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Strong self-trapping in semiconducting two-band systems

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Strong electron self-trapping is investigated at an energy gain exceeding (or close to) an interband gap width. Interactions between states in self-trapping and "nonparent" bands are taken into account. These interactions lead to changes in the occupation of the state in question: singly occupied or unoccupied states become doubly occupied. The shape of the adiabatic potentials is investigated for different initial occupation of the self-trapping state. A standard single-well potential can be to be transformed to a double-well potential. The extra minimum describes a strongly hybridized practically doubly occupied self-trapped state. The single-particle self-trapping energy and pair-correlation energy appear to depend strongly on these effects. The value of the pair self-trapping correlation energy is shown to be limited to about half of the gap width.

I. INTRODUCTION

Different aspects of the problem of self-trapping in solids appear when the self-trapping is strong, such as in disordered semiconductors.[1] The heart of the problem is the origin of the self-trapping process and the resulting self-trapped states, or the reconstruction of the bare electron state under self-trapping. The energy gain in this process, the self-trapping energy W_1 (<0), for a single particle is usually supposed to be small in the sense that $|W_1| \ll E_g$,[2,3] with E_g the interband gap width, or the mobility gap width in amorphous materials. In such cases, it is reasonable to consider a single-band self-trapping problem, so only the "parent" band states are essential.[4]

There are, however realistic situations for which this supposition is violated. For instance, in the harmonic approximation

$$|W_1| \simeq Q^2/2k \tag{1}$$

is comparable with E_g in glassy semiconductors with $E_g \simeq 1-3$ eV. This is because disorder in glasses gives rise to a high concentration of atoms in soft configurations with small random spring constants $k \ll k_0 \approx 10-30$ eV/Å,[2] while the electron-atomic configuration-coupling parameter Q is close to the typical value $Q \approx 3$ eV/Å.[1] Furthermore, self-trapping of a singlet electron pair in such a soft configuration turns out to be more favorable energetically than that of a single electron because the self-trapping energy (per particle) is considerably larger, $|W_2|/2 \simeq 2|W_1| \gg U_c$ in the harmonic approximation;[1] U_c denotes the Hubbard electron repulsion with typical values $U_c \lesssim 0.3$ eV in semiconductors.[5]

Another example is electron self-trapping in a crystal with a narrow gap between bands consisting of states of the same parity, at $E_g < |W_1|$.

In both examples interband interactions are expected to be important for the self-trapping, since the matrix elements with the valence-band states of the electron state under self-trapping (named for brevity the "self-trapping" state) are finite, either due to random fields (in glassy semiconductors), or to fulfilled selection rules (for narrow-gap semiconductors). Hence, the self-trapping problem considered here is essentially a two-band problem.

The purpose of this paper is to develop a theory of strong self-trapping (pair self-trapping, particularly) in two-band systems for which interband interactions become essential. The self-consistent Green's-function approach for a Haldane-Anderson-like Hamiltonian,[6] in a mean-field approximation, is applied to the problem under consideration.

The following specific features of self-trapping in two-band systems are most essential: (i) the repulsion of a true (renormalized) energy level of an electron "self-trapping" state from the valence-band edge or mobility edge[1,7] and (ii) an increase of hybridization of the "self-trapping" electron state with the valence-band states. The latter gives rise to an increase in occupation 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. Therefore, the pair self-trapping appears to be a highly favorable process despite the fact that repulsion of the "self-trapping" state from the valence band limits the energy gain.

Of course, the growth of atomic elastic energy due to the related atomic displacements also can prevent penetration of the true electron level into the valence band. A competition between this energy increase and the energy gain associated with increasing hybridization of the "self-trapping" state can give rise to the appearance of a double-well structure of adiabatic potentials for zero and single initial occupation. One of the two minima describes the standard self-trapped state of the system for which the hybridization with the valence-band states is not essential and can be neglected, in contrast to the extra minimum for the strongly hybridized self-trapped state.

The forms of the adiabatic potential and the existence of an extra minimum in particular depend strongly on the value of the single-polaron shift $|W_1|$, i.e, on the atomic spring constant, k, for a fixed electron-atomic configuration-coupling parameter, Q. The single minimum related to the polaronlike state exists for small values of $|W_1|$ ($|W_1| \ll E_g$), while the other minimum, describing an essentially hybridized state, appears for larger $|W_1| \sim E_g$ and becomes the lowest-energy minimum for $|W_1|$ comparable with E_g. In other words, the harmonic approximation[8] becomes irrelevant here.

Therefore, the self-trapping in two-band systems has essentially different features compared to those in single-band systems.

We discuss the model Hamiltonian in Sec. II. Its non-self-consistent and self-consistent solutions for different occupations of the electron levels are found in Secs. III and IV. Energy characteristics of self-trapping in two-band systems are calculated in Sec. V. Conclusions are given in Sec. VI.

II. MODEL

We discuss electron self-trapping in a two-band system, using the following total Hamiltonian of the system:

$$\hat{H}_{\text{tot}} = \hat{V}_{\text{at}}(x) + \hat{H}_e(x) + \hat{H}_{e\text{-at}}(x) \ . \tag{2}$$

Here

$$\hat{V}_{\text{at}} = kx^2/2 \tag{3}$$

is the classical elastic energy for atomic motion along a single essential configuration coordinate x. Indeed, in what follows we discuss atomic systems characterized by a single motion mode. This is shown[1] to be the case for the self-trapping in the soft atomic configurations mentioned above and can be a plausible (though simplified) approximation for self-trapping in narrow-band semiconductors.

Electron-atomic configuration interactions are approximated by a standard linear dependence on x:

$$\hat{H}_{e\text{-at}} = -Qx \sum_{\sigma} \hat{d}^{\dagger}_{\sigma}\hat{d}_{\sigma} \ , \tag{4}$$

as usually applied to the self-trapping problem.[1-3] Here the generation, $\hat{d}^{\dagger}_{\sigma}$, and annihilation, $\hat{d}_{\sigma}$, operators are referred to the state $|d\rangle$ under the self-trapping. It should be noted that terms $\propto x^2, x^3, x^4$ in expansion (4) can be taken into account and appear not to be essential.[9]

The electron subsystem is characterized by the Haldane-Anderson Hamiltonian[6]

$$\hat{H}_e = \sum_{i,\sigma} \varepsilon_i \hat{a}^{\dagger}_{i\sigma}\hat{a}_{i\sigma} + \tilde{E}^{(0)}_d \sum_{\sigma} \hat{d}^{\dagger}_{\sigma}\hat{d}_{\sigma} + \tfrac{1}{2}U_c \sum_{\sigma\neq\sigma'} \hat{d}^{\dagger}_{\sigma}\hat{d}_{\sigma}\hat{d}^{\dagger}_{\sigma'}\hat{d}_{\sigma'} + \sum_{i,\sigma}(V_{id}\hat{a}^{\dagger}_{i\sigma}\hat{d}_{\sigma} + \text{H.c.}) \ , \tag{5}$$

where ε_i stand for the bare (at $V_{id}=0$) spectrum of band (extended) states $|a_{i\sigma}\rangle$ and $\tilde{E}^{(0)}_d$ denotes an energy of the bare (at $V_{id}=0$ and $Q=0$) state $|d\rangle$. The last term in Eq. (5) just describes the interband interactions under consideration, and V_{id} denotes the matrix elements between the "self-trapping" state and valence-band states, $|V_{id}| \sim |V_1|/\sqrt{N}$, with $|V_1| \sim 1$ eV.[10]

In what follows we try to reach the synthesis of the results of both the single-band self-trapping problem[8] and the Haldane-Anderson approach[6] for taking into account the contributions of the interband interactions for non-self-trapped states.

The two-band self-trapping problem is analyzed further by studying adiabatic potentials $\Phi_n(x)$ of the system for different initial occupations n ($n=0,1,2$) of the state $|d\rangle$. The related self-trapping energies for a single electron,

$$\tilde{W}_1 = \Phi_1(x_1) - \Phi_1(x_0) \ , \tag{6}$$

and for a singlet electron pair,

$$\tilde{W}_2 = \Phi_2(x_2) - \Phi_2(x_0) \ , \tag{7}$$

as well as the pair correlation energy,

$$U = \Phi_2(x_2) + \Phi_0(x_0) - 2\Phi_1(x_1) \ , \tag{8}$$

can be calculated. Here x_n denotes the ground-state equilibrium atomic displacement which can be found from the equation

$$\left[\frac{d\Phi_n(x)}{dx}\right]_{x=x_n} = 0 \ . \tag{9}$$

All of these energies, particularly the correlation energy, are important characteristics of the system and will be found for different values of atomic spring constants.

III. SYSTEMS WITH NEGLIGIBLE HUBBARD REPULSION

One of the main difficulties in investigations of the problem described by the Hamiltonian (2)–(5) is associated with accounting for the Hubbard repulsion [the third term in (5)]. Therefore, following Ref. 6 we use here a mean-field approximation which results in energy renormalization of the solution of the Hubbard interaction-free problem. With this in mind, we start with the model Hamiltonian:

$$\begin{aligned}\hat{H}_{\text{tot}} &= \hat{V}_{\text{at}}(x) + \hat{H} \\ &= \tfrac{1}{2}kx^2 + \sum_{i,\sigma} \varepsilon_i \hat{a}^{\dagger}_{i\sigma}\hat{a}_{i\sigma} + \sum_{\sigma} E^{(0)}_d(x)\hat{d}^{\dagger}_{\sigma}\hat{d}_{\sigma} \\ &\quad + \sum_{i,\sigma}(V_{id}\hat{a}^{\dagger}_{i\sigma}\hat{d}_{\sigma} + \text{H.c.}) \ ,\end{aligned} \tag{10}$$

where

$$E^{(0)}_d(x) = \tilde{E}^{(0)}_d - Qx \tag{11}$$

is the single-band electron energy level (at $V_{id}=0$) and the Hubbard repulsion is ignored.

This Hamiltonian is solved by introducing a Green's operator, $\hat{G}$, according to

$$[E_d(x)-\hat{H}]\hat{G}=\hat{I}\ , \tag{12}$$

where $E_d(x)$ is the true electron level. The matrix elements of $\hat{G}$ for the Hamiltonian (10) and (11) can be easily found as follows:

$$G_{dd}=\langle d|\hat{G}|d\rangle=[E_d-E_d^{(0)}(x)-\Sigma(E_d)]^{-1}\ , \tag{13a}$$

$$G_{ii'}=\frac{\delta_{ii'}}{E_d-\varepsilon_i}+\frac{V_{id}V_{di'}}{(E_d-\varepsilon_{i'})}G_{dd}\ , \tag{13b}$$

with

$$\Sigma(\omega)=\sum_i\frac{|V_{di}|^2}{\omega-\varepsilon_i}=\int\frac{\rho(\varepsilon)|V_d(\varepsilon,\omega)|^2d\varepsilon}{\omega-\varepsilon} \tag{14}$$

the self-energy part of the Green's operator and $\rho(\varepsilon)$ the density of states of the two-band system. In fact, integration in (14) is reduced to that in the bands of extended states (see below). The true electron level is a pole of G_{dd} and can be found from the following equation:

$$E_d-E_d^{(0)}(x)=\Sigma(E_d)\ . \tag{15}$$

The resulting adiabatic potentials can be written as follows:

$$\overline{\Phi}_n(x)=\frac{1}{2}kx^2+\frac{1}{\pi}\sum_\sigma \mathrm{Im}\int\omega\,\mathrm{Tr}[\hat{G}^{(\sigma)}(\omega,x)]d\omega\ , \tag{16}$$

where the integration is taken over the occupied electron states only. We analyze the case of zero temperature, keeping in mind that the thermal equilibrium distribution function introduced in (16) for finite (not too high) temperatures T does not essentially change the results of the analysis presented below. This follows from the magnitudes of typical self-trapping energies (in the range $\sim$0.1–1 eV) which are much larger than the temperatures involved.

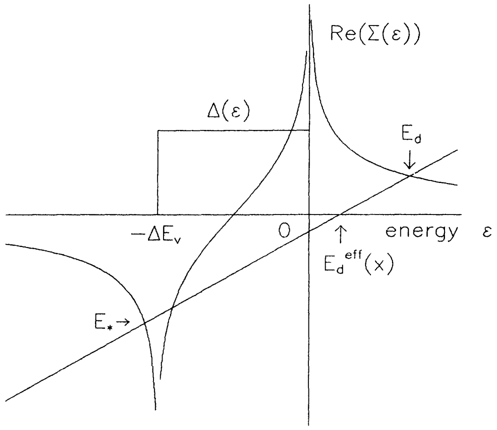

FIG. 1. Dependence of the effective interaction $\Delta(\varepsilon)$ and $\mathrm{Re}(\Sigma(\varepsilon))$ on energy. Cross points of the straight line, $\varepsilon-E_d^{\mathrm{eff}}(x)$, with $\mathrm{Re}(\Sigma(\varepsilon))$ correspond to the related energies E_* and E_d.

The integral in (14) can be calculated, if one knows the energy dependence of the effective interband interaction:

$$\Delta(\varepsilon,\omega)=\rho(\varepsilon)|V_d(\varepsilon,\omega)|^2\ . \tag{17}$$

Here we can use for the sake of simplicity a rectangular model for $\Delta(\varepsilon,\omega)$ (see Fig. 1) and neglect unimportant interactions with the "parent" (conduction) band states. Such an approximation of $\Delta(\varepsilon)$ results in the following energy dependence of the self-energy part (see Fig. 1):

$$\Sigma(\omega)=\begin{cases}-\Delta\ln[\omega/(\omega+\Delta E_v)]\ \text{ at } \omega<-\Delta E_v & (18\text{a})\\ \Delta\ln[(\omega+\Delta E_v)/(-\omega)]+i\pi\Delta\ \text{ at } -\Delta E_v<\omega<0 & (18\text{b})\\ \Delta\ln[(\omega+\Delta E_v)/\omega]\ \text{ at } \omega>0\ , & (18\text{c})\end{cases}$$

with ΔE_v the valence-band width. Taking into account the standard expression (16) for $\mathrm{Tr}\hat{G}$,[6]

$$\mathrm{Tr}\hat{G}=\mathrm{Tr}\hat{G}^{(0)}-\frac{d}{d\omega}\ln\hat{G}_{dd}\ , \tag{19}$$

with $\hat{G}^{(0)}$ the Green operator of the interaction-free system ($V_{di}=0$) and

$$\mathrm{Tr}\hat{G}^{(0)}=\sum_i\frac{1}{\omega-\varepsilon_i}\ , \tag{20}$$

one can rewrite the expression for the adiabatic potentials as follows (see Appendix A):

$$\overline{\Phi}_n(x)=\tfrac{1}{2}kx^2+E_{\mathrm{band}}^{(0)}-\sum_\sigma\Delta E_{*_\sigma}-\frac{1}{\pi}\sum_\sigma\int_{-\Delta E_v}^{0}\left[\frac{\pi}{2}+\arctan\left[\frac{\omega-E_d^{(0)}(x)-\mathrm{Re}(\Sigma(\omega))}{\pi\Delta}\right]\right]d\omega+\sum_{\sigma,\text{occupied}}E_{d\sigma}\ . \tag{21}$$

Here $E_{\mathrm{band}}^{(0)}$ (a reference point for energy) is the total energy of the valence-band states for interaction-free systems. The poles E_{*_σ} ($\Delta E_{*_\sigma}=-\Delta E_v-E_{*_\sigma}>0$) describe the level split off the bottom of the valence band (see Fig. 1) and are not essential here because they are small compared to other characteristic energies. The fourth term in (21) corresponds to a decrease of the valence-band energy due to its repulsion from the electron level in question. The last term in (21) describes the energy of the true states occupied in the gap.

IV. SYSTEMS WITH HUBBARD REPULSION: SELF-CONSISTENT SOLUTION

The mean-field approximation for electron-electron interactions, as well-known, results in a renormalization of the Hamiltonian $\hat{H}$ of Eq. (10):[6]

$$\hat{H}_{\text{tot}}=\hat{V}_{\text{at}}(x)+\hat{H}(E_d^{(0)}(x)\rightarrow E_{d\sigma}^{\text{eff}}(x)) -\tfrac{1}{2}U_c\sum_{\sigma\neq\sigma'}\langle\hat{n}_{d\sigma}\rangle\langle\hat{n}_{d\sigma'}\rangle\ ; \tag{22}$$

the single-band energy $E_d^{(0)}(x)$ defined in (11) should be replaced here by the effective single-band energy $E_{d\sigma}^{\text{eff}}(x)$. These effective energies for different spin projections can be found self-consistently from the following equations:

$$E_{d\sigma+}^{\text{eff}}=E_d^{(0)}(x)+U_c\langle\hat{n}_{d\sigma-}\rangle\ , \tag{23a}$$

$$E_{d\sigma-}^{\text{eff}}=E_d^{(0)}(x)+U_c\langle\hat{n}_{d\sigma+}\rangle\ . \tag{23b}$$

The average values of number operators $\hat{n}_{d\sigma}=\hat{d}_\sigma^\dagger\hat{d}_\sigma$ are defined as

$$\langle\hat{n}_{d\sigma}(x)\rangle=\frac{1}{\pi}\int\text{Im}[G_{dd}^{(\sigma)}(\omega,x)]d\omega\ . \tag{24}$$

Integration in (24) should be carried out over the occupied states only, and the respective substitution $E_{d\sigma}^{\text{eff}}(x)$ for $E_{d\sigma}(x)$ in $G_{dd}^{(\sigma)}(\omega)$, introduced by Eq. (13), must be performed.

The corresponding expression (21) for the adiabatic potentials can be rewritten as follows:

$$\Phi_n^{(0)}(x)=\Phi_n(x,E_d^{(0)}(x)\rightarrow E_{d\sigma}^{\text{eff}}(x)) -U_c\langle\hat{n}_{d\sigma+}\rangle\langle\hat{n}_{d\sigma-}\rangle\ . \tag{25}$$

For further analysis it is worth noting that a mean-field approximation results in a Hamiltonian (22) bilinear in the operators $\hat{a}_{i\sigma}$ and $\hat{d}_\sigma$. This feature provides that electron-electron interactions, of course, do not change the energy of the system of which all the levels in question are originally doubly occupied,[10] i.e.,

$$\text{Im}\int_{-\infty}^{\infty}\omega\,\text{Tr}[\hat{G}^{(\sigma)}(\omega,x)]d\omega =\text{Im}\int_{-\infty}^{\infty}\omega\,\text{Tr}[\hat{G}_0^{(\sigma)}(\omega,x)]d\omega\ . \tag{26}$$

An associated property is that also for such systems

$$\langle\hat{n}_{i\sigma}\rangle=\frac{1}{\pi}\text{Im}\int_{-\infty}^{\infty}G_{ii}^{(\sigma)}(\omega,x)d\omega=1\ , \tag{27}$$

because the interactions cannot change the occupation of the states in this case.

It should be stressed also that interactions of the "self-trapping" state with conduction-band states are inessential for the problem in question. Indeed, the electron level of the "self-trapping" state moves from the conduction band to the valence band so that interactions with the conduction-band states become unimportant as compared to those with the valence-band states. Therefore, in what follows we neglect interactions of the state $|d\rangle$ with the conduction-band states and, in fact, analyze the electron subsystem consisting of electron filled valence-band states and the state $|d\rangle$ with a variable occupation ($n=0,1,2$). In this case the properties (26) and (27) lead to the following relations:

$$E_{\text{band},\sigma}^{(0)}-\Delta E_{*\sigma}-\frac{1}{\pi}\int_{-\Delta E_v}^{0}\left[\frac{\pi}{2}+\arctan\frac{\omega-E_{d\sigma}^{(\text{eff})}(x)-\text{Re}(\Sigma(\omega))}{\pi\Delta}\right]d\omega+E_{d\sigma}=E_{\text{band},\sigma}^{(0)}+E_{d\sigma}^{\text{eff}} \tag{28}$$

and

$$\frac{1}{\pi}\int_{-\infty}^{0}\text{Im}[G_{dd}^{(\sigma)}(\omega,x)]d\omega=1-\frac{1}{\pi}\int_{0}^{\infty}\text{Im}[G_{dd}^{(\sigma)}(\omega,x)]d\omega=1-\gamma_{d\sigma}^2 \tag{29}$$

with

$$\gamma_{d\sigma}^2=\left[1-\frac{d\Sigma}{d\omega}\right]_{\omega=E_{d\sigma}}^{-1} \tag{30}$$

the parameter characterizing a degree of the hybridization of the state $|d\rangle$.

Expressions (28)–(30) essentially simplify the following analysis.

A. Initial zero occupation

It is clear in the case of zero initial occupation of the "self-trapping" state $|d\rangle$ that integration in (16) should be carried out only over the valence-band states. Therefore, the last sum equals zero in (21). Then, using the relation (28), one can easily get that

$$\Phi_0(x)=\tfrac{1}{2}kx^2+E_{\text{band}}^{(0)}-2[E_{d\sigma}-E_{d\sigma}^{\text{eff}}(x)]-U_c\langle\hat{n}_{d\sigma}\rangle^2\ . \tag{31}$$

The most interesting third term in (31) corresponds to the interband interactions. It describes a decrease of the valence-band state energy because of the repulsion off the "self-trapping" state. This decrease, as follows from Eq. (28), exactly equals the growth of the "self-trapping" level energy due to its repulsion from the valence band, as reflected in Eq. (31).

The occupation of the state $|d\rangle$ can be found from Eq. (24) when integrating over the valence band only,

$$\langle\hat{n}_{d\sigma+}\rangle=\langle\hat{n}_{d\sigma-}\rangle=\frac{1}{\pi}\int_{-\infty}^{0}\text{Im}[G_{dd}^{(\sigma)}(\omega,x)]d\omega =1-\gamma_{d\sigma}^2\ . \tag{32}$$

Here we take into account the property (29) and the symmetry for different spin projections.

The parameter $\gamma^2_{d\sigma}$ in Eq. (32) can be estimated within the frame of the simple model dependence of $\Delta(\varepsilon)$ according to Fig. 1,

$$\gamma^2_{d\sigma} = \left[1+\frac{\Delta\Delta E_v}{E_{d\sigma}(E_{d\sigma}+\Delta E_v)}\right]^{-1} . \tag{33}$$

The effective energy level $E^{\text{eff}}_{d\sigma}(x)$ and the true level $E_{d\sigma}$ from Eq. (31) can be found from the solution of Eq. (15) and the set of equations (23) which transform to the following:

$$E_{d\sigma} - E^{\text{eff}}_{d\sigma}(x) = \Delta \ln[E_{d\sigma}/(E_{d\sigma}+\Delta E_v)] , \tag{34a}$$

$$E^{\text{eff}}_{d\sigma}(x) = E^{(0)}_d(x) + U_c(1-\gamma^2_{d\sigma}(E_{d\sigma})) . \tag{34b}$$

These equations are solved numerically, the results being presented in Fig. 2. As is seen from Fig. 2, the interband interactions are unimportant, when a single-band level $E^{(0)}_d(x)$ is far from the valence band, $E^{(0)}_d(x) \gg \Delta$. Admixing of the valence-band states to the state $|d\rangle$ in such a situation is negligible, $\gamma^2_{d\sigma} \simeq 1$, and $E_{d\sigma} \simeq E^{\text{eff}}_{d\sigma}(x) \simeq E^{(0)}_d(x)$. The situation dramatically changes when a single-band state approaches the valence-band top, so the true level $E_{d\sigma}$ repulses off the valence band at $E^{(0)}_d(x) < \Delta$. The initially free state $|d\rangle$ is occupied now due to hybridization and becomes doubly occupied ($\gamma^2_{d\sigma} \to 0$) for further drop of $E^{(0)}_d(x)$ (<0), when $|E^{(0)}_d(x)| \gg \Delta$. The true level in this case is practically stopped near the valence-band top, $E_{d\sigma} \to 0$, while the effective one obeys the following relation:

$$E^{\text{eff}}_{d\sigma}(x) \simeq E^{(0)}_d(x) + U_c . \tag{35}$$

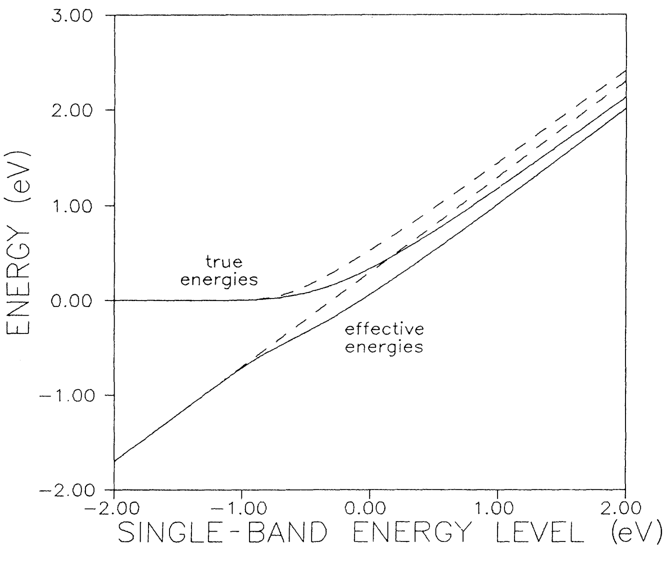

FIG. 2. True and effective energy levels as functions of the single-band energy level $E^{(0)}_d(x)$ for zero (solid lines) and single (dashed lines) initial occupation of the state $|d\rangle$ at $\Delta = 0.1$ eV, $\Delta E_v = 5$ eV, and $U_c = 0.3$ eV.

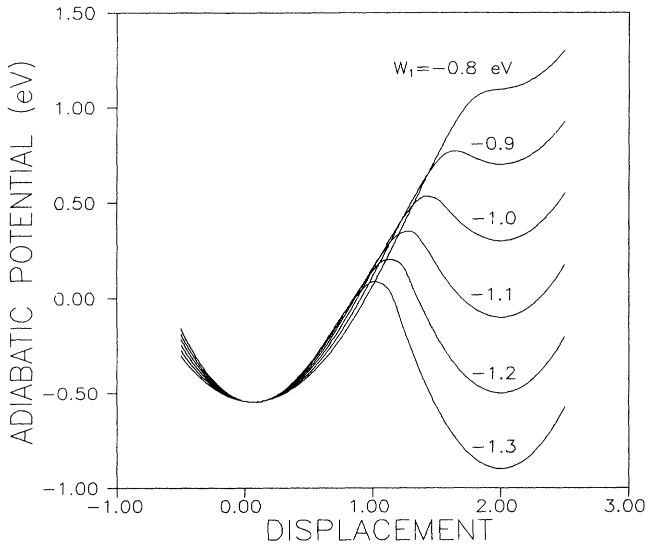

FIG. 3. Adiabatic potential of the system with an initially empty state $|d\rangle$ as a function of the dimensionless displacement $z = kx/Q$ for different polaron shifts ($\Delta = 0.1$ eV, $\Delta E_v = 5.0$ eV, $U_c = 0.3$ eV, and $\tilde{E}^{(0)}_d \simeq E_g = 2.0$ eV).

The effects described strongly influence the form of the adiabatic potential $\Phi_0(x)$. The results of the calculations of $\Phi_0(x)$ according to (31) are presented in Fig. 3. The form of the adiabatic potential strongly depends on the rigidity of the atomic potential or on the value of the polaron shift $|W_1|$ defined in (1). This results from the competition between the increase of elastic energy with atomic displacement [the first term in (31)] and the energy gain due to interband interactions [the third term in (31)], which can result in a double-well structure of the adiabatic potential. Indeed, the minimum of elastic atomic energy is realized at zero displacement. The deviations of x from this value give rise to an increase of elastic energy as well as to some energy gain because of the occupation of the "self-trapping" state due to interband interactions. This energy gain is inessential at small deviations of x, when energy levels $E_{d\sigma}$ and $E^{\text{eff}}_{d\sigma}(x)$ are far from the top of the valence band, but it strongly increases at large displacements when $E_{d\sigma}$ approaches the valence-band top. The "self-trapping" state becomes practically doubly occupied in this situation. This energy gain must be compared to the loss of elastic energy for such displacements. If the rigidity of the atomic potential is high enough (see below), then the increase in occupation of the "self-trapping" state does not change essentially the form of the adiabatic potential so that it has only a single minimum at $x_0 = x_{01} \simeq 0$. But in the case of soft atomic potentials (large values of polaron shift, $|W_1| \sim E_g$) the situation changes drastically. The energy gain resulting from the strong hybridization of the "self-trapping" state with the valence-band states now overcomes (at large displacements for which the true level reaches the valence-band top) the elastic energy growth. This gives rise to the appearance of an extra minimum of $\Phi_0(x)$ at

$x_0=x_{02}\simeq 2Q/k$. Further decrease leads to the lowering of the extra minimum, so that it corresponds to the lowest-energy state (see Fig. 3).

This qualitative picture is supported by the following estimations of the equilibrium displacements and the values of the polaronic shift W_1' (or W_1^*) giving rise to the extra minimum (lowest-energy extra minimum). The equilibrium displacements can be found from the following equation derived from (9) (see Appendix B):

$$kx-2Q[1-\gamma_{d\sigma}^2(x)]=0\ . \tag{36}$$

Its solution for a different $|W_1|$ is illustrated in Fig. 4(A). It is clearly seen from this figure that Eq. (36) has only a single root at $x_0=x_{01}\simeq 0$ for rigid potentials (large k and small $|W_1|$) when interband interactions are inessential. However, additional roots appear with decreasing k (increasing $|W_1|$) at a large atomic displacement $x\sim x_*\simeq E_g/Q$ for which the single-band level $E_d^{(0)}(x)$ reaches the valence-band top. In this situation $\gamma_{d\sigma}^2\to 0$, so it follows from Eq. (36) that $x_0-x_{02}\simeq 2Q/k$. This root is associated with the extra minimum.

To estimate the value of $|W_1'|$ related to the additional minimum, we compare at first the energies $\Phi_0(x_{01})$ and $\Phi_0(x_{02})$ in their minima. One can easily get from Eq. (31) that

$$\Phi_0(x_{01}\simeq 0)\simeq -2\Delta\ln\frac{\Delta E_v}{E_g}\ , \tag{37}$$

and taking into account the relations

$$E_{d\sigma}^{\rm eff}(x_{02})=\tilde{E}_d^{(0)}-2Q^2/k+U_c,\quad E_{d\sigma}\simeq 0\ , \tag{38}$$

that

$$\Phi_0(x_{02}\simeq 2Q/k)\simeq 2E_g-4|W_1|+U_c\ . \tag{39}$$

Here we keep in mind that $\tilde{E}_d^{(0)}\simeq E_g$ for the most essential states.[1] Comparison of (38) and (39) gives the following estimation of the polaronic shift $|W_1^*|$ for which the extra minimum becomes the ground-state minimum

$$|W_1^*|\simeq\frac{1}{2}\left[E_g+\Delta\ln\frac{\Delta E_v}{E_g}+U_c/2\right]\ . \tag{40}$$

As seen from Fig. 4(A), the extra minimum becomes the lowest-energy minimum very fast with increasing $|W_1|$ in the energy range of the scale $\sim\Delta$. Therefore, the energy $|W_1'|$ can be estimated as $|W_1'|\approx|W_1^*|-\gamma'\Delta$, $\gamma'\sim 1$.

Thus, the "ground-state" energy at zero initial occupation $\Phi_0(x_0)$ ($x_0=x_{01}$ for $|W_1|<|W_1^*|$ and $x_0=x_{02}$ for $|W_1|>|W_1^*|$), in fact, depends on the rigidity of the atomic potential (polaron shift $|W_1|$). This differs from the self-trapping in the single-band systems, when $\Phi_0(x_0)$ ($\simeq 0$) is practically independent of $|W_1|$.[1]

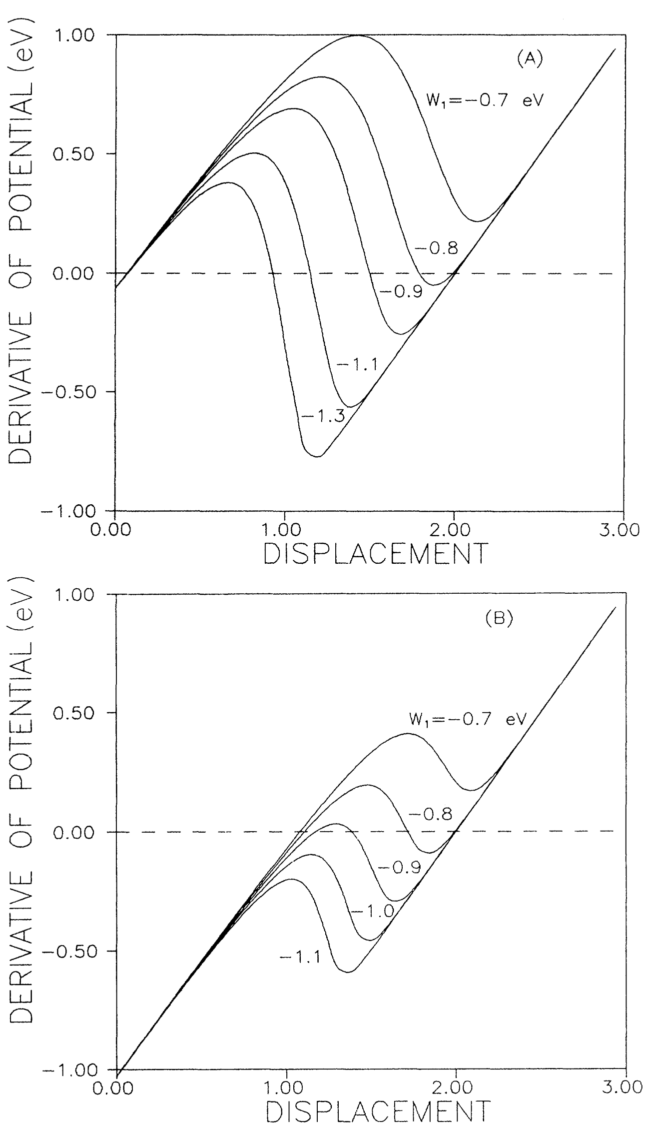

FIG. 4. Derivative of the adiabatic potential for (A) initially empty and (B) singly occupied states $|d\rangle$ as a function of the dimensionless displacement $z=kx/Q$ for different polaron shifts.

B. Single initial occupation

For the sake of definiteness let the state $|d\rangle$ be initially occupied by a single electron with spin projection $\sigma+$. Then the system in question contains only one empty state $|d_{\sigma-}\rangle$, and the general expression (25) for adiabatic potentials can be transformed as follows:

$$\Phi_1^{(\sigma+)}(x)=\tfrac{1}{2}kx^2+E_{\rm band}^{(0)}-\sum_{\sigma}\Delta E_{*\sigma}-\frac{1}{\pi}\sum_{\sigma}\int_{-\Delta E_v}^{0}\left[\frac{\pi}{2}+\arctan\frac{\omega-E_d^{\rm eff}(x)-{\rm Re}(\Sigma(\omega))}{\pi\Delta}\right]d\omega$$
$$+E_{d\sigma+}-U_c\langle\hat{n}_{\sigma+}\rangle\langle\hat{n}_{\sigma-}\rangle\ . \tag{41}$$

Using the relation (26) for both spin projections one can get

$$\Phi_1^{(\sigma+)}(x)=\tfrac{1}{2}kx^2+E^{(0)}_{\text{band}}+E^{\text{eff}}_{d\sigma+}(x)$$
$$-[E_{d\sigma-}-E^{\text{eff}}_{d\sigma-}(x)]-U_c\langle\hat{n}_{\sigma-}\rangle\langle\hat{n}_{\sigma+}\rangle\ . \tag{42}$$

The electron subsystem characterized by spin projection $\sigma+$ is insensitive to the interband interactions and gives the standard contribution [third term in (42)] to the total energy of the system like in a single-band problem. The electron subsystem with spin projection $\sigma-$ containing an empty state contributes to (42) as the fourth term similar to the case investigated of zero initial occupation. This term describes the decrease of valence-band energy due to the repulsion off the "self-trapping" state $|d_{\sigma-}\rangle$.

The average occupations of the states $|d\sigma\rangle$ can be calculated using relation (27):

$$\langle\hat{n}_{\sigma+}\rangle=1\ , \tag{43}$$

$$\langle\hat{n}_{\sigma-}\rangle=1-\gamma^2_{d\sigma-}\ , \tag{44}$$

with $\gamma^2_{d\sigma-}$ satisfying Eq. (33) at $\sigma=\sigma-$. Equation (43) simply reflects the total filling of states with $\sigma=\sigma+$.

The effective energies $E^{\text{eff}}_{d\sigma\pm}(x)$ are found self-consistently from the following set of equations:

$$E^{\text{eff}}_{d\sigma+}(x)=E^{(0)}_d(x)+U_c(1-\gamma^2_{d\sigma-})\ , \tag{45}$$

$$E^{\text{eff}}_{d\sigma-}(x)=E^{(0)}_d(x)+U_c\ . \tag{46}$$

The true energy levels $E_{d\sigma}$ can be found from Eq. (34a). The dependence of $E_{d\sigma+}$ on the single-band energy level position $E^{(0)}_d(x)$ is very similar to the case of zero initial occupation, while the dependence of $E_{d\sigma-}$ differs very much, as is clearly seen from relations (45) and (46) (see Fig. 2). This is a consequence of symmetry breaking for levels with different spin projections in the case under consideration.

The adiabatic potential $\Phi_1^{(\sigma+)}(x)$ can be investigated once the true level $E_{d\sigma-}$ is found (see Fig. 5). Its form and evolution with growing $|W_1|$ are similar to those in the case of zero initial occupation. The double-well structure of the potential $\Phi_1^{(\sigma+)}(x)$ is due to an increase of occupation of the "self-trapping" state from single to practically double because of admixing of the valence-band states with spin projection $\sigma-$ to the "self-trapping" state $|d_{\sigma-}\rangle$. The main difference of the case under consideration from that discussed above is that the extra minimum now appears for still smaller values of $|W_1|$ than in the case of zero initial occupation. The reason is that the atomic displacement from the equilibrium position $x_{11}\simeq Q/k$ to $x_{12}\simeq 2Q/k$, as well as the loss of the elastic energy, is smaller than the displacement from $x_{01}\simeq 0$ to $x_{02}\simeq 2Q/k$ at zero initial occupation. Indeed, equilibrium displacements x_{11} and x_{12} referred to the standard minimum and to the extra one, respectively, are found from the equation (see Appendix B)

$$kx-Q-Q(1-\gamma^2_{d\sigma-}(x))=0\ . \tag{47}$$

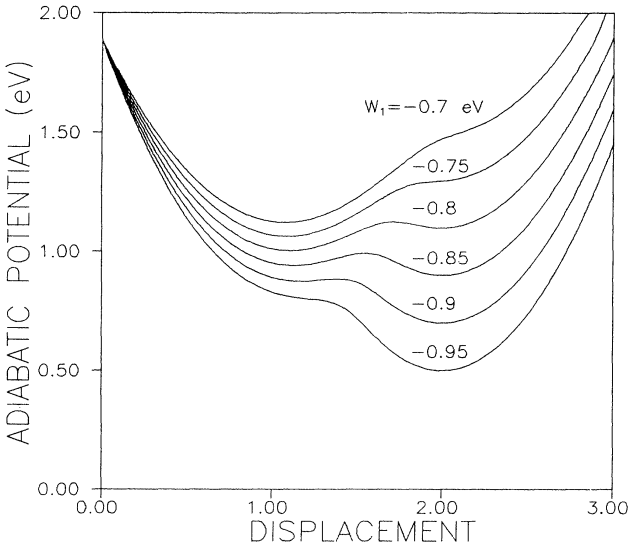

FIG. 5. Adiabatic potential of the system with an initially singly occupied state $|d\rangle$ as a function of the dimensionless displacement $z=kx/Q$ for different polaron shifts ($\Delta=0.1$ eV, $\Delta E_v=5.0$ eV, $U_c=0.3$ eV, $\tilde{E}^{(0)}_d\simeq E_g=2.0$ eV).

The equilibrium displacement equals $x_1=x_{11}\simeq Q/k$ for large enough values of spring constants k, when interband interactions are inessential ($\gamma^2_{d\sigma-}\simeq 1$). The extra minimum appears at $x_1=x_{12}\simeq 2Q/k$ for smaller k when $\gamma^2_{d\sigma-}(x)\to 0$. A comparison of the energies of the minima,

$$\Phi_1^{(\sigma+)}(x_{11})\simeq E_g-|W_1|-\Delta\ln\frac{\Delta E_v}{E_g} \tag{48}$$

and $\Phi_1^{(\sigma+)}(x_{12})\simeq\Phi_0(x_{02})$ [see Eq. (39)], gives rise to the following expression for $|W_1^{**}|$ for which the extra minimum becomes the lowest-energy minimum:

$$|W_1^{**}|\simeq\frac{1}{3}\left[E_g+\Delta\ln\frac{\Delta E_v}{E_g}+U_c\right]<|W_1^{*}|\ . \tag{49}$$

The energy $|W_1''|$ for which the extra minimum appears can be estimated in a similar way as in the case of zero initial occupation: $|W_1''|\approx|W_1^{**}|-\gamma''\Delta$, $\gamma''\sim 1$.

C. Double initial occupation

In the case of double initial occupation of the "self-trapping" state, all of the states in the system under consideration are filled and $\langle\hat{n}_{i\sigma+}\rangle=\langle\hat{n}_{i\sigma-}\rangle=1$ for both the band states and the state $|d\rangle$. This means that interband interactions, as follows from the property (26), do not influence the original adiabatic potential $\Phi_2(x)$. In fact, the energy growth due to the repulsion of the state $|d\rangle$ off the valence band is exactly compensated by the energy gain resulting from the repulsion of the valence-band states off the "self-trapping" level [see Eq. (28)], so that

$$\Phi_2(x)=\tfrac{1}{2}kx^2+E^{(0)}_{\text{band}}-\sum_{\sigma}E^{\text{eff}}_{d\sigma}-U_c \tag{50}$$

with $E^{\text{eff}}_{d\sigma}$ defined in (46) and (45).

Therefore, the adiabatic potential for double initial occupation has a standard single-well structure similar to that in the single-band systems. Equilibrium displacement equals $x_2 = 2Q/k$ (in harmonic approximation) and the ground-state energy $\Phi_2(x_2)$ depends on the polaron shift like in Eq. (39).[1-3]

V. SELF-TRAPPING AND CORRELATION ENERGIES

The interband interactions discussed above essentially influence the basic energy characteristics of the self-trapping in two-band systems: the single-particle self-trapping energy $\tilde{W}_1$ and the correlation energy $\tilde{U}$ [singlet pair self-trapping energy $\tilde{W}_2$ is not influenced because of unchanged $\Phi_2(x)$]. Within the frame of the single-band approach these energies are defined as[1,8]

$$\tilde{W}_1 = W_1 = -Q^2/2k \ , \tag{51}$$

$$\tilde{U} = U = 2W_1 + U_c \ . \tag{52}$$

In two-band systems the situation is rather different. The double-well structure of adiabatic potentials $\Phi_0(x)$ and $\Phi_1^{(\sigma)}(x)$ and the changes in the ground-state positions with increasing $|W_1|$ (from x_{n1} to x_{n2} at $n=0,1$) change the relations (51) and (52) and lead to the nonmonotonic dependence of $\tilde{U}$ on the polaron shift (see Fig. 6).

For sufficiently rigid atomic potentials at $|W_1| < |W_1^{**}|$ [see (49)] the interband interactions are practically unimportant, and all of the related energies satisfy the relations (51) and (52). At $|W_1^{**}| < |W_1| < |W_1^{*}|$ [the energy $|W_1^{*}|$ is defined in (40)], the ground state of the system with the initially singly occupied state $|d\rangle$ becomes related to the extra minimum at $x_{12} \simeq 2Q/k$. The result is that

$$\tilde{W}_1 = \Phi_1(x_{12}) - \Phi_1(x_{01}) \simeq E_g - 4|W_1| + U_c \tag{53}$$

and

$$\begin{aligned} \tilde{U} &= \Phi_2(x_2) + \Phi_0(x_{01}) - 2\Phi_1(x_{12}) \\ &= 4|W_1| - U_c - 2E_g \ . \end{aligned} \tag{54}$$

Further increase of $|W_1|$ results in the change of the ground-state position $(x_{01} \rightarrow x_{02} = x_{12})$ for $\Phi_0(x)$ at $|W_1| > |W_1^{*}|$, so that $\tilde{U} \simeq 0$ in this region, while $\tilde{W}_1$ is defined by Eq. (53) as before. For such large values of $|W_1|$ both initially free and singly occupied states $|d\rangle$ become doubly occupied, so that their energies practically coincide with each other, $\Phi_2(x_2) \simeq \Phi_1(x_{01}) \simeq \Phi_0(x_{02})$, and the correlation energy obviously equals zero.

Therefore, the correlation energy in two-band systems depends really nonmonotically on $|W_1|$. It decreases initially as $\propto -2|W_1|$, reaches a minimum at $|W_1| = |W_1^{**}|$,

$$U_{\min} \simeq -\tfrac{2}{3}E_g + \tfrac{1}{3}U_c \ , \tag{55}$$

and then rises as $\propto 4|W_1|$, up to zero at $|W_1| \simeq |W_1^{*}|$, remaining zero for larger $|W_1|$ (see Fig. 6). A principal moment here is that the correlation energy is limited by the value $U_{\min}$ of the order of half of the gap width. Many fundamental electron properties of glassy semiconductors follow from this fact.[1]

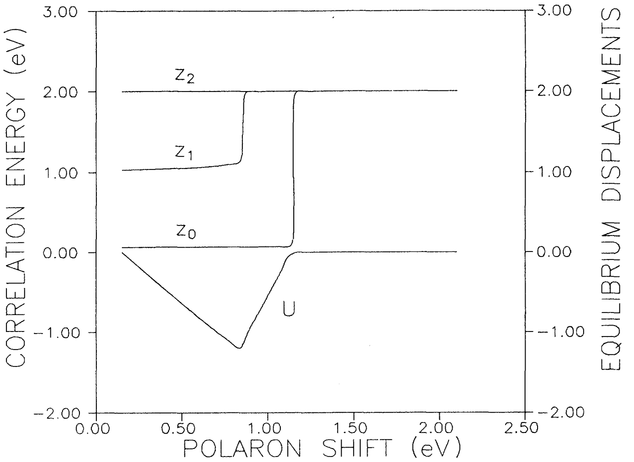

FIG. 6. The dependence of the pair correlation energy U and the equilibrium dimensionless displacements z_i on the polaron shift value $|W_1|$ at $\Delta = 0.1$ eV, $\Delta E_v = 5.0$ eV, $U_c = 0.3$ eV, and $\tilde{E}_d^{(0)} \simeq E_g = 2.0$ eV.

VI. CONCLUSIONS

Electron self-trapping in essentially two-band systems and its basic features (as compared to the self-trapping in single-band systems) are considered in detail. It is shown that interband interactions, i.e., interactions between a state split off the conduction (or valence) band and states of the "nonparent" valence (or conduction) band, are important in the formation of self-trapped electron (or hole) states, for strong enough self-trapping. The interband interactions lead to a strong hybridization of the state under the self-trapping with "nonparent" (valence) band states and to respective changes in the occupation of the initially singly occupied or empty states. These effects determine the shape of adiabatic potentials which can change their structure from single well to double well. An extra minimum of the adiabatic potential corresponds to a practically doubly occupied self-trapped state. This state becomes the ground-state for sufficiently soft atomic configurations.

The effects described here result in changes of the related self-trapping energies. The most important consequence is a nonmonotonic energy dependence of the pair correlation energy on the rigidity of the atomic configuration. The value of the correlation energy appears to be limited by approximately half of the gap width.

It should also be noted that anharmonicity of the soft atomic configurations can probably change some of the quantitative results presented above. We hope to investigate these effects elsewhere.

APPENDIX A

Using expression (19) one can rewrite the second term in Eq. (16) in the following form:

$$\frac{1}{\pi}\sum_{\sigma}\mathrm{Im}\int \omega\,\mathrm{Tr}[\hat{G}^{(\sigma)}(\omega,x)]d\omega$$

$$=E_{\text{band}}^{(0)}+\frac{1}{\pi}\sum_{\sigma}\mathrm{Im}\int \omega\frac{d}{d\omega}\ln[\hat{G}_{dd}^{(\sigma)}(\omega,x)]d\omega$$

$$=E_{\text{band}}^{(0)}+\sum_{\sigma}E_{*\sigma}+\frac{1}{\pi}\sum_{\sigma}\int_{-\Delta E_v}^{0}\omega\,\mathrm{Im}\frac{d}{d\omega}\ln\{\omega-E_d^{(0)}(x)-\mathrm{Re}(\Sigma(\omega))-i\pi\Delta\}d\omega+\sum_{\sigma,\text{occupied}}E_{d\sigma}\ . \qquad \text{(A1)}$$

Introducing a phase, $\phi(\omega)$, as

$$\omega-E_d^{(0)}(x)-\mathrm{Re}(\Sigma(\omega))-i\pi\Delta=ae^{i\phi(\omega)}\ , \qquad \text{(A2)}$$

or in the equivalent form

$$\phi(\omega)=-\frac{\pi}{2}+\arctan\left[\frac{\omega-E_d^{(0)}(x)-\mathrm{Re}(\Sigma(\omega))}{\pi\Delta}\right] \qquad \text{(A3)}$$

helps to integrate in (A1):

$$\frac{1}{\pi}\sum_{\sigma}\int_{-\Delta E_v}^{0}\omega\,\mathrm{Im}\frac{d}{d\omega}\ln\{\omega-E_d^{(0)}(x)-\mathrm{Re}(\Sigma(\omega))-i\pi\Delta\}d\omega$$

$$=\frac{1}{\pi}\sum_{\sigma}\int_{-\Delta E_v}^{0}\omega\frac{d\phi}{d\omega}d\omega=-2\Delta E_v-\frac{1}{\pi}\sum_{\sigma}\int_{-\Delta E_v}^{0}\left[\frac{\pi}{2}+\arctan\left[\frac{\omega-E_d^{(0)}(x)-\mathrm{Re}(\Sigma(\omega))}{\pi\Delta}\right]\right]d\omega\ . \qquad \text{(A4)}$$

Expressions (A1) and (A2) can be easily reduced to Eq. (21).

APPENDIX B

Taking the derivative of the adiabatic potential $\Phi_0(x)$ in Eq. (31) gives rise to the following expression:

$$\frac{d\Phi_0(x)}{dx}=kx-2\left[\frac{dE_{d\sigma}}{dx}-\frac{dE_{d\sigma}^{\text{eff}}}{dx}\right]-2U_c\langle\hat{n}_{d\sigma}\rangle\frac{d\langle\hat{n}_{d\sigma}\rangle}{dx}\ . \qquad \text{(B1)}$$

Taking into account that, as follows from Eqs. (33) and (34),

$$\frac{dE_{d\sigma}}{dx}=\frac{dE_{d\sigma}^{\text{eff}}}{dx}\gamma_{d\sigma}^2\ , \qquad \text{(B2)}$$

and substituting this into Eq. (B1) results in

$$\frac{d\Phi_0(x)}{dx}=kx+2(1-\gamma_{d\sigma}^2)\left[\frac{dE_{d\sigma}^{\text{eff}}}{dx}-U_c\frac{d\langle\hat{n}_{d\sigma}\rangle}{dx}\right]$$

$$=kx+2\frac{dE_d^{(0)}}{dx}(1-\gamma_{d\sigma}^2)\ . \qquad \text{(B3)}$$

Here we used relation (33) and the result of taking the derivative of Eq. (34b).

In the case of single initial occupation of the state $|d\rangle$ the derivation of Eq. (42) leads to

$$\frac{d\Phi_1(x)}{dx}=kx+2\frac{dE_d^{(0)}}{dx}-\frac{dE_{d\sigma-}}{dx}\ . \qquad \text{(B4)}$$

Substitution of Eq. (B2) with $\sigma=\sigma-$ in Eq. (B4) gives rise to Eq. (47).

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