

Electron self-trapping in a two-band system

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Strong electron self-trapping with energy gain close to the magnitude of the 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 the self-trapping state from initial single or zero up to almost double resulting in effective increase of electron–atom 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 electrons¹).^{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 $|W_1|$ of this process obviously is considerably smaller than the gap width, E_g . However, there are realistic situations in 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, $k \ll k_0 \approx 10\text{--}30 \text{ eV}/\text{\AA}^2$, where k_0 is the typical value of the spring constant in crystals. The self-trapping energy for this case is very large, so it can exceed $E_g/2$ (Ref. 2). Another example is the self-trapping in crystals with sufficiently narrow gaps ($E_g < |W_1|$) between bands consisting of states of the same parity. In each case the matrix elements of the 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 finite due to random fields in glassy semiconductors or due to symmetry factors in the second case. Therefore, the problem of self-trapping in these cases has an essentially two-band nature.

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

The essential specific features of the self-trapping in a two-band system are the following: (i) repulsion of a true (renormalized) self-trapped level from the valence band edge (mobility edge)^{2,4,5} and (ii) increase in hybridization of the self-trapped state with the states of the valence band. The latter gives rise to an increase of occu-

pancy of initially singly occupied or free "self-trapping" states up to almost double occupation, which results in an essential gain of the total energy of the system.

Increasing elastic energy in this process prevents the approach of the "self-trapping" state level to the valence band. This can result in the 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) which is closed to the valence band edge. It thus follows that the value of the pair correlation energy [Eq. (5)] is closed to $E_g/2$ as suggested in Ref. 2.

2. Model. Electron self-trapping in the two-band system can be described by the 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. The electron-atomic configuration interactions can be 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 $Q \sim 1 - 3 \text{ eV/\AA}$ is the respective coupling parameter of the self-trapping state $|d\rangle$, and σ is a spin projection. The electron subsystem is described by the Hamiltonian:

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

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

We are interested in what follows in the 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 $|\bar{d}\rangle$:

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

where the integration is carried out over the occupied electron states and the Green's operator of the problem, $\hat{G}^{(\sigma)}(\omega, x)$, satisfies the equation $(E_{d,\sigma} - \hat{H})\hat{G}^{(\sigma)} = \hat{I}$, where

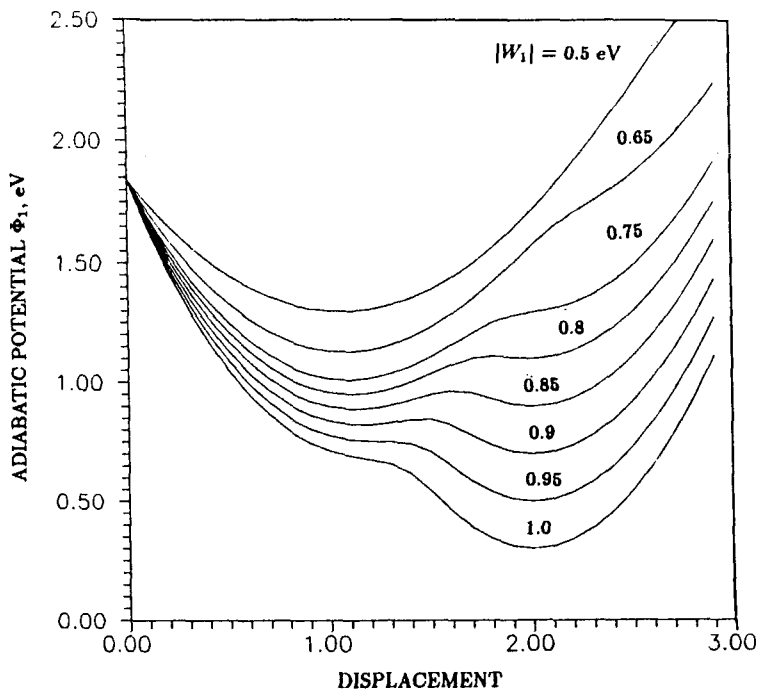


FIG. 1. Adiabatic potentials $\Phi_1(z)$ plotted as a function of the dimensionless atomic displacement $z = kx/Q$ for different values of the polaron shift $|W_1|$ and for $\Delta = 0.1$ eV, $U_c = 0.3$ eV, $\Delta E_v = 10$ eV, $\bar{E}_d^{(0)} \approx E_g = 2$ eV. The value of $E_{\text{band}}^{(0)}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

$E_{d,\sigma}$ is the true, renormalized level. The terms in (4) describe, respectively, the atomic elastic energy and the energy of the electron subsystem; the third term is characteristic of the mean-field approximation³ ($\langle \hat{n}_{d,\sigma} \rangle$ is the average of a number operator for the state $|d\rangle$ with the spin projection σ).

3. Results and discussion. The problem formulated above can be solved and adiabatic potentials $\Phi_n(x)$ can be explicitly found (some details of the solution are presented in Sec. 4). Here we analyze the case for the 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 shown in Fig. 1.

It is evident from Fig. 1 that only a single minimum of the adiabatic potential $\Phi_1(z)$ (for initial single occupation of the state $|d\rangle$) exists 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 , $E_d(z_1) - E_v \gg \Delta$; $\Delta = \rho|V|^2 \sim 0.1$ eV is the effective interband interaction energy,³ and ρ is a typical density of state in the valence band. Therefore, the interband interactions are unimportant and the minimum corresponds to the standard single-band polaron

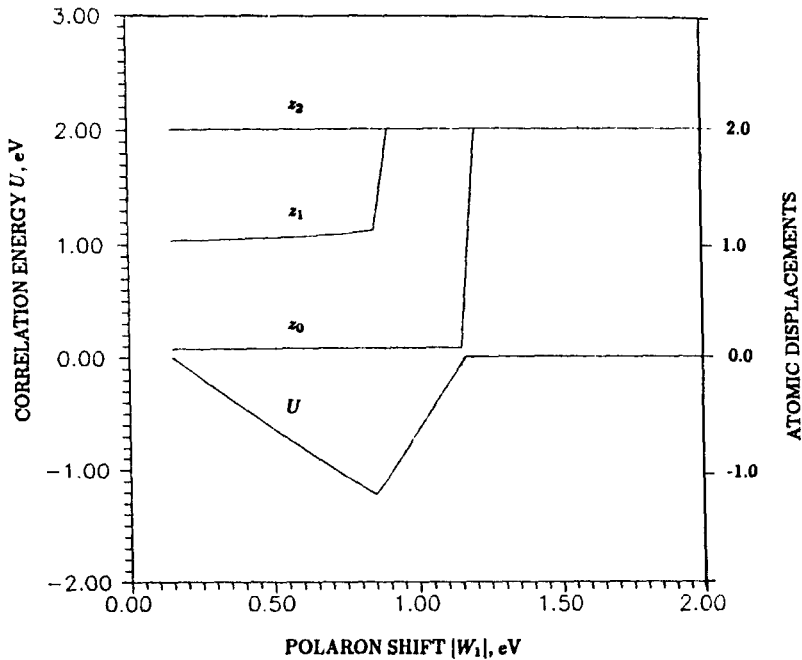


FIG. 2. Dependence of the pair correlation energy U and the dimensionless equilibrium displacements z_i on the polaron shift $|W_1|$ at $\Delta = 0.1$ eV, $U_c = 0.3$ eV, $\Delta E_v = 10$ eV, and $\tilde{E}_d^{(0)} \approx E_g = 2$ eV.

shift. An extra minimum at $z_1^* \approx 2$ appears with increasing $|W_1|$ at $|W_1| \sim E_g/2$ (see Figs. 1 and 2), so that $E_d(x_1) - E_v < \Delta$. In fact, the total energy initially increases for small enough atomic displacements (from the equilibrium position $z_1 \approx 1$), but for larger displacements it decreases, giving rise to the extra minimum at $z_1^* \approx 2$. The reason for 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 realized for even larger values of $|W_1|$. The reason is that the atomic displacement from the equilibrium position $z_0 \approx 0$ to $z_0^* \approx 2$, and the loss of the elastic energy, are large compared with 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.

A consequence of the interband interactions and of the related decrease in 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 unessential for small values of $|W_1|$, the correlation energy, as usual,² decreases linearly with increasing $|W_1|$, $U = -2|W_1| + U_c$. However, for $|W_1| > |W_1^*| \simeq (E_g + U_c)/3$, where the extra minimum of $\Phi_1(x)$ at $x_1^* \simeq 2Q/k$ corresponds to the ground state, the situation changes fundamentally. The magnitude of the correlation energy increases with increasing $|W_1|$ approximately as $U \simeq 4|W_1| - U_c - 2\tilde{E}_d^{(0)}$ (this follows from a detailed analysis). The maximum of the correlation energy is realized for $|W_1| \simeq |W_1^*|$, so that $U_{\max} \equiv \max|U| \simeq (2\tilde{E}_d^{(0)} - U_c)/3$ is close to half the interband gap (the mobility gap) width.⁴ 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 the correlation energy does not depend on $|W_1|$ since it is close to zero, $|U| \simeq 0$ (see Fig. 2).²⁾

4. Some details of the solution. To analyze the problem in question, we use a mean-field approximation in Eq. (3) for the electron-electron interaction at the state $|d\rangle$. The result is that the effective Hamiltonian is bilinear in the operators \hat{a}_σ and \hat{d}_σ . This feature accounts for the fact that the electron-electron interactions do not change the energy of the system, whose levels 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

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

Using relations (6) and (7), we easily find 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, the nonessential additive term, and $E_d^{(0)}(x) = \tilde{E}_d^{(0)} - Qx$ 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 follows:³

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

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

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 nonessential interactions of the self-trapping state with the states of the conduction band, we see that $\langle \hat{n}_{\sigma+} \rangle = 1$ and

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

where

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

the effective interaction; $\rho(\varepsilon)$ is the valence band density of states. To calculate the self-energy part of the Green's function, we have used for simplicity a rectangular approximation (similar to that in Ref. 3) for the energy dependence of the effective interaction, i.e., $\Delta(\varepsilon, E) = \Delta$ in 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 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, we can solve Eqs. (9) and (10) numerically and find the explicit dependence of the adiabatic potential on the configuration coordinate x (see Sec. 3).

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

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

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

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

describes the occupation probability of the state $|d\rangle$. It is clearly evident 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 is worth noting that the anharmonicity characteristic of the large atomic displacements for strong self-trapping in the wide-gap systems can change the qualitative characteristics of the problem in question. These effects will be analyzed elsewhere.

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

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

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