

ELECTRON SELF-TRAPPING IN TWO BAND SYSTEM

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Strong electron self-trapping with energy gain close to the magnitude of interband (or mobility) gap width is investigated. Interactions between the "self-trapping" state and the "non-parent" band states are taken into account. It gives rise to the change of occupation of self-trapping state from initial single or zero up to almost double resulting in effective increase of electron-atomic interaction. This effect restricts the value of pair self-trapping correlation energy.

1.Introduction. The problem of electron self-trapping in semiconductors and some insulators is usually considered for a single band system (e.g. self-trapping of conduction band states for electrons ¹⁾) ^{1,2}. Strong electron coupling with the atomic subsystem results in splitting of electronic levels off the "parent" (conduction) band into the interband gap or mobility gap. Therefore, as is well known, polarons appear with self-trapping energy $W_1 < 0$, in particular small polarons with $|W_1| > \Delta E/2$ (ΔE is the band width). The energy gain $|W_1|$ for this process obviously is to be considerably smaller than the gap width, E_g . However, there are realistic situations for which this condition is violated. In glassy semiconductors, for instance, the self-trapping takes place at soft atomic configurations characterized by random small spring constants $k \ll k_0 \simeq 10 - 30 eV/\text{\AA}^2$, with k_0 the typical value of spring constant in crystals. The self-trapping energy for this case is very large so it can exceed $E_g/2$ ². Another example is self-trapping in the crystals with sufficiently narrow gaps ($E_g < |W_1|$) between bands consisting of states of the same parity. In both situations the matrix elements of interactions between the state under self-trapping (referred to as "self-trapping" state in what follows) and the "non-parent" (valence) band states are, generally speaking, finite due to random fields in glassy semiconductors or to symmetry factors in the second situation. Therefore, the problem of self-trapping in these cases has an essentially two-band character.

The purpose of this communication is to analyze main features of the self-trapping in a two-band system, as compared with self-trapping in a single-band system. Green's functions approach, for Haldane-Anderson-like Hamiltonian ³, in a mean field approximation is applied for the problem under consideration.

The most essential specific features of the self-trapping in a two-band system are the following: (i) repulsion of a true (renormalized) self-trapped level off the valence band edge (mobility edge) ^{2,4,5} and (ii) increase of hybridization of the self-trapped state with the states of the valence band. The latter gives rise to an increase of occupancy of initially singly occupied or free "self-trapping" states up to almost double occupation, resulting in an essential gain of the total energy of the system.

¹⁾ Self-trapping of valence band states for holes can be analyzed in a similar way.

Increasing elastic energy at this process prevents the approach of the "self-trapping" state level to the valence band. This can result in appearance of a double-well structure of adiabatic potentials at zero and single initial occupation of the "self-trapping" state. The existence of an extra minimum and the mutual energy positions of the minima depend on the rigidity of the original atomic potential. If the latter is described by a small atomic spring constant $k \ll k_0$ a pair self-trapped ground state is characterized by an energy level (per particle) closed to the valence band edge. It follows from this that the value of the pair correlation energy (eq. (5)) is closed to $E_g/2$ as argued in ² .

2. Model. Electron self-trapping in the two-band system can be described by the following Hamiltonian:

$$\hat{H}_{tot} = \hat{V}_{at}(x) + \hat{H}_e(x) + \hat{H}_{e-at}(x), \quad (1)$$

where $\hat{V}_{at} = kx^2/2$ and x is the atomic configuration coordinate. Electron-atomic configurations interactions are approximated by a standard^{1,2} linear dependence on x :

$$\hat{H}_{e-at} = -Qx \sum_{\sigma} d_{\sigma}^{\dagger} d_{\sigma}, \quad (2)$$

where $Q \sim 1 - 3eV/\text{\AA}$ is the respective coupling parameter for the self-trapping state $|d\rangle$, and σ is a spin projection. The electron subsystem is described by the Hamiltonian:

$$\hat{H}_e = \sum_{i,\sigma} \epsilon_i a_{i,\sigma}^{\dagger} a_{i,\sigma} + \tilde{E}_d^{(0)} \sum_{\sigma} d_{\sigma}^{\dagger} d_{\sigma} + \frac{1}{2} U_c \sum_{\sigma \neq \sigma'} d_{\sigma}^{\dagger} d_{\sigma} d_{\sigma'}^{\dagger} d_{\sigma'} + \sum_{i,\sigma} (V_{i,d} a_{i,\sigma}^{\dagger} d_{\sigma} + h.c.). \quad (3)$$

Here ϵ_i is a spectrum of the original band states $|a_{i,\sigma}\rangle$, $\tilde{E}_d^{(0)}$ is an energy of a bare (with $\hat{V} = 0$ and $Q = 0$) state closed to the bottom of conduction band, U_c is the Hubbard electron repulsion energy for the state $|d\rangle$, $V_{i,d}$ is a matrix element of interaction between the "self-trapping" state and valence band states, $|V_{i,d}| \sim |V_1|/\sqrt{N}$, with $|V_1| \sim 1eV$ ⁶.

We are interested in what follows in adiabatic potentials $\Phi_n(x)$ of the system in the electronic ground state for different occupation numbers n ($n = 0, 1, 2$) of the state $|d\rangle$:

$$\Phi_n(x) = \frac{1}{2} kx^2 + \frac{1}{\pi} \sum_{\sigma} \text{Im} \int \omega Sp(\hat{G}^{(\sigma)}(\omega, x)) d\omega - \frac{1}{2} U_c \sum_{\sigma} \langle \hat{n}_{d,\sigma} \rangle \langle \hat{n}_{d,\sigma-} \rangle, \quad (4)$$

where integration is carried out over the occupied electron states and the Green operator of the problem, $\hat{G}^{(\sigma)}(\omega, x)$, satisfies the equation: $(E_{d,\sigma} - \hat{H})G^{(\sigma)} = \hat{I}$, with $E_{d,\sigma}$ the true, renormalized, level. The terms in (4) describe, respectively, the atomic elastic energy, the energy of the electron subsystem and the third one is characteristic of the mean field approximation³ ($\langle \hat{n}_{d,\sigma} \rangle$ is average of a number operator for the state $|d\rangle$ with spin projection σ).

3. Results and discussion. The problem formulated above can be solved and adiabatic potentials $\Phi_n(x)$ are explicitly found (some details of the solution are presented in Sec.4). Here we analyze the situation for initial single occupation of the state $|d\rangle$. The most specific and essential features of the problem are clearly seen in this case. The results of calculations for $\Phi_1(x)$ at different rigidities of the original atomic potential, i.e. for different values of the polaron shift $|W_1| = Q^2/2k$, as a function of the dimensionless displacement $z = kx/Q$ are presented in Fig.1.

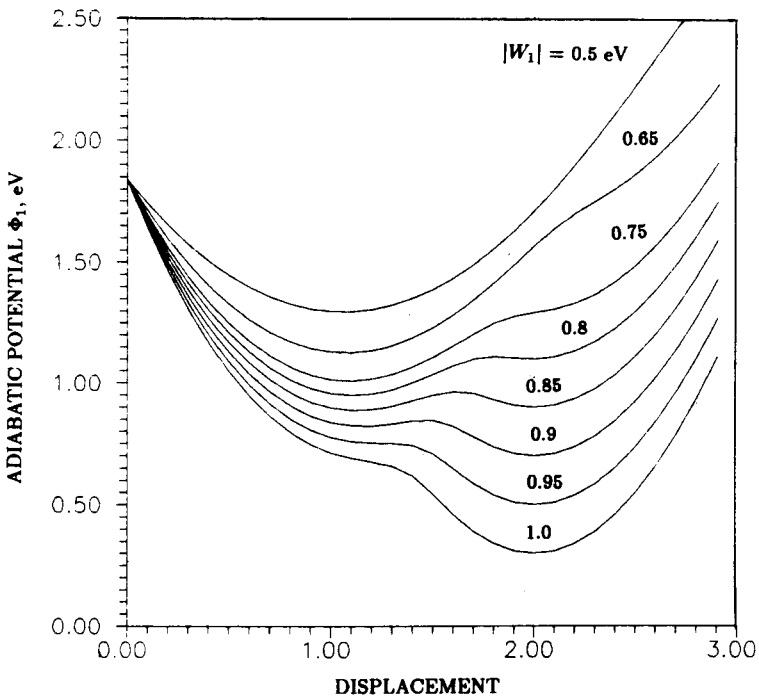


Fig.1. Adiabatic potentials $\Phi_1(z)$ as a function on the dimensionless atomic displacement $z = kx/Q$ at different values of the polaron shift $|W_1|$ and at $\Delta = 0.1eV, U_c = 0.3eV, \Delta E_v = 10eV, \hat{E}_d^{(0)} \approx E_g - 2eV$. The value of $E_{band}^{(0)} (-0)$ is proposed to be a reference point for $\Phi_1(z)$

It is seen from the Fig.1 that only a single minimum exists of adiabatic potential $\Phi_1(z)$ (for initial single occupation of the state $|d\rangle$) at $z_1 \approx 1$ for small values of $|W_1|$. The true level E_d in this case lies relatively far from the valence band edge E_v , $E_d(z_1) - E_v \gg \Delta$; $\Delta = \rho|V|^2 \sim 0.1eV$ is the effective interband interaction energy³, and ρ is a typical density-of-states in the valence band. Therefore, interband interactions are here inessential and the minimum corresponds to the standard single-band polaron shift. An extra minimum at $z_1^* \approx 2$ appears with increasing $|W_1|$ at $|W_1| \sim E_g/2$ (see Fig. 1 and Fig. 2), with $E_d(z_1) - E_v < \Delta$ thereby. In fact, the total energy initially grows for small enough atomic displacements (from the equilibrium position $z_1 \approx 1$), but for larger ones it drops giving rise to the extra minimum at $z_1^* \approx 2$. The reason of the total energy decrease is that the occupation of the state $|d\rangle$ increases due to admixing of the valence band states and the energy gain overcomes the relative elastic energy loss.

For zero initial occupation of the "self-trapping" state a similar effect is also realized for still larger values of $|W_1|$. The reason is that the atomic displacement from the equilibrium position $z_0 \approx 0$ to $z_0^* \approx 2$ as well as the loss of the elastic energy are large as compared to the case of the displacement from $z_1 \approx 1$ to $z_1^* \approx 2$ at single initial occupation.

If, however, the bare state initially is doubly occupied, the interband interactions do not change the occupation of the state and, therefore, the total energy of the system, so the effects discussed above are unimportant.

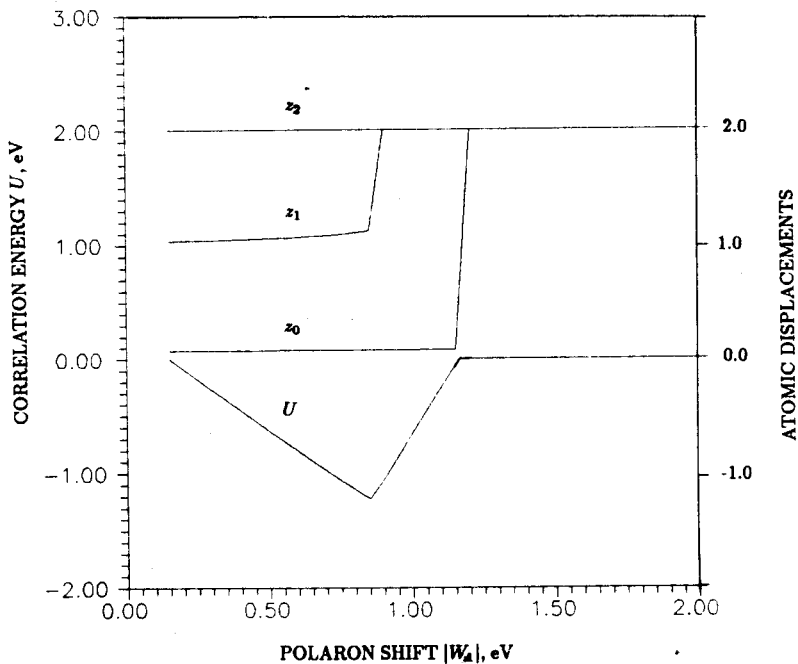


Fig.2. The dependence of the pair correlation energy U and the equilibrium dimensionless displacements z_i on the polaron shift value $|W_1|$ at $\Delta = 0.1eV$, $U_c = 0.3eV$, $\Delta E_v = 10eV$ and $\tilde{E}_d^{(0)} \approx E_g - 2eV$

A consequence of the interband interactions and the related decrease of the total energy is a nonmonotonic dependence of the pair correlation energy

$$U = \Phi_2(x_2) - 2\Phi_1(x_1) + \Phi_0(x_0) \quad (5)$$

on $|W_1|$ (see Fig. 2); here x_n is the equilibrium displacement for the ground state minima of the adiabatic potentials $\Phi_n(x)$. Since the interband interactions are inessential for small values of $|W_1|$ the correlation energy, as usual², linearly decreases with growing $|W_1|$, $U = -2|W_1| + U_c$. However, for $|W_1| > |W_1^*| \approx (E_g + U_c)/3$, when the extra minimum of $\Phi_1(x)$ at $x_1^* \approx 2Q/k$ corresponds to the ground state, the situation changes essentially. The magnitude of the correlation energy grows with increasing $|W_1|$ as approximately $U \approx 4|W_1| - U_c - 2\tilde{E}_d^{(0)}$ (this follows from detailed analysis). The maximum of the magnitude of the correlation energy is realized for $|W_1| \approx |W_1^*|$, so that $U_{\max} \equiv \max|U| \approx (2\tilde{E}_d^{(0)} - U_c)/3$ is close to half of the interband gap (mobility gap) width⁴. For a further increase of $|W_1|$ ($> (\tilde{E}_d^{(0)} + U_c/2)/2$) the extra minimum of $\Phi_0(x)$ corresponds to the ground state, so that correlation energy does not practically depend on $|W_1|$ being close to zero, $|U| \approx 0$ (see Fig. 2)².

4. Some details of the solution. To analyze the problem in question we use a mean field approximation in equation (3) for the electron-electron interaction at the state $|d\rangle$. The result is that the effective Hamiltonian is bilinear in

²) Such a conclusion follows from the detailed analysis of $\Phi_0(x)$ which will be presented elsewhere.

operators \hat{a}_σ and \hat{d}_σ . Of course this feature provides that electron-electron interactions do not change the energy of the system of which all the levels in question are originally doubly occupied, i.e.

$$Im \int_{-\infty}^{\infty} \omega Sp(\hat{G}^{(\sigma)}(\omega, x))d\omega = Im \int_{-\infty}^{\infty} \omega Sp(\hat{G}_0^{(\sigma)}(\omega, x))d\omega. \quad (6)$$

An associated property is that for such systems

$$\langle \hat{n}_{ii} \rangle = \frac{1}{\pi} Im \int_{-\infty}^{\infty} Sp(\hat{G}_{ii}^{(\sigma)}(\omega, x))d\omega = 1. \quad (7)$$

As well taking into account relations (6)-(7), one can easily get the following expression for the adiabatic potential $\Phi_1^{(\sigma+)}(x)$:

$$\Phi_1^{(\sigma+)}(x) = \frac{1}{2}kx^2 + E_{band}^{(0)} + E_d^{(0)}(x) - (E_{d,\sigma-} - E_{d,\sigma-}^{eff}). \quad (8)$$

Here $E_{band}^{(0)}$ is the original ($\hat{V} = 0, Q = 0$) total valence band energy, as non-essential additive term, $E_d^{(0)}(x) = \tilde{E}_d^{(0)} - Qx$ stands for a "single band" (at $\hat{V} = 0$) level. The energies $E_{d,\sigma-}$ and $E_{d,\sigma-}^{eff}$ can be found self-consistently, as follows³:

$$E_{d,\sigma-} - E_{d,\sigma-}^{eff} = \Sigma(E_{d,\sigma-}), \quad (9)$$

$$E_{d,\sigma-}^{eff} = E_d^{(0)}(x) + U_c \langle \hat{n}_{\sigma+} \rangle. \quad (10)$$

Here $\langle \hat{n}_{\sigma+} \rangle$ stands for the occupancy of the "single band" level with $\sigma = \sigma+$ and $\Sigma(E_{d,\sigma-})$ for the Green's function self-energy part. Ignoring the non-essential interactions of the "self-trapping" state with states of the conduction band, one can see that $\langle \hat{n}_{\sigma+} \rangle = 1$ and

$$\Sigma(E) = \int_{VB} \frac{\Delta(\varepsilon, E)d\varepsilon}{E - \varepsilon} \quad (11)$$

with

$$\Delta(\varepsilon, E) = \rho(\varepsilon)|V(\varepsilon, E)|^2 \quad (12)$$

the effective interaction; $\rho(\varepsilon)$ is the valence band density-of-states. To calculate the self-energy part of Green's function, we have used for the sake of simplicity a rectangular approximation (similar to³) for the energy dependence of the effective interaction, i.e. $\Delta(\varepsilon, E) = \Delta$ within the valence band and $\Delta(\varepsilon, E) = 0$ otherwise. Such an approximation leads to the following result for $\Sigma(E)$ for essential energies above the top of the valence band E_v ($E_v = 0$):

$$\Sigma(E) = \Delta \ln \frac{E + \Delta E_v}{E}; \quad (13)$$

ΔE_v is the valence band width. Using this expression one can solve equations (9)-(10) numerically and find the explicit dependence of the adiabatic potential on the configuration coordinate x (see Sec. 3).

Minimization of $\Phi_1^{(\sigma)}(x)$ with respect to x gives rise to the following equation:

$$kx - Q - Q(1 - \gamma_{d,\sigma}^2(x)) = 0, \quad (14)$$

determining the equilibrium displacement. Here the parameter $\gamma_{d,\sigma}^2$,

$$\gamma_{d,\sigma}^2 = \langle \hat{n}_{d,\sigma} \rangle = \frac{1}{1 + \sum_E' (E = E_{d,\sigma})}, \quad (15)$$

describes the occupation probability of the state $|d\rangle$. It is clearly seen from eq. (14) that the equilibrium position changes from $x_1 = Q/k$ for small admixing of extended states ($\gamma_{d,\sigma}^2(x_1) \simeq 1$) to $x_1^* \simeq 2Q/k$ for strong hybridization near the valence band edge for large $|W_1|$ ($\gamma_{d,\sigma}^2(x_1^*) \ll 1$).

It worth add that anharmonicity characteristic of large atomic displacements for strong self-trapping in wide gap systems can change qualitative characteristics of the problem in question. These effects will be analyzed elsewhere.

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