopping $|\uparrow\downarrow\rangle$-states are equal to a zero.

Let NEB is in the DMHI state with $n > 1$. In the Hubbard model physical properties of system of DMHI are equivalent both for $n < 1$ and for $n > 1$ when the condition $\langle X_i^0 \rangle = \langle X_i^2 \rangle$ is satisfied. This peculiarity of the Hubbard model (doublon-hole or electron- hole symmetry) is a result of hopping integrals equality in $\sigma - 0$- and $\uparrow\downarrow$-$\sigma$-subbands. In the proposed model hopping integrals in both subbands $t_{ij}(n)$ and $\tilde{t}_{ij}(n)$ can be essentially different, besides at the transition of system from the state DMHI with $n < 1$ to the state DMHI with $n > 1$ bandwidth have the jump equal to $2zT(ij)$ (and it continue to decrease with increase of $n$ in consequence of taking into account correlated hopping; see Fig. 15). So properties of narrow-band system with strong intra atomic interaction can be very different for cases $n < 1$ and $n > 1$ in consequence of the essential difference between subband widths (doublon-hole or electron-hole asymmetry).

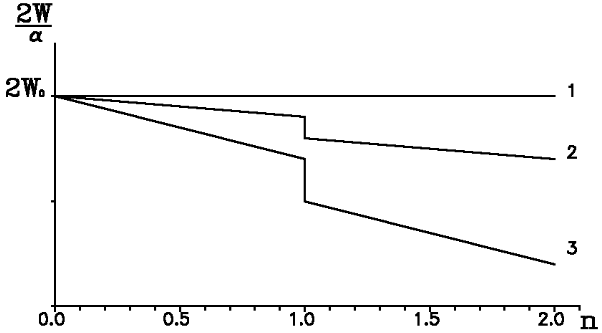

Fig. 15. The change of bandwidth at transition from hole ($n < 1$) to electron ($n > 1$) type of conductivity in doped Mott–Hubbard insulator: 1 — corresponds to Hubbard model ($\tau_1 = \tau_2 = 0$); 2 — $\tau_1 = \tau_2 = 0.1$; 3 — $\tau_1 = \tau_2 = 0.25$; $\alpha$ is the band narrowing factor.

This non-equivalence will be shown, in particular, in dependence of conductivity on degree of subband filling. In paper [22] had been shown that for DMHI conductivity at $n < 1$ $\sigma \sim cnw/(2-n)$, and for $n > 1$ $\tilde{\sigma} \sim d\tilde{w}(2-n)/n$, $(c = \langle X_i^0 \rangle, d = \langle X_i^2 \rangle)$. In the region of electron concentration for which $\partial\sigma/\partial n > 0 (n < 1)$ and $\partial\tilde{\sigma}/\partial n > 0 (n > 1)$ we have conductivity $n$-type, for $\partial\sigma/\partial n < 0)$, $\partial\tilde{\sigma}/\partial n < 0$ — conductivity $p$-type. One can see that $n$–$p$-type of conductivity of narrow-band system in the DMHI state is changed three time with change of electron concentration from 0 to 2: in a region of first and second maximums (if we neglect correlated hopping then $n_1 \simeq 0,6$ and $n_2 \simeq 1,4$) and at $n = 1$. In a region of some conductivity type the expressions for calculation of conductivity can be written in the Drude–Lorentz form with effective mass depending on electron concentration [22].

The non-equivalence of cases $n < 1$ and $n > 1$ in the concentration-dependence of $\sigma(n)$ is confirmed experimentally. In the paper [73] was shown that in metalooxides with less than half-filling of $3d$-shell ($Mn_2O$) conductivity is much higher than in the compounds with half or more than half-filling of $3d$-shell (MnO, NiO).

### *5.2. An application of the model to narrow-band materials*

Let us shortly consider a possibility of application of the obtained results for the explanation of some narrow-band systems properties.

**1.** Cohesive energy of $3d$-metals. The cohesive energy in our model is defined (for the case of weak and moderate intra atomic interaction) by the formula

$$E_b = -\sum_{k\sigma} \epsilon_{\boldsymbol{k}\sigma} \langle \alpha^{\dagger}_{k\sigma} \alpha_{k\sigma} \rangle - \nu U, \tag{5.1}$$

where $\epsilon_{\boldsymbol{k}\sigma}$ — Fourier-component of $t_{ij}$, $\nu = n^2/4$ for $n < 1$ and $\nu = 1 - n + n^2/4$ for $n > 1$. In the approximation of the rectangular density of states cohesive energy has the form

$$E_b = \frac{1}{2w(n)} \left[ w^2(n) - t_c^2 \right] - \nu U, \tag{5.2}$$

with

$$w(n) = w_0 \left[ 1 - n(\tau_1 + \tau_2) \right], \quad t_c = w(n)[n-1],$$

where $\tau_1$, $\tau_2$ are the parameters of correlated hopping, $2w_0$ — unperturbed bandwidth. The dependence of cohesive energy on the $d$-electron concentration in $3d$-systems can be determined by a generalisation of Eq. (5.1) for the case of five equivalent $d$-subbands. Fig. 16 shows that the obtained results explain the peculiarities of the dependence of cohesive energy on atomic number: minimum for Mn and a presence of two non-equivalent maximums (V, Co) (as the result of taking into account correlated hopping).

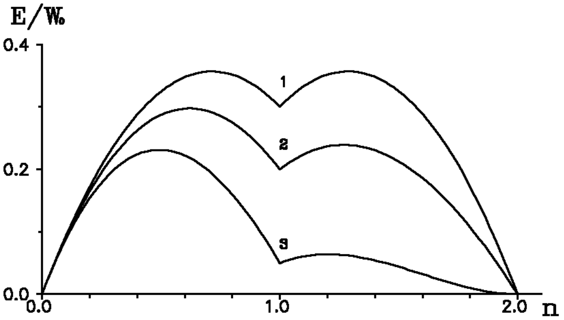

Fig. 16. The dependences of cohesive energy in considered narrow-band model on filling of the $s$-band; $U/(2w_0) = 0.8$; 1 — $\tau_1 = \tau_2 = 0$; 2 — $\tau_1 = \tau_2 = 0.1$; 3 — $\tau_1 = \tau_2 = 0.25$.

**2.** Change of $n-p$ type of conductivity. The noted change of conductivity type at half-filling is confirmed experimentally for some compounds, *e.g.* $\mathrm{VO}_x$; in the frame of the considered model the Mott–Hubbard insulator state at $x=1$ corresponds to the electron concentration $n=1$ (modelling half-filled $t_{2g}$-band). At $x>1$ in $\mathrm{VO}_x$ holes ($\mathrm{V}^{3+}$) appear and at $x<1$ doublons ($\mathrm{V}^{\dagger}$) appear. In accordance with our results the experiment [45] exhibits at $x \simeq 1$ the transition from $p$-type (at $x>1$) to $n$-type conductivity (at $x<1$). Analogous change of the conductivity type is observed also in $\mathrm{Co}_x\mathrm{Fe}_{3-x}\mathrm{O}_3$ [74].

**3.** Concentration-dependence of the activation energy. As a consequence of the concentration-dependence of the parameters in the quasiparticle energy spectrum in $\sigma$-0 and $\uparrow\downarrow$-$\sigma$-subbands, at the transition from the state with $n<1$ to the state with $n>1$, the activation energy has a jump at $n=1$. In this case both increase and decrease of activation energy are possible depending on a mutual arrangement of $\sigma$-0 and $\uparrow\downarrow$-$\sigma$-subbands relative to other bands. This jump of activation energy is confirmed experimentally for $\mathrm{Mn}_x\mathrm{Fe}_{3-x}\mathrm{O}_4$ [74] and $\mathrm{Co}_x\mathrm{Fe}_{3-x}\mathrm{O}_4$ [73].

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