

ON THE ROLE OF CONDUCTION BAND STATES IN FORMING OF ELECTRON NEGATIVE-U CENTRES

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Strong electron self-trapping of a bare state with energy located within the conduction band is investigated. Interaction of the "self-trapping" state with both conduction and valence band states are taken into account. These interactions are shown to give rise to variations of the self-trapping level occupation and can result in double-well and even triple-well adiabatic potentials of the system in question. The dependence of the correlation energy on the "rigidity" of the atomic configuration is found to be non-monotonic, resulting in a minimum of the correlation energy about of the gap width.

1. *Introduction.* A theory of strong electron (electron pair) self-trapping at soft atomic configurations characteristic of glasses, has been developed in some recent papers ^{1,2}. According to this theory, the strong self-trapping occurs when a bare state located in the mobility gap, actually, close to the "parent" band mobility edge (see ³), rather strongly localized at a soft configuration, is occupied by electron (hole) or a singlet electron (hole) pair. The electron state is here called "bare", if both electron-lattice and interactions of this state with both the "parent" and "non-parent" band states are neglected. For finiteness, self-trapping of electrons is explicitly analyzed, for which the conduction and valence bands are the "parent" and "non-parent" bands, respectively, while the situation for holes is quite similar. The strong self-trapping in question is due to strong interaction of electrons with just the soft local atomic configurations. The self-trapping electron generally also interacts with "parent" and "non-parent" band, mainly extended states ("inter-state" interactions), see ². In what follows, a "self-trapping" electron state, by definition, is an electron state under self-trapping when the "inter-state" interactions are neglected, whereas a true (renormalized) electron gap state takes into account both the electron-soft configuration and the "inter-state" interactions.

In this paper we analyse the strong self-trapping when the electron energy level of the bare site state (localized on a soft configuration) lies within the conduction band or in its nearest tail (below the mobility edge) consisting of macroscopically localized states. Interactions of the bare site state with extended states of the conduction band give rise to spreading out of the bare state , i.e. to dispersion of the site wave packet, so that self-trapping of this state, on a soft configuration of interatomic separation scale, seems at first glance to be weak, in contrast to strong self-trapping of a bare state strongly localized in the mobility gap. On the other side, realization of strong self-trapping does not seem to depend on whether the bare site level lies above or below the mobility edge, close to it at least. Therefore, the problem considered in what follows is whether strong

self-trapping in a soft-configuration can be realized even when the bare site state lies in the energy range corresponding to large-size or extended stationary states?

The answer is that strong self-trapping can be realized, even if the bare state level $\tilde{E}_{d\sigma}^{(0)}$ lies within the conduction ("parent") band at a strong enough electron-lattice coupling. The decisive parameter here is the value of the standard single-particle self-trapping energy, W , characterizing the electron-lattice coupling in a soft configuration. The reason is as follows. Let the bare state lie within the energy range of the extended band states. The energy level of the "self-trapping" state, $E_{d\sigma}^{(0)}(z)$, strongly coupled with the soft atomic configuration can move through the conduction band at atomic coordinate variations, so in standard linear approximation

$$E_{d\sigma}^{(0)}(z) = \tilde{E}_{d\sigma}^{(0)} - Qx = \tilde{E}_{d\sigma}^{(0)} - 2Wz. \quad (1)$$

Here $W = Q^2/2k$, the soft-configuration low spring constants are $k \leq 3 \text{ eV/\AA}^2$ ($\leq 0.1k_0$, with the standard spring-constant scale $k_0 \sim 30 \text{ eV/\AA}^2$) and the essential mode coordinate is x , or dimensionless $z = kx/Q$; the typical electron-atomic coupling parameter $Q \sim 3 \text{ eV}$. The subsequent analysis takes into account the difference between $\tilde{E}_{d\sigma}^{(0)}$ and $E_{d\sigma}^{(0)}(z)$. If $z \leq z_* = (\tilde{E}_{d\sigma}^{(0)} - E_g)/2W$, i.e. the level $E_{d\sigma}^{(0)}(z)$ lies within the conduction band, "inter-state" (intraband) interactions strongly disperse the wave packet related to the bare state, so that self-trapping effects are significantly suppressed. However, at $z \geq z_*$ the level $E_{d\sigma}^{(0)}(z)$ leaves the band of extended states and the wave function related to the true state becomes more or less localized. This means that self-trapping effects increase with growing z resulting in energy gain of the system. As usual, increasing elastic energy competes with the electron level lowering in the self-trapping. This competition can result in occurrence of an extra minimum of the adiabatic potential of the system. This extra minimum at $z > 0$ is a signature of the self-trapping state. Moreover, at appropriate values of W this extra minimum corresponds to the lowest energy state of the system.

The problem in question is analysed by Green's function approach for Haldane-Anderson-like Hamiltonian ⁴ using the mean-field approximation for Hubbard repulsion at localized states. We derived the analytical expressions for adiabatic potentials of the system at different initial occupations of localised state and calculate the correlation energy of self-trapped state ¹ as a function of the bare level energy position and standard single-particle self-trapping energy (or atomic spring constant). The self-trapping is shown to be efficient only at large enough standard self-trapping energies and at not very far position of the bare level from the bottom of the conduction band.

2. *Model.* We consider a two band system consisting of the valence $|v_{i\sigma}\rangle$ and conduction $|c_{i\sigma}\rangle$ band states and a bare state $|d\rangle$ localized at a soft atomic configuration. The state $|d\rangle$ is proposed to be coupled with a soft atomic configuration and interact with the band states. Then the total Hamiltonian of the system has the following form:

$$\hat{H} = Wz^2 + \sum_{i,\sigma}^{N_v} \epsilon_{iv} v_{i\sigma}^\dagger v_{i\sigma} + \sum_{i,\sigma}^{N_c} \epsilon_{ic} c_{i\sigma}^\dagger c_{i\sigma} + \sum_{\sigma} E_{d\sigma}^{(0)}(z) d_{\sigma}^\dagger d_{\sigma} + \frac{1}{2} U_c \sum_{\sigma \neq \sigma'} d_{\sigma}^\dagger d_{\sigma} d_{\sigma'}^\dagger d_{\sigma'} + \sum_{i,\sigma}^{N_v} (V_{id}^v v_{i\sigma}^\dagger d_{\sigma} + h.c.) + \sum_{i,\sigma}^{N_c} (V_{id}^c c_{i\sigma}^\dagger d_{\sigma} + h.c.). \quad (2)$$

The first term in eq.(2) describes an elastic atomic energy. The following two additives are the bare ($V=0$ and $Q=0$) band energies. The Hubbard repulsion at the state $|d\rangle$ is characterized by the energy $U_c(\leq 0.3eV^{-1})$. The last two terms are related to the interband ($\sim V_{i\sigma}^v$) and intraband ($\sim V_{i\sigma}^c$) interactions ($|V_{i\sigma}^v| \sim |V_{i\sigma}^c| \sim |V_1|/\sqrt{N}$; $N_v \sim N_c \sim N$, $|V_1| \sim 1eV^{-5}$).

The band energy spectrum is approximated as in ⁴ by rectangular distributions: $\rho_{v\sigma}(\varepsilon) = N_v/\Delta E_v$ at $-\Delta E_v < \varepsilon < 0$ and $\rho_{c\sigma}(\varepsilon) = N_c/\Delta E_c$ at $E_g < \varepsilon < E_g + \Delta E_c$ with $\Delta E_v, \Delta E_c, E_g$ the bands and gap widths ($\Delta E_v \sim \Delta E_c \sim 10eV$, $E_g \sim 1eV$), consequently. The bare energy level $\tilde{E}_{d\sigma}^{(0)}$ is assumed to lay within the conduction band $E_g < \tilde{E}_{d\sigma}^{(0)} < E_g + \Delta E_c$.

To study the self-trapping of state $|d\rangle$ we are interested in the adiabatic potentials $\Phi_n(z)$ of the system with totally filled valence band and various initial (before spreading due to interaction) occupation of the state $|d\rangle$ ($n=0, 1, 2$) at zero temperature. We solved the problem and found $\Phi_n(z)$ within the frame of mean-field approximation (detailed calculations will be presented in more a detailed paper, see also ²):

$$\Phi_n(x) = Wz^2 - \frac{1}{\pi} \sum_{\sigma} \int_{-\Delta E_v}^0 \left[\frac{\pi}{2} + \arctg \frac{\omega - E_{d\sigma}^{eff}(z) - \Sigma_2(\omega)}{\pi \Delta_v} \right] d\omega + \sum_{occupied} E_{d\sigma} - U_c \langle \hat{n}_{\sigma+} \rangle \langle \hat{n}_{\sigma-} \rangle. \quad (3)$$

Here the second term describes the repulsion of the valence band states off the state $|d\rangle$, the third term is the true energy of the "self-trapping" state which can be calculated from the equation:

$$E_{d\sigma} - E_{d\sigma}^{eff} = \Sigma_3(E_{d\sigma}). \quad (4)$$

The effective energies $E_{d\sigma}^{eff}$ can be found self-consistently from the following set of equations:

$$\begin{cases} E_{d\sigma+}^{eff} = E_d^{(0)}(z) + U_c \langle \hat{n}_{d\sigma-} \rangle; \\ E_{d\sigma-}^{eff} = E_d^{(0)}(z) + U_c \langle \hat{n}_{d\sigma+} \rangle, \end{cases} \quad (5a)$$

$$\quad (5b)$$

where $\langle \hat{n}_{d\sigma} \rangle$ is an average of a number operator for the state $|d\rangle$ with the spin projection σ ;

$$\langle \hat{n}_{d\sigma} \rangle = \Delta_v \int_{-\Delta E_v}^0 \frac{d\omega}{(\omega - E_{d\sigma}^{eff}(z) - \Sigma_2(\omega))^2 + (\pi \Delta_v)^2} + \left(1 - \frac{d\Sigma_3}{d\omega} \right)_{E_{d\sigma}, occupied}^{-1} \quad (6)$$

with

$$\Sigma_2(\omega) = \Delta_v \ln \frac{\omega + \Delta E_v}{-\omega} + \Delta_c \ln \frac{E_g - \omega}{E_g + \Delta E_c - \omega} \quad (7a)$$

$$\Sigma_3(\omega) = \Delta_v \ln \frac{\omega + \Delta E_v}{\omega} + \Delta_c \ln \frac{E_g - \omega}{E_g + \Delta E_c - \omega} \quad (7b)$$

the self-energy part of Green function and $\Delta_{v(c)} = \rho_{v(c)} |V^{v(c)}|^2$ are the effective interaction parameters ($\Delta_v \sim \Delta_c \sim \Delta \sim 0.1eV$).

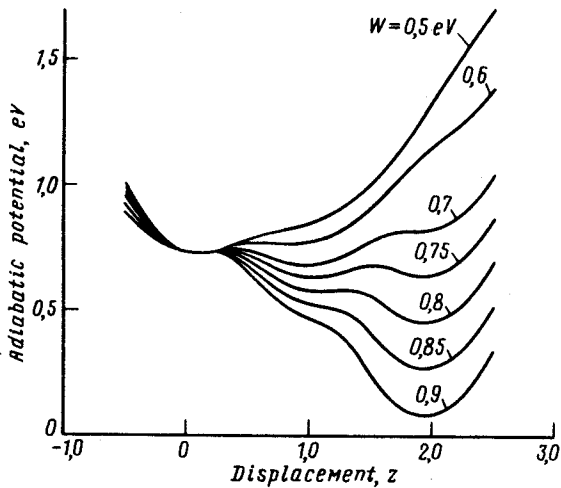


Fig.1: Evolution of the adiabatic potential $\Phi_1(z)$ with W at $\tilde{E}_{d\sigma}^{(0)} = 1.8 \text{ eV}$, $E_g = 1.0 \text{ eV}$, $\Delta E_c = \Delta E_v = 5 \text{ eV}$, $\Delta = 0.1 \text{ eV}$ and $U_c = 0.3 \text{ eV}$

3. *Results and discussions.* The adiabatic potentials given in eq.(3) were calculated by computer simulations. The results for $\Phi_1(z)$, as the most interesting example, are presented in Fig.1. The minima coordinates (equilibrium displacements) $z_{nj} = z_{1j}$ are shown to be close to $z_{11} = 0$, $z_{12} = 1$, or $z_{13} = 2$ where j denotes the minimum number. In case of zero and double initial occupation of the state $|d\rangle$ similar equilibrium displacements can be obtained for a sufficiently wide range of parameters ($\tilde{E}_{d\sigma}^{(0)}$, E_g and W) of the system under investigation. This result allows us to use very simple approximations for the lowest-energy state of the system at different site occupation n and to get simple analytical expressions for the pair correlation energy being an important characteristic of self-trapping ¹.

For investigating the shape of the adiabatic potentials and its transformation with variations of the parameters of the system (W and $\tilde{E}_{d\sigma}^{(0)}$) we derive eq.(3) and get the following equation for equilibrium displacements:

$$z - \sum_{\sigma} \langle \hat{n}_{d\sigma}(z) \rangle = 0. \quad (8)$$

It follows from eq.(8) that both the roots and the number of the roots essentially depend on the average occupation of the state $|d\rangle$ and its variations with the position of $E_{d\sigma}^{(0)}(z)$ (see eq. (1)). As it was mentioned before, if the atomic displacement is not very large ($z < z_*$) so that $E_{d\sigma}^{(0)}(z)$ does not split off the conduction band, the intraband interactions are essential and result in mixing the state $|d\rangle$ with conduction band states. Thereby, the occupation of the state $|d\rangle$ is negligible at any initial occupation. This means that for small $z (< 1)$ the adiabatic potentials, of course, have a single minimum only at $z_{01} \simeq z_{11} \simeq z_{21} \simeq 0$.

For larger atomic displacements the level $E_{d\sigma}^{(0)}(z)$ splits off the conduction band and the role of the intraband interactions decreases. This leads to an increase of the occupation of the state $|d\rangle$ to $\sum_{\sigma} \langle \hat{n}_{d\sigma}(z) \rangle \simeq 1$ for single initial occupation or to $\sum_{\sigma} \langle \hat{n}_{d\sigma}(z) \rangle \simeq 2$ in case of double initial occupation. Occurrence of an additional minimum of $\Phi_1(z)$ and $\Phi_2(z)$ at $z_{12} \simeq 1$ and $z_{22} \simeq 2$ can accompany

this process.

When the level $E_{d\sigma}^{(0)}(z)$ reaches the valence band at further increase of z , the interband interactions become essential and give rise to double occupation of initially free or singly occupied state $|d\rangle$ (see also ²). This process can also result in appearance of an additional minimum at $z_{02} \simeq z_{13}(z_{12}) \simeq 2$.

Occurrence of the additional minima of $\Phi_n(z)$ strongly depends on the value of the system parameters such as W and $\tilde{E}_{d\sigma}^{(0)}$. This is clearly demonstrated in Fig.1 presenting the evolution of a single-well potential to a double-well and triple-well and back to a double-well and a single-well one with increasing the standard self-trapping energy.

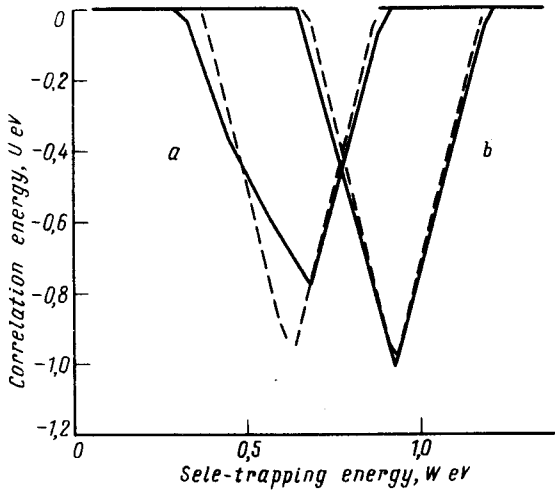


Fig.2: Dependence of the correlation energy U on the standard self-trapping energy W at different positions $\tilde{E}_{d\sigma}^{(0)}$ of the bare level within the conduction band: (a) sufficiently close to the band edge, $E_g < \tilde{E}_{d\sigma}^{(0)} < E_*$, $\tilde{E}_{d\sigma}^{(0)} = 1.6 \text{ eV}$; (b) sufficiently far from the band edge, $\tilde{E}_{d\sigma}^{(0)} > E_*$, $\tilde{E}_{d\sigma}^{(0)} = 2.2 \text{ eV}$ (solid curves - numerical solution according to eqs. (9) and (3); dashed curves - approximate depends according to eqs. (10), (11) and (12)); $E_g = 1.0 \text{ eV}$, $\Delta E_c = \Delta E_v = 5 \text{ eV}$, $\Delta = 0.1 \text{ eV}$ and $U_c = 0.3 \text{ eV}$

The relative energies of the different minima also depend on $\tilde{E}_{d\sigma}^{(0)}$, E_g and W . Therefore, the lowest-energy state of the system can be associated with one of the minima of the adiabatic potential and can transit from one minimum to another with variation of the system parameters. Such a transformation can be clearly demonstrated when investigating the correlation energy dependence on the standard self-trapping energy at different position of the bare site state level (see Fig. 2).

The correlation energy, U , defined as usually ¹,

$$U = \Phi_2(z_2) - 2\Phi_1(z_1) + \Phi_0(z_0) \quad (9)$$

is negative, so negative- U centres form the ground-state of the electron system while single-particle states are excited states of the negative- U centres. In other words, the lowest-energy state is the ground-state here only for double initial occupation. The values of z_i in eq.(9) denote the equilibrium atomic displacements at the ground-state. It is shown in Fig.2, that the shape of the curve $U(W)$ depends on the $\tilde{E}_{d\sigma}^{(0)}$ position.

If the bare level lies in the conduction band sufficiently close to the band (mobility) edge, i.e. $\tilde{E}_{d\sigma}^{(0)} < E_* \simeq 3E_g/2 + U_c/2$, then the situation can be described as follows. For small values of W , $W < W_1 \simeq \tilde{E}_{d\sigma}^{(0)}/2 - E_g/2 + U_c/4$, the equilibrium displacements $z_0 \simeq z_1 \simeq z_2 \simeq 0$ and the state $|d\rangle$ is practically not occupied for any initial occupation. Thereby, $U(z_0, z_1, z_2) \simeq U(0, 0, 0) = 0$.

For larger standard self-trapping energies, $W_1 < W < W_2 = \tilde{E}_{d\sigma}^{(0)} - E_g$, with the level $E_{d\sigma}^{(0)}(z)$ entering the gap, the second minimum of $\Phi_2(z)$ becomes the lowest-energy state one, so $z_2 \simeq 2$. The respective true level of the self-trapped state is located near (above) the valence band top, and the state $|d\rangle$ practically is occupied by two electrons because of very small admixing of conduction band states (at actual $\Delta_c \ll E_g$). At the same time the positions of the minima of the potentials $\Phi_1(z)$ and $\Phi_0(z)$ are close to $z_0 \simeq z_1 \simeq 0$ as before. Then,

$$U \simeq U(0, 0, 2) \simeq 2\tilde{E}_{d\sigma}^{(0)} - 2E_g - 4W + U_c. \quad (10)$$

This expression is derived from eq.(2) when neglecting inessential interactions of the state $|d\rangle$ with conduction band states at double initial occupation and valence band states at single or zero initial occupation of the state $|d\rangle$.

If $W_2 < W < W_3 = \tilde{E}_{d\sigma}^{(0)}/3 + U_c/3$, a change in the equilibrium position of z_1 takes place, with $z_1 \simeq 1$, instead of $z_1 \simeq 0$. The true level for such W and single initial occupation lies in the neighbourhood of midgap and its occupation is closed to unit. However, at zero initial occupation the true level lies within the conduction band as before, so that

$$U \simeq U(0, 1, 2) \simeq -2W + U_c. \quad (11)$$

This is the well-known expression for the correlation energy in the common negative- U centre theory¹. Indeed, this follows from eq.(2) when neglecting the interactions of the state $|d\rangle$ with extended band states.

A further growth of W results in a change of z_0 from $z_0 \simeq 1$ to $z_0 \simeq 2$ for $W_3 < W < W_4 = \tilde{E}_{d\sigma}^{(0)}/2 + U_c/4$. This is a result of a strong admixing of the valence band states to the state $|d\rangle$, which leads to almost double occupation of the state $|d\rangle$ at its single initial occupation. The true level of the self-trapped state at single initial occupation (like at double) lies now near (above) the top of the valence band while the true level at zero initial occupation is located near the conduction band bottom, so that

$$U \simeq U(0, 2, 2) \simeq 4W - 2\tilde{E}_{d\sigma}^{(0)} - U_c. \quad (12)$$

It is clearly seen from eq.(12), that this correlation energy increases with the standard self-trapping energy in contrast to eqs. (10) and (11). This means that U reaches the minimum value at $W = W_3$,

$$U_{min} = U(W_3) \simeq -\frac{2}{3}\tilde{E}_{d\sigma}^{(0)} + \frac{1}{3}U_c \quad (13)$$

(see also ² where similar effects are studied but in case of inessential intraband interactions).

At $W > W_4$, the second minimum of $\Phi_0(z)$ at $z_2 \simeq 2$ becomes the lowest-energy-state one, so an initially non-occupied state $|d\rangle$ becomes doubly occupied

because of strong admixing of the valence band electrons. The correlation energy in this case, obviously, equals zero, $U(2, 2, 2) \approx 0$.

When the bare energy lies within the conduction band sufficiently far from its bottom, $\tilde{E}_{d\sigma}^{(0)} > E_*$, the shape of $U(W)$ is changed (see Fig. 2): the region $W_2 < W < W_3$ disappears and W_2 should be replaced by $W_2^* = \tilde{E}_{d\sigma}^{(0)}/2 - E_g/4 + U_c/4$. This results in a change of U_{min} from eq.(13) to $U_{min} \approx U(W_2^*) \approx E_g$.

We have presented above some approximate expressions for $U(W)$, which agree rather well with the exact solution calculated by computer simulations (see Fig.2).

4. *Conclusions.* To conclude, self-trapping is investigated here of a bare site state of energy $\tilde{E}_{d\sigma}^{(0)}$ lying within the conduction band, the interactions of this state with states of both the "parent" and "non-parent" bands being taken into account. Self-trapping takes place if the standard self-trapping energy W , is large enough so that the level $E_{d\sigma}^{(0)}(z)$ reaches the neighbourhood of the band (mobility) edge. Then, the wave function related to this state becomes localized and a strong electron-atomic interaction at the state $|d\rangle$ can be realized. The related atomic adiabatic potentials of the system appear to become anharmonic, in particular double-well and even triple-well, although the original bare adiabatic potential is a standard harmonic single-well potential Wz^2 in eq.(3). In this connection the interactions of state $|d\rangle$ with extended states can be considered as an additional source of atomic double-well potentials and related two-level systems determining the universal very-low-temperature properties of glasses (see e.g. ¹). The origin of atomic anharmonic, in particular double-well potentials in glasses, of course, cannot be reduced to the influence of the hybridization effects under discussion, as the well-known low temperature properties characteristic of glasses are universal, whereas hybridization effects and negative-U centres are essential largely in glassy semiconductors. It is worth noting in this connection that a model ⁶ different from the present one in some essential respects, has recently been proposed for studying the role of hybridization effects in forming negative-U centres. Despite of the essential differences but also some similar features appear in the behaviour of the adiabatic potentials $\Phi_n(z)$ and the negative correlation energy U .

The negative correlation energy, $U(\tilde{E}_{d\sigma}^{(0)}, W)$, is shown to depend on the bare level ($\tilde{E}_{d\sigma}^{(0)}$) position in the conduction band, or close to the band (mobility) edge, and to be a nonmonotonous function of the standard single-particle self-trapping energy (W), the minimal value of the correlation energy being $U_{min} \sim -E_g$.

The effects analysed can be essential for self-trapping in condensed systems with atomic soft configurations (e.g. in glassy semiconductors ¹). It should be noted also that similar effects can be observed at high pressure when the bare level can enter the band of the extended states.

A detailed investigation of electron and atomic-dynamical properties of the systems under discussion is supposed to be presented elsewhere.

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