# Theory of electron two-band self-trapping in atomic soft configurations: Hybridization of states, formation of negative-$U$ centers, and anharmonic atomic dynamics

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A consistent theory of two-band self-trapping of electrons (holes) in semiconductors is presented, in which negative-$U$ centers in the interband (mobility) gap are formed as singlet electron (hole) pairs self-trapped in atomic soft configurations. Both the configuration softness and hybridization of the bare single-electron state with extended band states are essential for formation of the self-trapped states and negative-$U$ centers. The hybridization significantly changes appropriate soft configurations, introducing additional anharmonic features in the related atomic dynamics. Examples are mobility-gap states and negative-$U$ centers and the related atomic dynamics in glassy semiconductors, the properties of which are discussed.

## I. INTRODUCTION

The type of self-trapping of quasiparticles in condensed matter, in particular of electrons (holes) in semiconductors, depends on the properties of both the quasiparticle spectrum and atomic dynamics and of their interactions (see, e.g., Refs. 1–10). Whatever the origin of the self-trapping, in most work (see, e.g., Refs. 1–8) the essential contributions are due largely to states of a single energy band, the parent band (e.g., the conduction band, for electrons). In this sense, single-band self-trapping has been considered earlier, and occurs if the characteristic total energy gain, the self-trapping energy $W_{ST}$ ($< 0$), is substantially less in magnitude than the interband (or mobility) gap width $E_g$, $|W_{ST}| \ll E_g$. A well-known example is polaron formation due to self-trapping of a localized electron for which coupling to a harmonic atomic-motion mode ($x$), characterized by an effective spring constant ($k$), is linear in the mode.[11] Increasing atomic displacement in this mode gives rise to an increase of the elastic energy ($kx^2a_0^2/2$) of the atomic configuration and to a competing coupling-induced decrease [$\Delta\varepsilon_d \equiv \varepsilon_d(x) - \varepsilon_d(0) \simeq -Q_d x$] of the bare single-electron energy and results in a minimum total energy of the system which corresponds to an equilibrium mode position ($x_1 = -Q_d/ka_0$) shifted from the original one $x_0 = 0$ ($a_0$ is the atomic length scale, $a_0 \simeq 1$ Å). The related self-trapping energy of $n$ electrons is

$$W_n = -n^2 W \quad \text{and} \quad W = Q_d^2/2ka_0^2 \qquad (1.1)$$

with $x_n = -nQ_d/(ka_0)$, for $n = 0, 1$, or 2, in orbitally nondegenerate bare-states,[11] if the characteristic self-trapping energy is small in magnitude, $|W_{ST}| \ll E_g$. The energy $W_{ST} = W_1$ if single-polaron states with positive singlet-pair correlation energy $U > 0$ are ground states,

whereas $W_{ST} = W_2$ if bipolaron states with $U < 0$ are ground states. It is worth adding that the singlet-pair correlation energy[11,9]

$$U = W_2 + W_0 - 2W_1 + U_d, \qquad (1.2)$$

where $U_d$ is the effective Mott-Hubbard repulsion energy in the bare single-electron state $\psi_d$ of energy $\varepsilon_d$. Let us note also that in the semiconductors mainly implied, typical values of the parameters mentioned are

$$ka_0^2 \equiv M_0\omega^2 \approx k_0a_0^2 \equiv M_0\omega_0^2 \approx 30 - 60 \text{ eV},$$

$$Q_d \approx 3\text{–}5 \text{ eV (Refs. 1 and 5)},$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1.3)$$

$$E_g \approx 1 - 3 \text{ eV} \quad \text{and} \quad U_d \ll E_g, \quad \text{e.g.,} \quad U_d \leq 0.3 \text{ eV}$$

$$\text{(Refs. 12 and 13)}.$$

Therefore the mentioned criterion of single-band self-trapping is expected usually to be satisfied in crystalline semiconductors.

There are, or actually may exist, however, materials for which $|W_{ST}|$ is comparable to $E_g$. For such materials, contributions from the states of both the conduction ($c$) and the valence ($v$) bands to electron (hole) self-trapping are essential and hybridization of states in the gap becomes important. One may refer to this type of self-trapping as two-band self-trapping. The theory of two-band self-trapping is just what is discussed in essential detail in the present paper (some aspects of the theory have been noted earlier[9(b),10]). Apart from the parameters of single-band self-trapping theories [see Eqs. (1.3)], the theory under discussion contains two additional basic parameters: the gap width $E_g$ and the effective hybridization energy $\Delta$ ($\ll E_g$). The related aspect of the theory is introducing the hybridization of states into the

         

self-trapping phenomenon, of which $E_g$ and $\Delta$ are characteristic.

The characteristic self-trapping energy $W_{ST}$ becomes comparable in magnitude to $E_g$ if the effective spring constant $k$ is sufficiently small,

$$|W_{ST}| \geq E_g \quad \text{for} \quad k \ll k_0 . \tag{1.4}$$

In this connection, the two-band self-trapping is actually expected to occur in local atomic soft configurations characterized by soft modes and related potentials with small spring constants $k \ll k_0$. Moreover, the two-band self-trapping is so strong due to configuration softness that it favors formation of self-trapped singlet electron pair states with $U < 0$, rather than of the more usual self-trapped single-electron (-hole) states with $U > 0$, in the gap. Furthermore, this trend to formation of self-trapped electron pair states is strongly enhanced by the hybridization of states in the gap, which gives rise to double occupation of even the nominally empty $(n = 0)$ single-electron energy level $\varepsilon_d(x)$ as it drops and approaches the valence band (mobility) edge during self-trapping. This is another aspect which the theory appears to add to the earlier studies of the self-trapping phenomenon.

As noted, the two-band self-trapping is essentially related to the hybridization of a bare single-electron (site) state $\psi_d$ of energy $\varepsilon_d$ with states $\psi_i$ of energy $\varepsilon_i$, in both the conduction $(\psi_i^{(c)})$ and the valence $(\psi_i^{(v)})$ bands. In fact the hybridization matrix elements $V_{id}$ contribute to the true, renormalized, single-electron state $\Psi_{d\sigma}$ in a soft configuration,

$$\Psi_{d\sigma} = \sum_i C_{id}^{(\sigma)} \psi_i + C_{dd}^{(\sigma)} \psi_d, \tag{1.5}$$

corresponding to the true single-electron energy level $E_{d\sigma}$ ($\sigma$ stands for the spin projection, $\sigma = \pm 1/2$). An important characteristic of this *self-trapping* is the contribution of the hybridization to $\Psi_{d\sigma}$,

$$\sum_i |C_{id}^{(\sigma)}|^2 = 1 - |C_{dd}^{(\sigma)}|^2 \equiv 1 - \gamma_{d\sigma}^2, \tag{1.6}$$

so that $\gamma_{d\sigma}^2 \to 0$ as the hybridization becomes strongest, and $\gamma_{d\sigma}^2 \to 1$ alternatively (e.g., with $|C_{id}^{(\sigma)}| \to 0$ as $V_{id} \to 0$). Another related characteristic is the true occupation $\nu_{d,\sigma}$ of the bare state $\psi_d$. Both characteristics vary with the soft-mode $(x)$ variations during the self-trapping, the hybridization effects becoming strongest as $\varepsilon_d(x)$ approaches the appropriate band (mobility) edge. As noted, the self-trapped state is realized as the equilibrium soft-mode displacement is reached in a competition between the soft-mode potential growth and the bare energy decrease, the equilibrium displacement being large due to the mode softness.

The main problem of the theory is to describe the basic properties of two-band self-trapping, in particular, the behavior of $\gamma_{d\sigma}^2$ and $\nu_{d\sigma}$, as the soft-mode displacement increases to the equilibrium value. This problem is eventually reduced to calculations of the related soft-configuration adiabatic potentials $\Phi_n$ depending on the soft-mode displacement, as the bare level $\varepsilon_d$ is occupied

by $n$ electrons. For the sake of simplicity, the bare state $\psi_d$ is assumed to be orbitally nondegenerate, so its nominal occupation $n = 0, 1$, or 2. This appears to be relevant for the amorphous (glassy) semiconductors mainly implied, because of their lack of symmetry. Another problem is to calculate the self-trapping energies $W_n$ and the singlet-pair correlation energy $U$ and to find whether the hybridization effects actually favor formation of singlet-pair self-trapped states with $U < 0$, i.e., of negative-$U$ centers, as noted above.

Most important examples of systems exhibiting such two-band self-trapping are glassy semiconductors, largely the chalcogenide glasses like $g$-As$_2$S$_3$ and $g$-GeS$_2$, which are mainly implied in what follows. In these materials, the actual mobility-gap states are commonly considered to be singlet electron (hole) pair states with negative correlation energy, or negative-$U$ centers, as assumed in Refs. 11 and 14 and applied in a series of papers for interpreting a large variety of experimental data (see Ref. 15). In the theory under discussion, the gap states in glassy semiconductors actually are shown to be negative-$U$ pair states, with typically large $|U| \simeq E_g/2$, in accordance with earlier assumptions.[11,14] This holds because $|W_2| > 2|W_1| + U_d$ for the characteristic values noted in Eqs. (1.3) and (1.4), and because the related characteristic value $|U| \approx |W_2|/2$, with $|W_2|$ close to $E_g$. The latter is related to the hybridization-induced repulsion of the true single-electron level off the valence-band edge, as demonstrated in direct calculations (Sec. IV).[9,10] Then the spectral and thermodynamic properties of the pair self-trapped states are found to be similar, in some respects at least, to those of the negative-$U$ centers introduced in Refs. 11 and 14 as also follows from calculations (Sec. V). The apparently conflicting models[11,14] in which, respectively, discrete or continuous features of the gap spectrum predominate, may be considered in a sense as limiting cases of the present theory. In this respect the theory of two-band self-trapping may also contribute to the physical insight into the problem of electron gap states and related properties of glassy semiconductors.

It is worth adding that the basic concept of the soft-configuration model of glasses[9,16,17] is that soft configurations with a relatively high atomic concentration $c_d \leq 10^{-2}$ (rather than $c_d \leq 10^{-1}$ as earlier assumed), are characteristic of a glass. Moreover, the related soft modes are shown to be actually slow, corresponding to low effective frequencies, and the related potentials exhibit anharmonic features and generate low-energy excitations responsible for the universal low-temperature properties of glasses (see, e.g., Refs. 9 and 18). Then correlations may be expected between the low-temperature properties and the electron properties determined by negative-$U$ centers in glassy semiconductors.

Another example of two-band self-trapping may be related to deep soft defects in narrow-gap semiconductors (perhaps, like PbTe:In, exhibiting peculiar electronic properties; see, e.g., Ref. 19).

Two principal factors are taken here into account together in the self-trapping problem:

(i) *Hybridization* of the bare state $\psi_d$ with extended states $\psi_i$ of both bands, largely the nonparent band (e.g.,

the valence band for electrons), in the gap;

(ii) Anharmonicity of the substrate atomic soft configuration.

The resulting properties of the self-trapped states and related local atomic dynamics are found to substantially differ in some important respects from those of single-band self-trapping in a harmonic lattice. The purpose of this paper is to develop the theory which gives a description in essential detail of two-band self-trapping in soft configurations and of the related local atomic dynamics, particularly in glassy semiconductors. The basic properties only are discussed, whereas concrete related phenomena will be discussed elsewhere.

Actually many data concerning thermal equilibrium and steady-state phenomena may be qualitatively interpreted within the framework of the well-known "chemical" or "defect" model of negative-$U$ centers,[14,15] which is related to discrete features of the gap spectrum. On the other side, non-steady-state effects in these materials rather reflect continuous features of the gap spectrum,[20] which are basic in an alternative model of negative-$U$ centers.[11] In this respect, it seems important to derive these models as limiting cases of the theory of two-band self-trapping, which is intended to be done elsewhere. Therefore only general experimental findings, like electron-hole symmetry in the characteristics of negative-$U$ centers and the coexistence of discrete and continuous features of the gap spectrum, are discussed and no detailed comparison of the theory to the large variety of data available for glassy semiconductors is given in this paper.

The basic relations and approximations of the model system under discussion are presented in Sec. II. The total electron energy and the related adiabatic potentials are analyzed in Sec. III. The main results of numerical calculations and analytical approximations for the characteristics of two-band self-trapping are discussed in Sec. IV. In these calculations appropriate parameters of the theory characterize the hybridization of states ($V_{id}$) and electron-mode coupling. Microscopic calculations based on explicit expressions of the bare states ($\psi_d, \psi_i$) and hybridization matrix elements ($V_{id}$), even for the glassy semiconductors implied, are beyond the scope of this paper. The density of states of the ground self-trapped states and low-temperature thermal equilibrium properties of negative-$U$ centers, including the mentioned electron-hole symmetry and coexistence of discrete and continuous features of the gap spectrum of glassy semiconductors, are considered in Sec. V. Concluding remarks in Sec. VI summarize the results described and concern some other effects (and approaches) in the theory of two-band self-trapping.

Electron self-trapping is mainly considered in what follows, whereas hole self-trapping is similar (with trivial substitutions of the valence-band characteristics for the conduction-band ones and vice versa).

## II. MODEL: BASIC RELATIONS AND APPROXIMATIONS

The quantum-mechanical system under discussion contains electrons characterized by a two-band energy spec

trum, including energy levels in the interband (mobility) gap, which interact with atoms moving in soft configurations, their soft-mode potentials. The model takes into account interactions with a single most important atomic-motion mode $x$ while interactions with other motion modes are neglected as less important. This approximation not only simplifies the theory, retaining the basic features of the two-band self-trapping, but is relevant for soft configurations in glasses.[9]

The Hamiltonian of the model can be described as follows:[10]

$$\hat{H}(x) = \hat{V}_{\text{at}}(x) + \hat{H}_{\text{el}}(x) \equiv \hat{V}_{\text{at}}(x) + \hat{H}_{\text{el}}^{(0)} + \hat{H}_{\text{el-at}}(x),$$

$$(2.1)$$

where $V_{\text{at}}(x)$ is the substrate soft-configuration potential energy, $\hat{H}_{\text{el}}^{(0)}$ is the Haldane-Anderson Hamiltonian introduced in a different context in Ref. 21, and $\hat{H}_{\text{el-at}}$ characterizes the electron–soft-mode interaction.

It is shown in the soft-configuration model that actually a single soft mode $x$ is important for the local atomic dynamics and the related soft-mode potential energy for not very large displacements $|x| \equiv |u|/a_0 \leq 1$ can be approximated as follows:[9,16]

$$V_{\text{at}} \simeq A(\eta x^2 + \xi x^3 + \gamma x^4),$$

$$(2.2)$$

where $A = k_0 a_0^2/2$, $k_0 = M_0 \omega_0^2$, and $\gamma = 1$. Generally speaking, the substrate potential energy (2.2) is anharmonic, with the basic parameters $\eta$ and $\xi$ of either sign ($\eta > 0$ or $\eta < 0, \xi > 0$ or $\xi < 0$) and small in magnitude $\{|\eta|, \xi^2\} \ll 1$, e.g., $\{|\eta|, \xi^2\} \leq \eta^* \approx 0.1$. The related effective spring constants $k$ are small, $k \ll k_0$ (e.g., $k = k_0 \eta \ll k_0$ at $0 < \eta \ll 1$) and typical displacements $|x|$ may be rather large, $|x| \leq 0.1 - 0.3$, whereas large $k \approx k_0$ and small $|x| \ll 1$ are characteristic of normal harmonic single-well potentials $V_{\text{at}} \simeq A\eta x^2 \equiv kx^2 a_0^2/2$ at $\eta \approx 1$. Both single-well and non-single-well soft mode potentials (2.2) are available. Single-well potentials occur at $9\xi^2/32 < \eta \ll 1$, and are quasiharmonic for $\eta$ separated from the curve $\eta = 9\xi^2/32$ by a gap significantly exceeding the important parameter $\eta_L \equiv (\hbar^2/2M_0 a_0^2 A)^{1/3} \sim 10^{-2}$ of the soft-mode dynamics.[9,16] However, essentially anharmonic potentials are characteristic of the alternative range of $\eta < 9\xi^2/32$ ($\ll 1$), a true double-well potential with a pronounced interwell barrier for $\eta < 0$ and $|\eta| > 3\eta_L$ while an intermediate, strongly anharmonic one for $|\eta| < 3\eta_L$, e.g., $|\eta| \leq \eta_L$.

For disordered systems like glasses, $\eta$ and $\xi$ are random quantities which obey a probability distribution density $F(\eta, \xi)$, exhibiting its highest maximum at $\eta = \bar{\eta} \approx 1$ (and $\xi^2 = \bar{\xi}^2 \ll 1$) for the overwhelming majority of atoms in quasiharmonic single-well potentials. Generally speaking, the parameter $A$ in Eq. (2.2) is also a random quantity, as well as the effective mass $M_0$ of atoms cooperatively moving in the soft mode (see, e.g., Refs. 9 and 17). Commonly, however, a representative average value $A$ is used, corresponding to an implied narrow distribution, with the typical value $k_0 a_0^2 \approx 30$–$60$ eV mentioned above. Two limiting types of $F(\eta, \xi)$, and in this sense of glasses, may be expected, depending on the

properties of the basic interatomic forces. One, $F_1(\eta, \xi)$, exhibits analytical (not necessary monotonic) behavior near $\eta = 0$, $F(\eta, \xi) \approx F_0^{(1)} = \text{const} \neq 0$, for variations $\{\delta\eta, \delta(\xi)^2\} < \eta_c$,[9(a),16] whereas the other, $F_2(\eta, \xi)$, contains a nonanalyticity of the type $F_2(\eta, \xi) = |\eta| F_0^{(2)}$ with $F_0^{(2)} = \text{const}$ for the noted variations[17] [the variation scale $\eta_c$ of $F(\eta, \xi)$ in $\eta$ and $\xi^2$ exceeds $\eta_L$, with typical $\eta_c \approx 0.1 \gg \eta_L$]. For real glasses one can assume [9(c)] that $F(\eta, \xi) = c_1 F_1(\eta, \xi) + c_2 F_2(\eta, \xi)$ with $0 \leq c_{1,2} \leq 1$ and $c_1 + c_2 = 1$, so it is qualitatively similar to $F_1(\eta, \xi)$, rather than to $F_2(\eta, \xi)$, near $\eta = 0$, at actual not too small $c_1$. Although the difference between $F_1$ and $F_2$ may be reflected in some properties of the anharmonic soft-mode dynamics, it is not essential in the two-band self-trapping (as results from the following calculations) and therefore can be neglected.

The Hamiltonian[21] (see also Ref. 22)

$$\hat{H}_{\rm el}^0 \equiv \hat{H}_{\rm el}(x=0) = \sum_{i,\sigma} \varepsilon_i \hat{n}_{i\sigma} + \sum_\sigma \varepsilon_d^{(0)} \hat{n}_{d\sigma}$$
$$+ \frac{1}{2} U_d \sum_{\sigma \neq \sigma'} \hat{n}_{d\sigma} \hat{n}_{d\sigma'} + \sum_{i,\sigma} \left\{ V_{id}^{(0)} \hat{a}_{i\sigma}^\dagger \hat{d}_\sigma + \text{H.c.} \right\} \tag{2.3}$$

takes into account hybridization of the bare localized state $[\psi_d^{(0)}, \varepsilon_d^{(0)} \equiv \varepsilon_d(x=0)]$ in a reference $(x=0)$ atomic configuration, with the band states $(\psi_i, \varepsilon_i)$, where $\hat{n}_{j\sigma} = \hat{a}_{j\sigma}^\dagger \hat{a}_{j\sigma}$, $j = i$ or $d$, $\hat{a}_{d\sigma} \equiv \hat{d}_\sigma$, and $\{\hat{a}_{j\sigma}^\dagger, \hat{a}_{j\sigma}\}$ are the electron operators. Coulomb interactions of electrons in band states with each other and with electrons in the localized state $(\psi_d)$, as often, are not taken into account explicitly in $\hat{H}_{\rm el}^0$. These interactions and the associated polarization of the configuration environment by a true local charge appear to reduce the bare Hubbard energy to the effective parameter $U_d$, with, as noted in Eq. (1.3), typically relatively small values in semiconductors, $U_d \ll E_g$.[12,13]

Finally, the electron (hole)–soft-mode interaction contains contributions both diagonal $[\Delta\varepsilon_d(x)]$ and nondiagonal $[\Delta V_{id}(x)]$ in the local electron state,

$$\hat{H}_{\rm el\text{-}at}(x) = \Delta\varepsilon_d(x) \sum_\sigma \hat{n}_{d\sigma}$$
$$+ \sum_{i,\sigma} \left\{ \Delta V_{id}(x) \hat{a}_{i\sigma}^\dagger \hat{d}_\sigma + \text{H.c.} \right\}, \tag{2.4}$$

with $\Delta\varepsilon_d(x) \equiv \varepsilon_d(x) - \varepsilon_d^{(0)} \simeq -Q_d x$ and $\Delta V_{id}(x) \equiv V_{id}(x) - V_{id}(0) \simeq Q_{id} x$ in the usual linear approximation. The higher-order expansion terms [e.g., up to $x^4$, as in Eq. (2.2)] can be accounted for approximately by renormalizing the parameters of $V_{\rm at}(x)$ without essential changes in the estimations (e.g., $\eta \to \eta + \Delta\eta$ and $\xi \to \xi + \Delta\xi$ at $|\Delta\eta| \sim |\Delta(\xi^2)| < Q_d/A \ll 1$).[9,23] The bare electron state $\psi_d$ is considered (as well as in Ref. 21) as a localized state of which the reference energy level $\varepsilon_d^{(0)} \equiv \varepsilon_d(x=0)$ belongs either (mainly) to the gap or to the conduction band not too high above its (mobility) edge $E_c$:[10]

$$E_v < \varepsilon_d^{(0)} < E_c \quad \text{or} \quad E_c < \varepsilon_d^{(0)} < E_c + W_0.$$

Here $E_v$ is the valence-band (mobility) edge and the typical magnitude of the single-band self-trapping energy $W_0 \simeq Q_d^2/2k_0 a_0^2 \ll E_g$.

Generally speaking, the bare single-electron energy level $\varepsilon_d \equiv \varepsilon_d(x) \simeq \varepsilon_d^{(0)} - Q_d x$ and hybridization matrix elements $V_{id} \equiv V_{id}(x) \simeq V_{id}^{(0)} + Q_{id} x$ are random quantities depending on $x$, and obey appropriate distribution densities $P_0(\varepsilon_d^{(0)}, Q_d)$ and $P_1(V_{id}^{(0)}, Q_{id})$. It is assumed for disordered systems like glassy semiconductors that

$$P_0(\varepsilon_d^{(0)}, Q_d) \simeq g_0(\varepsilon_d^{(0)}) P_0(Q_d)$$

and

$$P_1(V_{id}^{(0)}, Q_{id}) \simeq g_1(V_{id}^{(0)}) P_1(Q_{id})$$

and that $P_{0,1}(Q)$ and $g_1(V_{id}^{(0)})$ are narrow distributions around the respective average values $(\bar{Q}_d, \bar{V}_{id}^{(0)})$, whereas the bare density of states $g_0(\varepsilon_d^{(0)})$ usually varies weakly around $E_c$ and steeply drops in the mobility gap for $E_c - \varepsilon_d^{(0)} > w_t$, the band-tail width. Since the displacements $x$ may be of either sign, the parameter $\bar{Q}_d$ can be chosen positive without loss of generality, $0 < \bar{Q}_d \leq D_c$, e.g., $\bar{Q}_d \approx 3\text{--}5$ eV.[24] The width of the conduction $(D_c)$ or valence $(D_v)$ band actually exceeds $E_g$ noticeably for the semiconductors in question, e.g., $D_{c,v} \approx 5\text{--}10$ eV $\gg E_g \approx 1\text{--}2$ eV. It is also expected that, generally speaking,

$$|\bar{Q}_{id}| \equiv |\bar{Q}_{id}^{c,v}| < \bar{Q}_d \equiv \bar{Q}_{dd} \equiv \bar{Q}_{dd}^{c,v}, \tag{2.5a}$$

and for the valence ("nonparent") band

$$|\bar{V}_{id}^{(0)v}| \neq 0 \quad \text{while} \quad V_{id}^{(0)c} = 0 \tag{2.5b}$$

for any given random configuration, as long as the bare state $\psi_d$ originates from the conduction band (i.e., it is not a true defect state).

As noted in Sec. I, one of the essential problems in this theory is to calculate the correlation energy $U$ of a self-trapped singlet electron pair state in a soft atomic configuration and to find out whether and under what conditions $U$ is negative for the system under discussion, for which hybridization of states is essential or even decisive. The correlation energy can be expressed in terms of adiabatic potentials $\Phi_n(x)$ of the configuration distorted at self-trapping in the bare state, for different nominal electron occupations $n = 0, 1$, or 2:[9–11]

$$U = \Phi_2(\bar{x}_2) + \Phi_0(\bar{x}_0) - 2\Phi_1(\bar{x}_1) \equiv U(\eta, \xi). \tag{2.6}$$

A related problem is to calculate the self-trapping energies

$$W_n = \Phi_n(\bar{x}_n) - \Phi_n(0) \equiv W_n(\eta, \xi), \tag{2.7}$$

which are negative as self-trapping occurs. The potential extrema (minima, maxima), including the equilibrium self-trapping displacements $\bar{x}_n$ along the mode $x$, are found as usual from the equation

$$\frac{d\Phi_n(x)}{dx} = 0 \quad \text{at} \quad x = x_n \equiv x_n(\eta, \xi). \quad (2.8)$$

Equations (2.6)–(2.8) take into account the adiabaticity of the self-trapping electron motion with respect to atomic motion in the slow soft mode $x$, as the related parameter

$$\frac{\varepsilon_{\text{exc}}}{|E_{d\sigma}(x) - \varepsilon_d^{(0)}|} \approx \frac{\varepsilon_{\text{exc}}}{E_g} \ll 1 \quad (2.9)$$

for actual large equilibrium displacements $|x| \approx |x_n| \sim 1$ and low energies $\varepsilon_{\text{exc}}$ ($\ll \hbar\omega_D$) of the soft-mode excitations.[9,10] However, since $V_{id}$ depends on $x$, the true occupation of the bare level is also a function of $x$, so the adiabaticity of the atomic motion ($x$) with respect to variations of the electron state occupation often supposed for single-band self-trapping (see, e.g., Ref. 11) does not hold precisely.

The Green's function method is applied and the total electron energy $E_{\text{el}}^{(n)}(x)$ of the system (2.1) is calculated, in the Hartree-Fock mean-field approximation taking into account the Hubbard interaction. Then the total electron Hamiltonian in (2.1) is approximated in a standard way as[10,21]

$$\hat{H}_{\text{el}}(x) \equiv \hat{H}_{\text{el}}[\varepsilon_d(x), V_{id}(x)]$$

$$\simeq \hat{H}_{\text{HF}}(x) \equiv \hat{\tilde{H}}_{\text{el}}[\varepsilon_{d\sigma}^{\text{eff}}(x), V_{id}(x)] - \delta E. \quad (2.10)$$

Here

$$\hat{\tilde{H}}_{\text{el}}[\varepsilon, V_{id}] \equiv \hat{H}_{\text{el}}[\varepsilon, V_{id}] - \frac{1}{2} U_d \sum_{\sigma \neq \sigma'} \hat{n}_{d\sigma} \hat{n}_{d\sigma'},$$

$$\delta E \equiv \frac{1}{2} U_d \sum_{\sigma \neq \sigma'} \nu_{d\sigma} \nu_{d\sigma'},$$

and

$$\varepsilon_{d\sigma}^{\text{eff}} = \varepsilon_{d\sigma}^{\text{eff}}(x) = \varepsilon_d(x) + U_d \nu_{d,-\sigma}(x)$$

is the effective single-particle energy level substituted for the bare energy level $\varepsilon_d$ in $\hat{H}_{\text{el}}(x)$, so that $\hat{H}_{\text{HF}}(x)$ is bilinear in the electron operators, whereas $\nu_{d\sigma}(x)$ is the true occupation of the bare state ($\psi_d$) with spin projection $\sigma$ ($= \pm 1/2$). This approximation is assumed to be relevant, since in the semiconductors in question the Hubbard energy $U_d \ll E_g$,[12,13] while the resulting pair correlation energy $U$ is negative and much larger in magnitude, $|U| \sim E_g$, for most pairs in the soft configurations in question. In the Green's function approach the electron energy contribution $E_{\text{el}}^{(n)}(x)$ to the adiabatic potential $\Phi_n(x)$ and the bare state occupation $\nu_d$ are described by the following relations:[10,21]

$$\Delta\Phi_n(x) = E_{\text{el}}^{(n)}(x) \equiv \Phi_n(x) - V_{\text{at}}(x) = \sum_\sigma \int_{(R_n)} d\omega \; \omega \pi^{-1} \text{Im} \text{Tr} \hat{G}^{(\sigma)}(\omega) - \delta E$$

$$= \sum_\sigma \int_{(R_n)} d\omega \; \omega \pi^{-1} \text{Im} \hat{G}_{dd}^{(\sigma)}(\omega) \left[1 - d\Sigma_d'(\omega)/d\omega\right] - \delta E, \quad (2.11)$$

and

$$\nu_d(x) = \sum_\sigma \nu_{d\sigma},$$

$$\nu_{d\sigma}(x) \equiv \langle \hat{n}_{d\sigma}(x) \rangle = \int_{(R_n)} d\omega \pi^{-1} \text{Im} \hat{G}_{dd}^{(\sigma)}(\omega). \quad (2.12)$$

Here $(R_n)$ stands for the range of energies $\omega$ of the nominally occupied states only, and the following formula is applied:[21]

$$\text{Tr} \hat{G}^{(\sigma)}(\omega) = \hat{G}_{dd}^{(\sigma)}(\omega) \left[1 - \frac{d\Sigma_d'}{d\omega}\right]$$

$$= \frac{d}{d\omega} \ln \left\{\omega - \varepsilon_{d\sigma}^{\text{eff}} - \Sigma_d\right\}.$$

In Eqs. (2.11) and (2.12),

$$\hat{G}_{dd}^{(\sigma)}(\omega) = \langle \psi_d | \hat{G}^{(\sigma)}(\omega) | \psi_d \rangle = \left[\omega - \varepsilon_{d\sigma}^{\text{eff}} - \Sigma_d\right]^{-1} \quad (2.13)$$

is the respective diagonal matrix element of the Green's function operator for the Hamiltonian (2.10), whereas the self-energy

$$\Sigma_d \equiv \Sigma_d(\omega, x) = \sum_i |V_{id}(x)|^2 (\omega - \varepsilon_i)^{-1}$$

$$= \int d\varepsilon \Delta(\varepsilon, \omega)(\omega - \varepsilon)^{-1} \quad (2.14)$$

is determined by the effective hybridization energy

$$\Delta(\varepsilon, \omega) = g_0(\varepsilon)|V(\varepsilon, \omega; x)|^2 \equiv \Delta(\varepsilon, \omega; x), \quad (2.15)$$

with $N^{1/2} V_{id}(x) \equiv V(\varepsilon, \omega; x)$, $N$ the total number of atoms, and $g_0(\varepsilon)$ the bare electron density of states (DOS). Moreover, an important characteristic of two-band self-trapping is the degree of hybridization of the bare state with the band states:

$$0 \leq \gamma_{d\sigma}^2(x) = \int_{E_v}^{E_c} d\omega \pi^{-1} \text{Im} \hat{G}_{dd}^{(\sigma)}(\omega)$$

$$= \left(1 - \frac{d\Sigma_d'}{d\omega}\right)^{-1} \Bigg|_{\omega = E_{d\sigma}(x)} \leq 1. \quad (2.16)$$

The degree of hybridization $\gamma_{d\sigma}^2(x)$ is the probability to find the bare state electron in the cloud of the true state $\Psi_{d\sigma}$ [Eq. (1.5)] with energy $E_{d\sigma}$ in the gap. In particular, $\gamma_{d\sigma}^2(x) \simeq 0$ corresponds to nearly complete hybridization

at large displacements $|x| \sim 1$ and $\gamma^2_{d\sigma}(x) \simeq 1$ to negligible hybridization at small $|x|$. The true, hybridization-renormalized single-electron energy level $E_{d\sigma} \equiv E_{d\sigma}(x)$ is the pole of $\hat{G}^{(\sigma)}_{dd}(\omega; x)$ in the (mobility) gap and can essentially differ from the effective energy level $\varepsilon^{\text{eff}}_{d\sigma}(x)$ for large displacements $|x| \sim 1$:

$$E_{d\sigma} - \varepsilon^{\text{eff}}_{d\sigma}(x) - \Sigma'_d(E_{d\sigma}) = 0, \quad (2.17)$$

where $\Sigma'_d(\omega) \equiv \text{Re}\Sigma_d(\omega)$ while $\Sigma''_d(\omega) \equiv \text{Im}\Sigma_d(\omega) = 0$ for $E_v \equiv 0 < \omega = E_{d\sigma} < E_c \equiv E_g$. The last relation in the right-hand side (RHS) of (2.16) just follows from Eqs. (2.13) and (2.17).

Then the problem of the two-band self-trapping characteristics and related hybridization effects is reduced to calculations of $E^{(n)}_{\text{el}}(x)$, $E_{d\sigma}(x)$ and $\nu_d(x)$, $\gamma^2_{d\sigma}(x)$, as well as of $\bar{x}_n(\eta, \xi)$. The basic parameters of the theory, besides those for a reference $(x = 0)$ configuration, $\{\varepsilon^{(0)}_d/E_g, \ U_d/E_g, \ \Delta(\varepsilon, \omega; x = 0)/E_g\}$,[21] are also soft-mode-related characteristics[10]

$$\Delta(\varepsilon, \omega; x)/E_g, \quad Q_d/E_g, \quad A/E_g. \quad (2.18)$$

The calculations are performed by applying the following approximation for $\Delta(\varepsilon, \omega; x)$:[10,21]

$$\Delta(\varepsilon, \omega; x) \simeq \Delta_v(x)\theta(\varepsilon - E'_v)\theta(E_v - \varepsilon)$$
$$+ \Delta_c(x)\theta(E'_c - \varepsilon)\theta(\varepsilon - E_c). \quad (2.19)$$

Here $\theta(z) \equiv \{1$ at $z > 0$; $0$ at $z < 0\}$, while $\Delta_{v,c}(x)$ are, generally speaking, $x$-dependent characteristics of extended states of the valence and conduction bands, with $E'_v \equiv E_v - D_v$, $E'_c \equiv E_c + D_c$, and $D_{c,v}$ the bandwidths. The approximation (2.19), taking into account the gross features of the two-band single-particle energy spectrum, assumes that the dependence of $\Delta$ on $\varepsilon$, the band state energy, does not affect the qualitative features of the self-trapping in question and the related estimations. Moreover, hybridization of the bare electron state $(\varepsilon_d)$ with the gap states $(\omega)$ far from the edges $(E_{c,v})$ is shown[25] to be also relatively unimportant for the qualitative features of the self-trapping, so the $\omega$ dependence of $\Delta$ may be neglected for the estimations as well. In fact, the important variations of both $\varepsilon$ near $E_{c,v}$ and $\omega$ in the gap are small in the sense that $\{\delta\varepsilon, \delta\omega\} \ll E_g$ and $\{\delta\varepsilon, \delta\omega\} \ll D_{c,v}$ for the $D_{c,v}$ and $E_g$ implied. Typical values of $\Delta_{c,v}(x)$ can be estimated as

$$\Delta_{c,v}(x) \approx N|V_{id}(x)|^2 g_0(E_{c,v})$$
$$\approx |V_1|^2/D_{c,v} \approx 0.01\text{--}0.1 \text{ eV}$$
$$\ll E_g \approx 1\text{--}3 \text{ eV}, \quad (2.20)$$

with $V_{id} \equiv V_1 N^{-1/2}$, $|V_1| \approx 0.3\text{--}0.5$ eV,[24] and $g_0(E_{c,v}) \sim 1/D_{c,v}$, $5 \leq D_{c,v} \leq 10$ eV.

## III. TOTAL ELECTRON ENERGY

As noted, hybridization of states significantly influences the total electron energy $E^{(n)}_{\text{el}}(x)$ of the system in question. The hybridization of the bare state $(\psi_d)$ is taken into account not only with the nonparent band states but also, under self-trapping $(x \neq 0)$, with the parent band states, the efficiency of hybridization depending on the position of the bare energy level $\varepsilon_d(x)$ in the gap. If the level is far from the band edges $E_{c,v}$,

$$\Delta \ll |\varepsilon_d(x) - E_{c,v}| \ll E_g,$$

the interactions of the bare state with the band states are not essential and the true occupation $\nu_d$ of the self-trapping state within the mobility gap is close to its nominal occupation $n$. However, the situation changes drastically as the bare level approaches a band edge or penetrates a band. If the energy level $\varepsilon_d(x)$ is located within the conduction band $[\varepsilon_d(x) > E_c]$, the hybridization of the state $\psi_d$ with unoccupied conduction-band states gives rise to such an electron (or electron pair) state, which mainly consists of the conduction-band states, rather than of the state $\psi_d$. Therefore, as follows from Eq. (2.12), the true occupation of the state $\psi_d$ becomes close to zero, $\nu_d \simeq 0$, independently of its nominal occupation $n$, actually due to the well-known quantum-mechanical dispersion of the wave packet in the conduction band. A similar situation takes place when the bare level $\varepsilon_d(x)$ appears within the valence band $[\varepsilon_d(x) < E_v]$. The difference is that hybridization leads to almost complete occupation of the state $\psi_d$ by two electrons coming from the valence-band states, so that $\nu_d \simeq 2$, independently of the nominal state occupation $n$. Essential changes $\Delta\nu_d \equiv \nu_d - n$ in the state occupation occur within an energy range around the appropriate band edge, of which the width is of the order of magnitude of the effective interaction energy $\Delta$. Since actually $\Delta/E_g \ll 1$ and $U_d/E_g \ll 1$, simple approximate relations can be derived for the electron energies $E^{(n)}_{\text{el}}(x)$ of the system, taking into account the obvious expressions characteristic of the hybridization-free case:

$$E^{(n)}_{\text{el}}(x) = n\varepsilon_d(x) + U_d\delta_{n,2}. \quad (3.1)$$

In this connection let us assume, for the sake of simplicity, that the hybridization generates abrupt changes in the state occupation as the energy level $\varepsilon_d(x)$ crosses a band edge with increasing soft-mode displacement. As just noted, if the energy level $\varepsilon_d(x)$ is located in the conduction band $[\varepsilon_d(x) > E_c]$ and the state $\psi_d$ is singly occupied $(n = 1)$, the true occupation of the state becomes close to zero, $\nu_d \simeq 0$, and the electron occupies the band bottom, $E^{(1)}_{\text{el}}(x) \simeq E_c$. Then the true and nominal occupations nearly coincide $(\nu_d \simeq n \simeq 1)$, if $E_v < \varepsilon_d(x) < E_c$, so the relation (3.1) at $n = 1$ is still applicable. On the other hand, if $\varepsilon_d(x)$ is located within the valence band, the true occupation $\nu_d \simeq 2$, so the relation (3.1) may be applied for $n = 2$. In a similar way the cases of other nominal occupation can be described. The approximate expressions for $E^{(n)}_{\text{el}}(x)$ follow:

$$E^{(0)}_{\text{el}}(x) \equiv E^{(n=0)}_{\text{el}} \approx \begin{cases} 0 & \text{at } \varepsilon_d(x) > E_v \equiv 0, \\ 2\varepsilon_d(x) + U_d & \text{at } \varepsilon_d(x) < 0 \, ; \end{cases}$$

$$(3.2)$$

$$E_{\rm el}^{(1)}(x) \approx \begin{cases} E_g & \text{at } \varepsilon_d(x) > E_c \equiv E_g, \\ \varepsilon_d(x) & \text{at } 0 < \varepsilon_d(x) < E_g, \\ 2\varepsilon_d(x) + U_d & \text{at } \varepsilon_d(x) < 0 \, ; \end{cases} \quad (3.3)$$

and

$$E_{\rm el}^{(2)}(x) \approx \begin{cases} 2E_g & \text{at } \varepsilon_d(x) > E_g, \\ 2\varepsilon_d(x) + U_d & \text{at } \varepsilon_d(x) < E_g \, . \end{cases} \quad (3.4)$$

In accordance with the note above, it is taken into account that $E_{\rm el}^{(n)}(x) \approx nE_g$, if $\varepsilon_d(x) > E_g \gg U_d$. The expressions (3.2)–(3.4) give a simple qualitative picture of the electron energy changes under self-trapping. This is supported and quantified by the results of numerical calculations presented and discussed in the next section for actual positive soft-mode displacements which correspond to $\varepsilon_d(x)$ approaching and penetrating the valence band, i.e., to $\varepsilon_d(x) < E_g$ in Eqs. (3.2)–(3.4). Although the hybridization energy $\Delta$ is finite and therefore the related changes in the state occupation are continuous, the latter indeed are rather sharp for actual $\Delta/E_g$, the sharper the smaller $\Delta/E_g$.

The expressions for $E_{\rm el}^{(n)}(x)$, as well as for the other characteristics $E_{d\sigma}(x)$, $\nu_{d\sigma}$, and $\gamma_{d\sigma}^2(x)$, and for the equation determining the equilibrium self-trapping displacements, which are applied in the numerical calculations, can be derived in the approximation (2.19) from Eqs. (2.11)–(2.17). It follows that (see also Ref. 10)

$$\begin{aligned} E_{\rm el}^{(n)}(x) = &-\frac{1}{\pi} \sum_{\sigma} \int_{\rm VB} \phi_\sigma(\omega, x) d\omega \\ &+ \sum_{\sigma({\rm occupied})} E_{d\sigma}(x) - \delta E, \end{aligned} \quad (3.5)$$

$$\nu_{d\sigma}(x) \equiv \langle \hat{n}_{d\sigma} \rangle = \frac{1}{\pi} \int_{\rm VB} d\omega \left[ -\frac{d\phi_\sigma(\omega; x)}{d\varepsilon_{d\sigma}^{\rm eff}(x)} \right] + \gamma_{d\sigma}^2(x),$$

$$(3.6)$$

and

$$\phi_\sigma(\omega; x) = \frac{\pi}{2} + \arctan\left\{ \frac{\omega - \varepsilon_{d\sigma}^{\rm eff}(x) - \Sigma_d'(\omega; x)}{\Sigma_d''(\omega; x)} \right\}. \quad (3.7)$$

Here the self-energy

$$\begin{aligned} \Sigma_d(\omega) \simeq &\, \Delta_v(x) \ln\left| \frac{\omega - E_v'}{E_v - \omega} \right| + \Delta_c(x) \ln\left| \frac{\omega - E_c}{E_c' - \omega} \right| \\ &+ i\pi \bigg[ \Delta_v(x)\theta(E_v - \omega)\theta(\omega - E_v') \\ &\quad + \Delta_c(x)\theta(\omega - E_c)\theta(E_c' - \omega) \bigg] \end{aligned} \quad (3.8)$$

and

$$\gamma_{d\sigma}^2(x) \simeq \left\{ 1 + \frac{\Delta_v D_v}{(\omega - E_v)(\omega - E_v')} + \frac{\Delta_c D_c}{(E_c - \omega)(E_c' - \omega)} \right\}_{E_v < \omega = E_{d\sigma}(x) < E_c} \quad (3.9)$$

with $E_c' \equiv E_c + D_c$, $E_v' \equiv E_v - D_v$, $E_v \equiv 0$, and $E_c \equiv E_g$. The integrals in Eqs. (3.5) and (3.6) are taken over the energies ($\omega$) of the (fully occupied) states of the valence-band, and the reference energy for $E_{\rm el}^{(n)}(x)$ is the total energy of the unperturbed, hybridization-free, valence-band states.

The first term in Eq. (3.5) characterizes the decrease of the total valence-band energy due to the hybridization of states, while the first term in Eq. (3.6) describes the respective change in the true occupation of the bare single-electron state. The second term in Eqs. (3.5) and (3.6) corresponds to the energy of the occupied energy levels $E_{d\sigma}(x)$ and to the related contribution to the occupation of the bare state, respectively. Note that the conduction-band states only slightly contribute to $E_{\rm el}^{(n)}(x)$, $\nu_{d\sigma}(x)$, and $\gamma_{d\sigma}^2(x)$, i.e., to $\Sigma_d(\omega = E_{d\sigma})$, as long as $E_{d\sigma}(x)$ approaches $E_v$ and $\varepsilon_d(x)$ penetrates the valence band at large displacements $|x|$, $1 \geq |x| \geq x_g = E_g/Q_d$. In this actual case (see Sec. IV) implied in what follows, the expressions for $E_{\rm el}^{(n)}(x)$ and $\gamma_{d\sigma}^2(x)$ can be simplified, with[10]

$$E_{d\sigma}(x) - \frac{1}{\pi} \sum_{\sigma} \int_{\rm VB} \phi_\sigma(\omega, x) d\omega \simeq \varepsilon_{d\sigma}^{\rm eff}(x) \quad (3.10)$$

and

$$\gamma_{d\sigma}^2(x) \simeq \left[ 1 + \frac{\Delta}{E_{d\sigma}(x)} \right]^{-1}. \quad (3.11)$$

The latter corresponds to practically complete hybridization with the valence-band states at $0 < E_{d\sigma}(x) < \Delta_v$ and to negligible hybridization at $E_{d\sigma}(x) \simeq \varepsilon_{d\sigma}^{\rm eff}(x) \gg \Delta_v$, in agreement with the corresponding note in Sec. II.

As noted above, applying quantitatively more adequate expressions for $\Delta(\varepsilon, \omega; x)$ is not expected to give rise to essential changes in the basic features of $E_{\rm el}^{(n)}(x)$, $E_{d\sigma}(x)$ and $\nu_{d\sigma}(x)$, $\gamma_{d\sigma}^2(x)$, althogh quantitative corrections may occur.

## IV. BASIC FEATURES OF SELF-TRAPPED STATES AND RELATED ATOMIC DYNAMICS. FORMATION OF NEGATIVE-$U$ CENTERS

Equations (2.8), with Eqs. (2.12) and (3.5), and also Eq. (2.17) have been numerically solved and the basic characteristics (3.5), (3.6), (3.9), (2.6), and (2.7) have been calculated for the self-trapped states at equilibrium soft-mode displacements $\bar{x}_n(\eta, \xi)$, for different nominal occupations $n = 0, 1$, or 2 of the bare state. In what follows the main results are presented and discussed. The situation is considered in detail for the case of a nominally free bare state ($n = 0$), which exhibits in a most pronounced way the basic features of the self-trapped states and the related atomic dynamics. Hybridization effects, giving rise to these features, actually are strong just for the substrate soft configurations (2.2) of which anharmonicity limits the equilibrium displacements to realistic $|\bar{x}_n(\eta, \xi)| \leq 1$. Characteristic values $(\eta_n^{**}, \xi_n^{**})$ of the soft-mode parameters $(\eta, \xi)$, which mark essen-

tial changes in the bare state occupation $\nu_d$ and related atomic adiabatic potentials (atomic dynamics), are also calculated. However, analytical approximations for estimating $(\eta_n^{**}, \xi_n^{**})$ can be obtained only for quasiharmonic soft configurations belonging to the range of $(\eta, \xi)$, actually at $1 \gg \eta \gg \eta_L$ (since most important contributions come from $\xi \simeq \bar{\xi}$, the mean value, which is small, $\bar{\xi}^2 \ll 1$, and practically can be chosen $\bar{\xi} \simeq 0$).

It is worth noting that two-band self-trapping is realized as long as the bare electron energy level $\varepsilon_d(x) \simeq \varepsilon_d(x) - Q_d x$ moves toward and penetrates the valence, nonparent, band with increasing soft-mode displacements $x$ $(> 0)$, and strong hybridization of the electron state with the valence-band states occurs at large enough positive equilibrium displacements $\bar{x}_n(\eta, \xi) \sim 1$. The soft-mode asymmetry $(\xi)$ in Eq. (2.2) does favor $x > 0$ and $\bar{x}_n(\eta, \xi) > 0$ at $\xi < 0$ while it does not at $\xi > 0$. Therefore a finite subrange of $(\eta, \xi > 0)$ may exist, in which $\bar{x}_n(\eta, \xi) < 0$ and $\varepsilon_d(x)$ moves toward (and may penetrate) the conduction, parent, band and hybridization with these band states becomes strong. Self-trapping in such soft configurations does not contribute to the two-band self-trapping under discussion and is a special type of single-band self-trapping which does not favor formation of negative-$U$ centers. Numerical calculations of $\bar{x}_n(\eta, \xi)$ show that such a subrange $A_2$ of $(\eta, \xi)$, although finite, is small compared to the main subrange $A_1$ of $(\eta, \xi)$, which corresponds to two-band self-trapping with large $\bar{x}_n(\eta, \xi) \geq x_g = E_g/Q_d$ and $\varepsilon_d(\bar{x}_n) < 0 < \varepsilon_d(0) \sim E_g$. As shown in the next section, only the contribution of the main subrange $A_1$ of $(\eta, \xi)$ to the electron density of states (DOS) and thermal equilibrium statistics of the system under consideration is important. In this connection in what follows we focus on the two-band self-trapping and related soft modes in the main subrange $A_1$ of their parameters $(\eta, \xi)$. In fact, as seen in Sec. V, only a small part of this subrange $A_1$ is important in thermal equilibrium properties, and corresponds to quasiharmonic single-well soft-mode potentials (2.2 ), at $1 \gg \eta \gg \eta_L$. However, the whole subrange $A_1$, including anharmonic non-single-well soft-mode potentials, and the related spectrum of self-trapping energies $W_n(\eta, \xi)$, pair correlation energies $U(\eta, \xi)$, and atomic adiabatic potentials $\Phi_n(x; \eta, \xi)$ are considered in what follows, since those may be important for nonequilibrium properties of the system. An example is a correlation between photoinduced electron effects, associated with generation of negative-$U$ center excitations (photoluminescence, photoconductivity, etc.), and changes in atomic structure (photostructural changes[9,26]), in atomic soft-mode potentials and low-energy dynamics, as well as in the associated low-temperature properties, of glassy semiconductors, which will be discussed elsewhere.

Three most important effects can be revealed, which are due to hybridization of states in the gap and are characteristic of the two-band self-trapping and the related spectrum of $W_n(\eta, \xi)$, $U(\eta, \xi)$, and $\Phi_n(x, \eta, \xi)$ under consideration.

(i) As the electron level $\varepsilon_{d\sigma}^{\text{eff}}(x) = \varepsilon_d(x) + U_d \nu_{d,-\sigma}(x)$ approaches under self-trapping the (mobility) edge $E_v$, increasing hybridization of states gives rise to repulsion
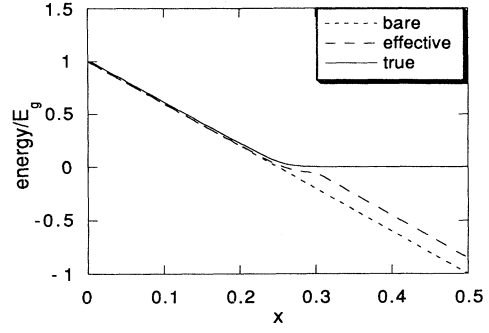


FIG. 1. Dependence of bare $[\varepsilon_d(x)]$, effective $[\varepsilon_{d\sigma}^{\text{eff}}(x)]$, and true $[E_{d\sigma}(x)]$ energies on $x$ at $\varepsilon_d^{(0)} \equiv \varepsilon_d^{(0)}/E_g = 1$, $Q_d^c = 4$; $V_{id(c)}^{(0)} = 0 = Q_{id(v)}$, $N^{1/2} Q_{id(c)} = 0.5$, $N^{1/2} V_{id(v)}^{(0)} = 0.2$, i.e., $\Delta_v = 0.01$, $U_d = 0.15$, and $D_v = 5$, with $E_g$ taken here as the energy unit (the same set of parameters is used in the subsequent figures).

of the true level $E_{d\sigma}(x)$ off $E_v$. As seen from Fig. 1, hybridization is negligible as $\varepsilon_{d\sigma}^{\text{eff}}(x)$ is far from $E_v = 0$,

$$E_{d\sigma}(x) \simeq \varepsilon_{d\sigma}^{\text{eff}}(x) \gg \Delta \quad \text{and} \quad \nu_{d\sigma}(x) = 1 - \gamma_{d\sigma}^2(x) \ll 1,$$
$$(4.1)$$

whereas it becomes decisive as $\varepsilon_{d\sigma}^{\text{eff}}(x)$ approaches $E_v$ and penetrates the band, $\varepsilon_{d\sigma}^{\text{eff}}(x) \leq 0$. In the latter case, $E_{d\sigma}(x)$ is stopped near $E_v$,

$$0 < E_{d\sigma}(x) < \Delta \quad \text{and} \quad \nu_{d\sigma}(x) \simeq 1. \qquad (4.2)$$

In fact, the effective electron-mode coupling energy $Q_{d\sigma}^{(\text{eff})}(x)$ can be defined, for large displacements and $E_{d\sigma}(x)$ close to $E_v$ at least, as

$$Q_{d\sigma}^{(\text{eff})}(x) \equiv dE_{d\sigma}(x)/dx \simeq \gamma_{d\sigma}^2 Q_d, \qquad (4.3)$$

as follows from Eqs. (2.16) and (2.17). As seen, $Q_{d\sigma}^{(\text{eff})}(x) \ll Q_d$ and $\gamma_{d\sigma}^2(x) = 1 - \nu_{d\sigma}(x) \ll 1$ for large $|x|$, in accordance with Eq. (3.11). The essential decrease of $Q_{d\sigma}^{(\text{eff})}(x)$ can be considered as the ultimate cause of repulsion of the true energy level off $E_v$. It follows from Eqs. from Eqs. (2.17) and (3.8) that $E_{d\sigma}(x)$ approximately approaches the (mobility) edge $E_v$ in an exponential way,

$$E_{d\sigma}(x) \approx D_v \exp\left\{ \frac{\varepsilon_{d\sigma}^{\text{eff}}(x)}{\Delta} \right\} \qquad (4.4)$$

for $|\varepsilon_{d\sigma}^{\text{eff}}| = -\varepsilon_{d\sigma}^{\text{eff}} \gg \Delta$.

(ii) The hybridization of states also is responsible for an increase of the bare state occupation from the nominal $n = 0$ to the true occupation $\nu_{d\sigma} > 0$ (Fig. 2). This corresponds to a change in the equilibrium self-trapping displacement from $x_0 \simeq 0$ to a finite $x_0 \neq 0$, as follows from Eq. (2.8) and discussed also below. Solutions of Eq. (2.8) are illustrated in Fig. 3 for different possible values of the substrate softness parameter $\eta$ and for $\xi = \bar{\xi} \approx 0$ corresponding to the main maximum of the distribution density $F(\eta, \xi)$. A single solution $x_0 = x_{01} \simeq 0$ only occurs for large enough $\eta > \eta_0^* \equiv \eta_{n=0}^*$, at weak hybridiza-
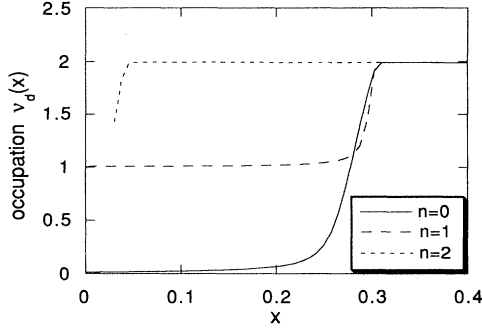
FIG. 2. True occupation of the defect state at different nominal occupations as a function of $x$.

tion, with $\nu_{d\sigma}(x_{01}) = 1 - \gamma_{d\sigma}^2(x) \approx \Delta/E_g \ll 1$. However, an additional solution $x_{02} \neq 0$ appears for smaller $\eta < \eta_0^*$, for a large displacement $|x_{02}| \sim x_g = E_g/Q_d \leq 1$, which corresponds at first to a metastable minimum and, for still smaller $\eta$, to an equilibrium (absolute) minimum, as discussed below. Thereby, the effective electron level $\varepsilon_{d\sigma}^{\mathrm{eff}}(x)$ reaches $E_v$ and penetrates the valence band, the true level $E_{d\sigma}(x)$ is repelled off $E_v$, and nearly complete hybridization occurs, $\gamma_{d\sigma}^2(x) \ll 1$, so $x_{02}$ should be close to the equilibrium self-trapping displacement $x_2$ for a nominally doubly occupied state ($n = 2$) in the hybridization-free case:

$$|x_{02}| \simeq |x_2| \leq 1, \tag{4.5}$$

for soft enough configurations.

The characteristic value $\eta_0^*$, corresponding to appearance of an inflection point for $\Phi_0(x;\eta)$, is found to be $\eta_0^* \simeq 0.08$ for the representative values of the parameters used in the calculations. A value $\eta_{0h}^* \approx 0.10$ close in scale to $\eta_0^*$ follows from the approximate expression

$$\eta_{0h}^* \leq \frac{Q_d}{A} \sim 0.1 \tag{4.6}$$

obtained in the harmonic approximation.

It is worthy of note that self-trapping of the nominally free state ($n = 0$) is entirely determined by hybridization. The latter originally is weak [$\nu_{d\sigma}(x) \simeq \Delta/E_g \ll 1$ for

$|x| \ll 1$] but finite, and then increases with growing $|x|$ up to $x_{02} \approx x_2$, due to increasing contributions from extended valence-band states. The resulting self-trapped pair state is still localized, but its effective size $\rho$ increases as compared to the bare state size $\rho_0 \approx (1-2)a_1$, $a_1$ being the average nearest neighbor separation ($a_1 \approx 2.0$ Å). A rough estimation of $\rho/\rho_0$ can be obtained from Eq. (3.11) and the approximate relation

$$\gamma_{d\sigma}^2(x_{02}) \approx \int_0^{\rho_0} dr \; 4\pi r^2 |\Psi_{d\sigma}(r|x = x_{02})|^2$$
$$\leq \frac{1}{6}\left(\frac{2\rho_0}{\rho}\right)^3, \tag{4.7}$$

with $\Psi_{d\sigma}(r|x_{02}) \equiv C_{d\sigma}\exp(-r/\rho)$ and $\psi_d = C_0\exp(-r/\rho_0)$, so that

$$1 < \rho/\rho_0 \approx [1 + \Delta/E_{d\sigma}(x_{02})]^{1/3} \leq 5 \tag{4.8}$$

for realistic not too small $E_{d\sigma}(x_{02})$, $1 < \Delta/E_{d\sigma}(x_{02}) \leq 10^2$.

The related effects of the true single-electron energy level $E_{d\sigma}(x)$ being repelled off the valence-band edge $E_v$ and of the increase of the bare state occupation may be interpreted as follows. The true occupation $\nu_{d\sigma}(x)$ with increasing $|x|$ changes from $n_\sigma = 0$ to $\nu_{d\sigma} = 1$ due to contributions of the valence-band electrons which flow into the region of the bare state, strongly interacting with the soft mode. Thereby, in accordance with the behavior of the total electron energy, the bare level efficiently drops and penetrates the valence band, effectively as $\varepsilon_d(0) - \nu_d Q_d x$ at $\nu_d \to 2$. However, the contributions of the bare state to the true, hybridization-renormalized state $\Psi_{d\sigma}$ are characterized by $\gamma_{d\sigma}^2(x) \to 0$ for the large displacements $|x| \to x_{02}$. This may correspond to the fact that the true energy level, as a solution of the effective Schrödinger equation (2.17), behaves in such a way as if it is unaffected by the true occupation of the bare level, and may be characterized by the nominal occupation which is zero in the case in question.

(iii) A competition between an increase of the substrate atomic potential energy and an electron energy gain due to growing hybridization, with increasing $|x|$, can generate for sufficiently soft substrate configurations additional anharmonic features of the adiabatic potential

$$\Phi_0(x) = V_{\mathrm{at}}(x) - U_d\left[\nu_{d\sigma}(x)\right]^2 - 2\left[E_{d\sigma}(x) - \varepsilon_{d\sigma}^{\mathrm{eff}}(x)\right], \tag{4.9}$$

and thus of the related local atomic dynamics. A signature of the potential anharmonicity is softness and/or appearance of an extra potential minimum as a metastable one for an excited self-trapped state at $\eta < \eta_0^*$, and then as a lowest-energy minimum for a ground state at smaller $\eta < \eta_0^{**} < \eta_0^* \ll 1$ (Fig. 4). The value $\eta_0^{**} \simeq 0.01$ is found for the representative values of the parameters. An approximate expression of $\eta_{0h}^{**}$ for a harmonic substrate follows from

$$\Phi_0(x_{01} \simeq 0) \simeq 2\Delta \ln(D_v/E_g)$$
$$\simeq \Phi_0(x_{02} \simeq x_2) \simeq 2E_g - Q_d^2/A\eta_{0h}^{**} + U_d,$$
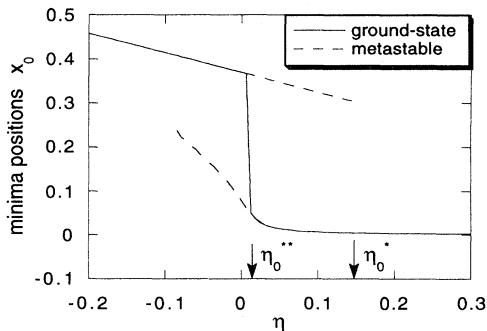


FIG. 3. Minima positions of the adiabatic potential $\Phi_0(x)$ depending on the softness parameter $\eta$ (for the same set of parameters noted in Fig. 1 and $A = 40$, $\xi = \bar{\xi} = 0$, as also used in Figs. 4–9 and Figs. 11–13).
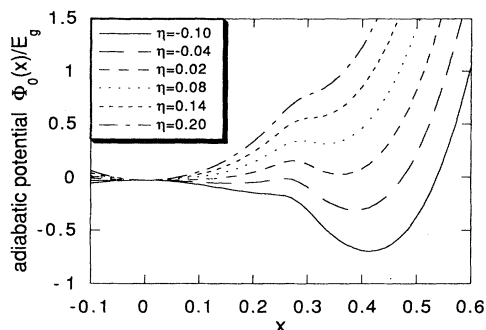
FIG. 4. Dependence of the adiabatic potential $\Phi_0(x)$ on $x$ for different values of the softness parameter $\eta$.

i.e.,

$$\eta_{0h}^{**} \simeq Q_d^2/A(2E_g + U_d), \qquad (4.10)$$

so that $\eta_{0h}^{**} \approx 0.05$ is not far in scale from $\eta_0^{**}$ (cf. Ref. 10).

One can conclude that the lowest-energy minimum position of the adiabatic potential depends on the value of $\eta/\eta_0^{**}$, unlike the universal single minimum at $x_0 = 0$ for single-band self-trapping. For $\eta < \eta_0^{**}$, the electron ground state related to the lowest-energy potential minimum at $x_{02} \simeq x_2$ is the self-trapped state for a singlet electron pair $[\nu_d(x_{02}) \simeq 2]$, so the self-trapping rather requires overcoming the interwell barrier. It is seen that actually $\eta_0^{**}$ is rather small, so the related extra anharmonic features appear for soft enough configurations occurring in a glassy semiconductor.

The situation shown in Fig. 5 for a nominally singly occupied state ($n = 1$) is similar to that for $n = 0$. The main difference is that the respective $\eta_1^*$ and $\eta_1^{**}$ are larger and characteristic of more numerous and less soft configurations: $\eta_1^* > \eta_0^*$ and $\eta_1^{**} > \eta_0^{**}$, at $\eta_1^{**} < \eta_1^*$, e.g., $\eta_1^* \simeq 0.12 > \eta_0^* \simeq 0.08$ and $\eta_1^{**} \simeq 0.05 > \eta_0^{**} \simeq 0.01$. Of course, in this case self-trapping occurs even without hybridization although the latter changes it substantially for soft enough configurations.

The situation is essentially different for a nominally doubly occupied bare state ($n = 2$) which is weakly sensitive to hybridization, since it is filled originally. There-
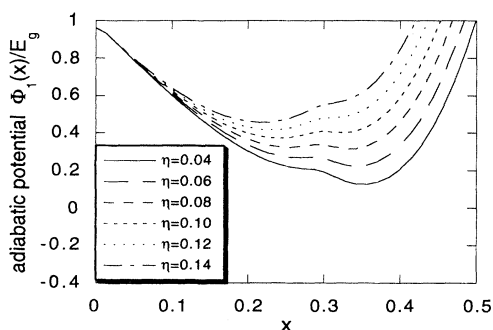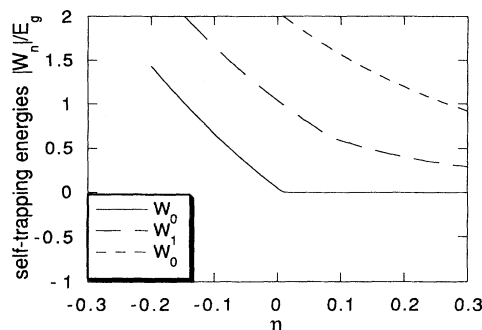


FIG. 6. Self-trapping energies: dependence on the softness parameter $\eta$.

fore,

$$\Phi_2(x) \simeq V_{at}(x) + U_d + 2\varepsilon_d(x) \qquad (4.11)$$

and

$$\Phi_2(x_2) \simeq 2\varepsilon_d^{(0)} + U_d + W_2, \qquad (4.12)$$

as if the influence of the valence-band states vanishes. Then the adiabatic potential has the same structure as the substrate one $V_{at}(x)$. For instance, it would be harmonic, with

$$W_{2h} \equiv W_{2h}(x_2) \simeq -Q_d^2/A\eta a_0^2 \qquad (4.13)$$

at $x_2 \simeq Q_d/A\eta$ if $V_{at}(x) \simeq A\eta x^2$.

The hybridization-induced changes in $\Phi_0(x)$ and $\Phi_1(x)$, as well as in $x_n$, for the lowest-energy minima, give rise to significant deviations of the total electron energies $E_{el}^{(n)}(x)$, self-trapping energies $W_n$ ($n = 0, 1$), and the pair correlation energy $U$ in Eqs. (2.6) and (2.7) from the standard formulas[1-5]

$$W_0 = 0, \quad W_1 = W_2/4 = -W = -Q_d^2/2ka_0^2,$$
$$E_{el}^{(n)} = n(\varepsilon_d^{(0)} - Q_d x) + \delta_{n2} U_d, \quad \text{and} \quad U = -2W + U_d \qquad (4.14)$$

for single-band self-trapping in a harmonic substrate configuration $V_{at}(x) \simeq A\eta x^2 = kx^2 a_0^2/2$. In Eqs. (4.14) $U$ decreases linearly with $W$ and is negative for $k < Q_d^2/2U_d a_0^2 \leq k_0$. The deviations of $W_0$, $W_1$, $E_{el}^{(n)}(x)$ ($n = 0, 1$), and $U$ from Eqs. (4.14) are schematically shown in Figs. 6 and 7. Those become essential for small



FIG. 5. Dependence of the adiabatic potential $\Phi_1(x)$ on $x$ for different values of the softness parameter $\eta$.
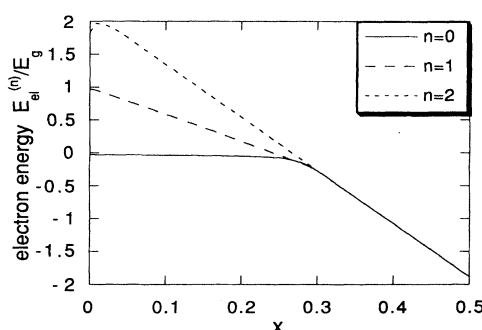


FIG. 7. Total electron energy gain $E_{el}^{(n)}$: dependence on $x$ for different nominal occupations.

enough $\eta \leq \eta_1^{**}$ as the electron ground state, nominally singly occupied ($n = 1$), is related to the extra minimum at $x_1 = x_{12} \simeq x_2$ for $\Phi_1(x)$ and is actually doubly occupied [$\nu_d(x_{12}) \simeq 2$]. This behavior might be illustrated for self-trapping in a harmonic substrate configuration with $W_{2h}$ from Eq. (4.13),

$$W_1 = E_g - 4W + U_d = W_2(x_2) + E_g + U_d < 0,$$
$$U_h = 4W - U_d - 2E_g < 0,$$
(4.15)

for $\eta_{0h}^{**} < \eta < \eta_{1h}^{**}$ at $|\eta| \ll 1$ and typical $\varepsilon_d^{(0)} \simeq E_c \equiv E_g$ [with accuracy to small corrections $O(\Delta/E_g)$]. In Eq. (4.15), $W_1$ decreases linearly with $W \sim \eta^{-1}$, whereas the negative $U$ passes through the lowest value $U_{mh}$ at $\eta = \eta_{1h}^{**}$, increasing in the range $\eta_{0h}^{**} < \eta < \eta_{1h}^{**}$. Further decrease of $\eta$ ($\leq \eta_{0h}^{**}$) changes the lowest-energy minimum position for $\Phi_0(x)$ from $x_0 = x_{01} \simeq 0$ to $x_0 \simeq x_{02} \simeq x_{12} \simeq x_2$, so that [with accuracy to small corrections $O(\Delta/E_g)$] $\Phi_2(x_2) \simeq \Phi_1(x_{12}) \simeq \Phi_0(x_{02})$, and

$$U_h \geq -\Delta, \quad \text{i.e.,} \quad |U_h| \leq \Delta \ll E_g.$$
(4.16)

In fact, $U$ asymptotically tends to zero, not becoming positive, at $\eta < \eta_{0h}^{**}$. Then the negative correlation energy $U$ exhibits a nonmonotonic dependence on $W$, and the lowest value

$$U_{mh} = U_h(\eta_{1h}^{**}) \simeq -\frac{2}{3}E_g\left(1 + \frac{U_d}{2E_g}\right)$$
(4.17)

is actually close to, though slightly less than, $(-E_g/2)$ for $E_g \gg U_d$, $|U_{mh}| \simeq E_g/2$.

As noted above, the basic features of $U(\eta)$ shown in Fig. 8 (solid line) for self-trapping in anharmonic substrate configurations (2.2) are similar to those of the nonmonotonic dependence $U_h(\eta)$ from the formulas (4.15)–(4.17). On the other hand, even in the absence of hybridization, the behavior of $U(\eta)$ shown in Fig. 8 (dashed line) for the self-trapping in the anharmonic configurations with double-well potentials is similar to that described by the solid line in Fig. 8 and by formulas (4.15)–(4.17). This similarity can be interpreted to mean that hybridization effects give rise to anharmonic features of the same type as the original anharmonicity of Eq. (2.2). The difference is that hybridization prevents occurrence of positive correlation energies for anharmonic configu-
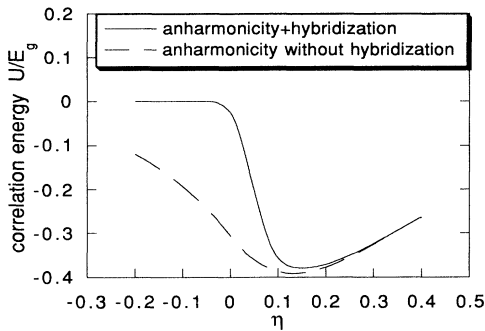
rations ($\eta < \eta_0^{**}$), whereas the anharmonicity itself does not. A quantitative difference exists between $U_{mh}$ in Eq. (4.17) and the true lowest value $U_m$ of $U$ for self-trapping in anharmonic configurations, which is, however, relatively small, so that

$$0 < U_{mh} - U_m \ll |U_{mh}|, \quad \text{i.e.,} \quad U_m \simeq -E_g/2,$$
(4.18)

as seen from Fig. 8 as well.

It is worth adding that the behavior of $U(\eta)$ and its hybridization-induced features, as also the scale of the magnitude, do not essentially depend on whether $V_{id}^{(0)} = 0$ or $V_{id}^{(0)}$ is finite (e.g., $|V_{id}^{(0)}|N^{1/2} = |V_1| \leq 1$ eV) in $V_{id}(x) \simeq V_{id}^{(0)} + Q_{id}x$, as shown in Fig. 9. Presumably this holds because of the relatively large magnitude $|x_2| \approx 1$.

It follows from the above that the hybridization of states in two-band self-trapping in general changes the relationships between $E_{d\sigma}(\bar{x}_n)$ and $W_n(\eta,\xi)$ ($n = 0,1,2$), as well as the behavior of $U(\eta,\xi)$, compared to those for single-band self-trapping. The difference is minor in the subrange of not very soft configurations at $1 > \eta \geq \eta_1^{**} > \eta_0^{**}$ and $\xi \approx \bar{\xi} = 0$, in which actually the substrate soft-mode potentials (2.2) are quasiharmonic. The deviations, however, become essential for softer configurations at $\eta < \eta_1^{**}$ and even more at $\eta < \eta_0^{**}$ ($< \eta_1^{**}$), for which the substrate potentials are rather anharmonic and even non-single-well, e.g., double-well ones. Then in the subrange of ($\eta,\xi$) at $1 \gg \eta \gtrsim \eta_1^{**}$ and $\xi \approx \bar{\xi} \simeq 0$, in which $U$ is close to its lowest value $U_m$, $U \approx U_m \simeq -E_g/2$, an approximate electron-hole symmetry exists, as introduced for single-band self-trapping in an earlier theory,[9] in the sense that

$$U_m^{(e)} \simeq -E_g/2 \simeq U_m^{(h)},$$
(4.19)

with accuracy to small corrections $\leq \Delta/E_g \ll 1$, $\leq U_d/E_g \ll 1$, and $|\Delta U|/E_g \ll 1$, with $\Delta U = |U_m| - E_g/2$. Correspondingly, with the same accuracy, the pair self-trapping energies also exhibit this symmetry in the sense that
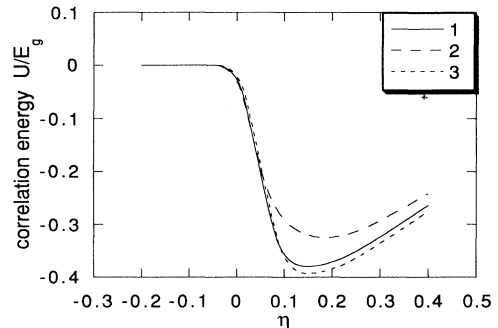
$$W_{2e} \simeq -E_g \simeq W_{2h},$$
(4.20)



FIG. 9. Variations of the pair correlation energy behavior for different dependence of the hybridization energy on the soft-mode displacement $x$. Curve 1: $N^{1/2}V_{id(v)}^{(0)} = 0.2$, $Q_{id(v)} = 0$. Curve 2: $N^{1/2}V_{id(v)}^{(0)} = 0.2$, $Q_{id(v)} = 0.5$. Curve 3: $N^{1/2}V_{id(v)}^{(0)} = 0$, $Q_{id(v)} = 0.5$. (The other parameters are the same as in Fig. 3.)



FIG. 8. Dependence of pair correlation energy on the softness parameter $\eta$ for different cases.

although $1/4 \leq |W_1/W_2| < 1/3$, rather than $W_2 = 4W_1$ for single-band self-trapping in a harmonic lattice. This kind of symmetry is important since just the subrange of $(\eta, \xi)$, in which the relations (4.19) and (4.20) hold, determines the principal spectral and thermal equilibrium properties of the gap states. That is why the earlier theory of the gap states in soft configurations,[9] though applying relations of single-band self-trapping theories, still might approximately be used for interpreting thermal equilibrium properties of negative-$U$ centers in glassy semiconductors.

## V. DENSITY OF STATES AND THERMAL EQUILIBRIUM PROPERTIES AT LOW TEMPERATURES

For the semiconductors under discussion (e.g., for glassy semiconductors) for which the electron subsystem is not excited, the principal spectral characteristic of the gap states, their density of states (DOS) per particle

$$g(E) = g^{(e)}(E) + g^{(h)}(E), \tag{5.1}$$

additively contains electron $(e)$ and hole $(h)$ contributions of both single-particle states of positive correlation energy $U$ (positive-$U$ states) $g_1^{(e,h)}(E)$ and singlet-pair states of $U < 0$ (negative-$U$ states) $g_2^{(e,h)}(E)$. The respective expressions are as follows:

$$g^{(e,h)}(E) = g_1^{(e,h)}(E) + g_2^{(e,h)}(E), \tag{5.2}$$

$$g_1^{(e,h)}(E) = \int_{-\infty}^{\eta^*} d\eta \int_{-\infty}^{\infty} d\xi \int d\varepsilon_d^{(0)} g_0^{(e,h)}(\varepsilon_d^{(0)})$$
$$\times F(\eta, \xi) \delta \left[ E - E_1(\varepsilon_d^{(0)}; \eta, \xi) \right], \tag{5.3}$$

and

$$g_2^{(e,h)}(E) = \int_{-\infty}^{\eta^*} d\eta \int_{-\infty}^{\infty} d\xi \int d\varepsilon_d^{(0)} g_0^{(e,h)}(\varepsilon_d^{(0)})$$
$$\times F(\eta, \xi) \delta \left[ E - E_2(\varepsilon_d^{(0)}; \eta, \xi)/2 \right], \tag{5.4}$$

with the total energies of the system nominally occupied by $n = 0, 1$, or 2 electrons (or holes) being

$$E_0 = 0, \quad E_1(\varepsilon_d^{(0)}; \eta, \xi) = \varepsilon_d^{(0)} + W_1(\eta, \xi) - W_0(\eta, \xi),$$

$$E_2(\varepsilon_d^{(0)}; \eta, \xi) = 2\varepsilon_d^{(0)} + W_2(\eta, \xi) - W_0(\eta, \xi) + U_d,$$

and

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\eta d\xi F(\eta, \xi) = 1, \quad \int g_0(\varepsilon_d^{(0)}) d\varepsilon_d^{(0)} = 1. \tag{5.5}$$

The DOS $g(E)$ determines both the total concentration of the self-trapped states and the related thermal equilibrium properties, such as the concentration $c_2$ of the occupied negative-$U$ pair states, or negative-$U$ centers, and the position of the chemical potential $\zeta$, or the Fermi-level $\zeta_0$ (at low temperatures $T \to 0$), in the gap.

The concentration of the positive-$U$ or negative-$U$ centers is

$$c_n = c_n^{(e)} + c_n^{(h)} \tag{5.6}$$

at $n = 1$ or $n = 2$, where

$$c_n^{(e,h)} = \int_{-\infty}^{\eta^*} d\eta \int_{-\infty}^{\infty} d\xi \int d\varepsilon_d^{(0)} g_0^{(e,h)}(\varepsilon_d^{(0)})$$
$$\times F(\eta, \xi) \phi_n^{(e,h)}(\varepsilon_d^{(0)}; \eta, \xi), \tag{5.7}$$

and the Gibbs occupation factor

$$\phi_n(\varepsilon_d^{(0)}; \eta, \xi) = Z^{-1} g_n \exp \left[ \frac{n\zeta - E_n(\varepsilon_d^{(0)}; \eta, \xi)}{T} \right], \tag{5.8}$$

$$Z = \sum_{n=0}^{2} g_n \exp \left[ \frac{n\zeta - E_n(\varepsilon_d^{(0)}; \eta, \xi)}{T} \right],$$

$$g_0 = g_2 = 1, \quad \text{and} \quad g_1 = 2 \tag{5.9}$$

In what follows low temperatures $T$ are only implied $[\zeta_0 \equiv \zeta(T = 0) \gg T \to 0]$ and temperature-dependent effects, in particular in $c_n$, are not considered in detail in the present paper. Some approximations are introduced, which may simplify the discussion and are justified below by calculations concerning in particular the electroneutrality equation

$$c_2^{(e)}(\zeta) \simeq c_2^{(h)}(\zeta) \tag{5.10}$$

for an actually intrinsic glassy semiconductor. As also may follow from general qualitative arguments,[9] the electron-hole symmetry in Eqs. (4.19) and (4.20) corresponds to $\zeta$ near the midgap $\bar{E} = E_g/2$,

$$\zeta \simeq \zeta_0 \equiv \zeta(T = 0) = E_g/2 + \Delta\zeta \simeq E_g/2 \gg |\Delta\zeta|. \tag{5.11}$$

It is also taken into account here (see below) that

$$g(\zeta) \simeq g_2(\zeta) \gg g_1(\zeta). \tag{5.12}$$

In this connection most important $(\varepsilon_d^{(0)}; \eta, \xi)$ obey, e.g., the equation

$$E_{2e}(\varepsilon_d^{(0)}; \eta, \xi) = 2\varepsilon_{de}^{(0)} + W_{2e}(\eta, \xi) - W_{0e}(\eta, \xi) + U_d^{(e)}$$
$$\simeq 2\zeta \simeq E_g \tag{5.13}$$

so

$$\zeta - E_{1e} = \zeta - \varepsilon_{de}^{(0)} - (W_{1e} - W_{0e})$$
$$= \frac{1}{2}\left( W_{2e} - W_{0e} + U_d^{(e)} \right) - (W_{1e} - W_{0e}) < 0$$

for actual

$$|W_{2e} - W_{0e}| > 2|W_{1e} - W_{0e}| + U_d^{(e)}.$$

Therefore,

$$Z \simeq 1 + \exp\left[\frac{2\zeta - E_2}{T}\right] \gg 2\exp\left[\frac{\zeta - E_1}{T}\right] \quad (5.14)$$

for the low temperatures in question. It is worth noting that the subrange ( 5.13) of $(\eta, \xi)$ still corresponds to small $\Phi_0(x_0 \simeq 0) \approx \Delta \ll |U_m| \simeq E_g/2$, not much different from the situation for negative-$U$ centers in the mentioned earlier theory applying the relations of single-band self-trapping.

In the approximation (5.11) and (5.14) the total low-temperature concentration of negative-$U$ and positive-$U$ centers in the gap,

$$c_{\rm tot} = c_1 + c_2 \simeq c_2 = c_2^{(e)} + c_2^{(h)} \gg c_1^{(e)} + c_1^{(h)}, \quad (5.15)$$

and $c_2$ can be expressed in terms of $g_2(E)$ and $\phi_2(\varepsilon_d^{(0)}; \eta, \xi)$, e.g.,

$$c_2^{(e)} = \int d\varepsilon_d g_0(\varepsilon_d^{(0)})\psi(\varepsilon_d^{(0)})$$
$$= \int_{E_v}^{E_c} dE g_{2e}(E)\bar{\phi}_{2e}(E) \ . \quad (5.16)$$

Here

$$\psi(\varepsilon_d^{(0)}) = \int_{-\infty}^{\eta^*} d\eta \int_{-\infty}^{\infty} d\xi F(\eta, \xi)\phi_{2e}(\varepsilon_d^{(0)}; \eta, \xi)$$

and

$$\bar{\phi}_{2e}(E) \equiv \bar{\phi}_{2e}(E_2/2) = 1 - \bar{\phi}_{2h}(E)$$
$$\equiv \phi_{2e}(\varepsilon_d^{(0)}; \eta, \xi)$$
$$\simeq \left\{1 + \exp\left[-\frac{2(\zeta - E)}{T}\right]\right\}^{-1} \quad (5.17)$$

with $E = E_2(\varepsilon_d^{(0)}; \eta, \xi)/2$, so

$$\bar{\phi}_{2e}(E) = 1 - \bar{\phi}_{2h}(E) \to 0 \quad \text{for} \quad E > \zeta$$

while

$$\bar{\phi}_{2e}(E) \to 1 \quad \text{for} \quad E < \zeta$$

at $T \to 0$.

Numerical calculations of Eqs. (5.10) and (5.15)–(5.17) justify the relations (5.11)–(5.14). The calculations were carried out by finding $\varepsilon_d^{(0)} = f(E, \eta, \xi)$ from the definition of $E$,

$$2E = E_2(\varepsilon_d^{(0)}; \eta, \xi),$$

so that

$$g_2(E) = \int_{-\infty}^{\eta^*} d\eta \int_{-\infty}^{\infty} d\xi F(\eta, \xi)Q(\eta, \xi; E) \quad (5.18)$$

with $g_0(\varepsilon_d^{(0)}) \equiv Q(\eta, \xi; E)$.

The bare DOS $g_0(\varepsilon_d^{(0)})$ of the two-band system and the distribution density $F(\eta, \xi)$ are approximated by often applied Gaussian-like functions:

$$g_0^{(e)}(\varepsilon_d^{(0)}) = g_{0e}^*\left\{\exp\left[-\left(\frac{E_c - \varepsilon_d^{(0)}}{w_t^{(e)}}\right)^2\right]\right.$$
$$\left. \times\theta(E_c - \varepsilon_d^{(0)}) + \alpha_e\theta(\varepsilon_d^{(0)} - E_c)\right\},$$
$$(5.19a)$$

$$F(\eta, \xi) = F_0(\eta)\exp\left[-\left(\frac{\bar{\eta} - \eta}{\Delta\eta}\right)^2 - \left(\frac{\bar{\xi} - \xi}{\Delta\xi}\right)^2\right].$$
$$(5.19b)$$

Here $g_{2e,h}^* \equiv g_0^{(e,h)}(E_{c,v})$, $\alpha_{e,h} = \text{const}$, $\bar{\eta} \approx 1$, $\bar{\xi}^2 \ll 1$; $\Delta\eta$ and $\Delta\xi$ stand for the respective distribution widths, and

$$F_0(\eta) = F_0 = \text{const}$$

or

$$F_0(\eta) = |\eta|\Phi_0, \quad \Phi_0 = \text{const} \quad (5.20)$$

for the two mentioned limiting types of $F(\eta, \xi)$ at $|\eta| \ll 1$ in the soft-configuration model (see, e.g., Refs. 9 and 16). The constant $F_0$ (or $\Phi_0$), as well as ratio $\alpha_e/\alpha_h$, can be estimated by taking into account the normalization Eqs. (5.5), actually with $\alpha_e \approx \alpha_h$, and $w_t^{(e,h)}$ are the band-tail widths, $w_t^{(e,h)}/E_g \ll 1$, e.g., $w_t^{(e,h)}/E_g \approx 0.1$. The variation scale $\delta\eta$ of $F(\eta, \xi)$ in $\eta$ for $|\eta| \ll 1$ is

$$\delta\eta \simeq (\Delta\eta)^2/2\bar{\eta} \approx 0.1 \sim (\Delta\xi)^2 \quad (5.21)$$

for typical soft-mode concentrations $c_d \sim 10^{-2}$ in glasses (see Sec. I). The parameters in the calculations include both the basic parameters of the theory [Eq. (2.18)] and those introduced in Eqs. (5.19)–(5.21).

The results of the numerical calculations for $g(E)$, $c_2(\zeta)$, and $\zeta$ are presented in Figs. 10–13 and discussed below. At least qualitatively and in order-of-magnitude estimates, the DOS $g(E)$ around the midgap and the related thermal equilibrium properties do not change at typical variations of the parameters in Eqs. (2.18) and (5.19)–(5.21) and of the type of $F_0(\eta)$ in Eqs. (5.20). The results are weakly sensitive to the type of $F_0(\eta)$, since quasiharmonic soft modes with not very small $|\eta| \gg \eta_L \sim 10^{-2}$ mostly contribute to the properties under discussion (see also below) while the difference in $F_0(\eta)$ is important here for very small $|\eta| \le \eta_L$.

Rough estimates also show, and it is implied in what follows, that other realistic approximations of $g_0(\varepsilon_d^{(0)})$ and $F(\eta, \xi)/F_0(\eta)$, e.g.,

$$g_0^{(e)}(\varepsilon_d^{(0)}) = g_{0e}^*\left\{\exp\left[-\left(\frac{E_c - \varepsilon_d^{(0)}}{w_t^{(e)}}\right)\right]\right.$$
$$\left. \times\theta(E_c - \varepsilon_d^{(0)}) + \alpha_e\theta(\varepsilon_d^{(0)} - E_c)\right\},$$

do not give rise to essential changes in the qualitative behavior and order-of-magnitude estimates of the DOS
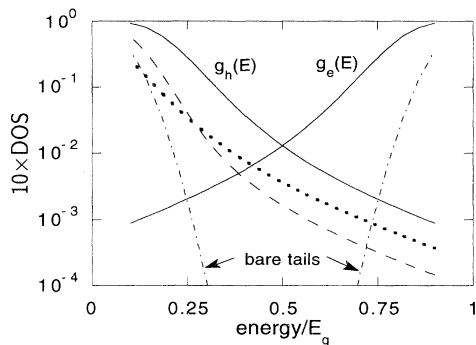
FIG. 10. Partial DOS's (per particle): $g_e(E)$ for electrons (solid line) and $g_h(E)$ for holes ($g_{0e}^* = g_{0h}^* = 0.1$, $\alpha_e 2 = \alpha_h = 1$, $\bar{\eta} = 1$, $\bar{\xi} = 0$, $\Delta\eta = 0.4$, $\Delta\xi = 0.3$; other parameters are noted in Fig. 3). For $g_h(E)$: solid line in the symmetric case (all the parameters are the same as for electron states), dashed line at $Q_d^v = 3$, and dotted line at $\Delta_v = 0.1$ (other parameters are the same as for electron states).

$g(E)$ and thermal equilibrium properties under discussion compared to the results of calculations presented in Fig. 10.

As seen, the symmetric shape of $g(E) \simeq g_2(E)$ around $\bar{E}$ at complete electron-hole symmetry ($X_e = X_h$ with $X = Q_d$, $g_0^*$, $w_t$, $\alpha$, and $U_d$) is weakly distorted at realistic non-symmetric values of the parameter $X$, with deviations from symmetry less than 10% in accordance with Eqs. (4.19) and (4.20). The largest deviations are associated with variations of the parameters $Q_d$ and $\Delta$, whereas variations of the other parameters give rise to smaller deviations not exceeding about 1% in magnitude. It follows also from the calculations that the variation scale $\delta E$ for $g(E)$ around $\bar{E}$ much exceeds $w_t$, $\delta E \sim E_g/2 \gg w_t$, i.e., the variations of $g(E)$ at $E \sim \bar{E}$ are much slower than in the band tails. Indeed, since most of the soft modes (2.2) are quasiharmonic at $1 \gg \eta \gg \eta_L$ Eqs. (4.14) and



FIG. 12. The truncated sector $A = A_1 + A_2$ in the $(\eta, \xi)$ plane, in which the electron negative-$U$ centers exist at $T = 0$, for actual $\varepsilon_{de}^0 \simeq 1$ (for the same set of parameters noted in Figs. 3 and 10).

(5.13) give rise to

$$\delta E \approx \delta\eta k_0 a_0^2 Q_d^{-2}(\varepsilon_d^{(0)} + U_d/2 - E)^2$$

$$\approx \frac{E_g}{2}\frac{0.1A}{Q_d}\frac{E_g}{Q_d} \sim \frac{E_g}{2} \gg w_t \qquad (5.22)$$

for typical $\delta\eta \approx 0.1 \approx \eta^*$ and, as shown below, $\varepsilon_d^{(0)} \approx E_c$, $E \approx \bar{E}$. This means that the variations of $g(E)$ at $E \approx \bar{E}$ are due to variations in $\eta$, rather than in $\varepsilon_d^{(0)}$.[9,27] Moreover, even the lowest value $g_L$ of $g(E) \simeq g_2(E)$, at $E = E_L \approx \bar{E}$, is very high compared to the corresponding value of the bare DOS,

$$g_0(\bar{E}) \ll g_L = g_2(E_L) \approx g_2(\bar{E}) \leq 10^{-3}. \qquad (5.23)$$

In this connection, a rough estimate $g_L \sim c_d f_t$ corresponds, for typical $c_d \sim 10^{-2}$, to an effective concentration of the related tail states in the gap $f_t \leq 10^{-1}$, which does not seem implausible in scale in a glassy semiconductor.

Actually, the electron (and hole) negative-$U$ centers are formed, with their Fermi level position near $\bar{E}$, as long as the conduction-band split DOS $g_{2e}(E)$ for electron pairs and the valence-band split DOS $g_{2h}(E)$ for
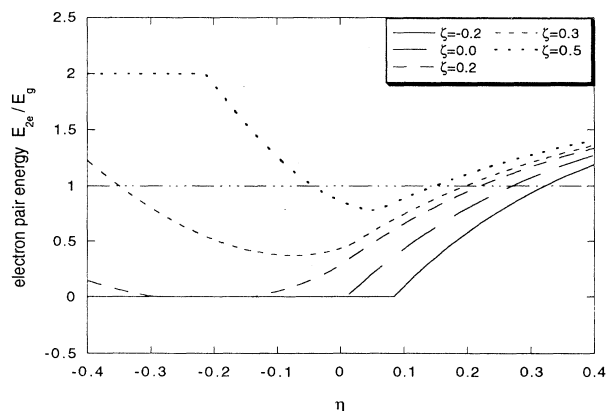


FIG. 11. Dependence of the singlet electron pair energy $E_{2e}(\varepsilon_d^0; \eta, \xi)$ on the soft configuration parameters $(\eta, \xi)$ at important $\varepsilon_{de}^0 \simeq 1$.
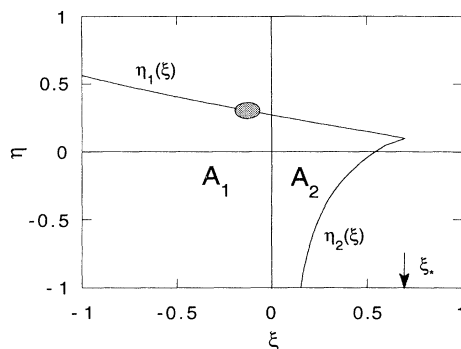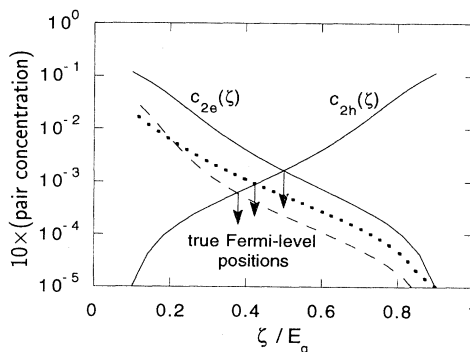


FIG. 13. The Fermi level position for the negative-$U$ centers, in the mobility gap, as found from the electroneutrality equation (the same parameters and notations as in Fig. 10).

hole pairs are overlapped in a noticeable energy range $\Delta E_{\rm eff} \leq \delta E$ around the midgap. As long as the overlap occurs, electrons from the valence-band split DOS flow to and occupy the pair states in the DOS $g_{2e}(E)$ below $\zeta$, whereas holes occupy the pair states above $\zeta$. This redistribution gives rise to formation of electron $(E_{2e} < 2\zeta)$ and hole $(E_{2h} > 2\zeta)$ negative-$U$ centers in the gap. The overlap indeed takes place, since for the actually important $\varepsilon_{de} \simeq E_c$, $\varepsilon_{dh} \simeq E_v$ assumed (see below) and $U \approx U_m \simeq -E_g/2$, $E_g/2 \leq 2|W_1| < 2E_g/3$,

$$E_{2e} \simeq 2E_c + 2W_1^{(e)} + U^{(e)} + U_d^{(e)}$$

$$\leq 2\zeta \leq E_{2h} \simeq 2E_v + 2W_1^{(h)} + U^{(h)} + U_d^{(h)} \quad (5.24)$$

(it is taken into account that $W_0 = 0$ for the implied $U \approx U_m$, i.e., $\eta \geq \eta_1^{**} > \eta_0^{**}$; see Sec. IV).

The total subrange $(\eta, \xi)$ for soft modes at $\{|\eta|, \xi^2\} \leq \eta^* \approx 0.1$, in which electron negative-$U$ centers are formed, can be found from the mentioned relation

$$E_{2e}(\varepsilon_d^{(0)}; \eta, \xi) \leq 2\zeta \simeq E_g \quad (5.25)$$

for the actual variety of $\varepsilon_d^{(0)}$ in question. However, as noted (and justified below), the bare energy level $\varepsilon_d^{(0)}$ lies near $E_c$ in the actual cases with $\zeta \simeq \bar{E} \equiv E_g/2$, $\varepsilon_d^{(0)} \simeq E_c \equiv E_g$. For such $\varepsilon_d^{(0)}$, the variation of $E_{2e}$ with $\eta$, found from numerical calculations for different $\xi$, is shown in Fig. 11. As follows for $\xi \leq 0$, $E_{2e} - 2E_g$ monotonically decreases with decreasing $\eta$, because of complete hybridization with the valence-band states for small enough $\eta$. In contrast, a nonmonotonic dependence of $E_{2e}$ on $\eta$ is rather expected at $\xi > 0$, as long as complete hybridization with the conduction-band states occurs at $\nu_2 \simeq 0 \simeq \nu_0$, $\Phi_0(x_0) \simeq 0$, and $\Phi_2(x_2) \simeq 2E_g$, so that $E_{2e}$ increases with decreasing $\eta$ and approaches $2E_g$ at small enough $\eta$.

Then the equation $E_{2e}(E_c; \eta, \xi) = E_g$ has a single real solution $\eta_1(\xi)$ at $\xi \leq 0$, whereas two real solutions $\eta_{1,2}(\xi)$ with $\eta_1(\xi_*) = \eta_2(\xi_*)$ occur at $0 \leq \xi \leq (\eta^*)^{1/2} < \xi_*$ (and no real solutions exist at $\xi > \xi_*$). The related subrange of $(\eta, \xi)$, at $\{|\eta|, \xi^2\} \leq \eta*$ is the truncated sector $A = A_1 + A_2$ in Fig. 12, which mainly corresponds to $\xi < 0$ and thus to positive equilibrium soft-mode displacements $\bar{x}_n(\eta, \xi) > 0$. The latter just give rise to the two-band self-trapping and negative-$U$ centers in question. Those, however, do not occur in practice for $\xi > 0$ and related negative displacements $\bar{x}_n(\eta, \xi) < 0$, for which complete hybridization of the electron bare state with the conduction-band states actually takes place in the soft configurations, corresponding to wave-packet dispersion in the conduction band. In this case $\nu_2 \simeq 0 \simeq \nu_0$, $\Phi_0(x_0) \simeq 0$, and $\Phi_2(x_2) \simeq 2E_g$, the state being almost nonoccupied, and the relation (5.25) does not hold. Actually, a kind of single-band self-trapping occurs for $\xi > 0$, which is not important in the characteristic truncated sector $A = A_1 + A_2$ and therefore not considered in what follows.

The question is what are the $(\eta, \xi)$ in the characteristic range $(A)$ which correspond to the states occupied by singlet electron pairs, i.e., to the electron negative-

$U$ centers? The integrand in the corresponding integral of Eq. (5.16) exhibits a pronounced maximum at $\xi_{\rm max} \simeq \bar{\xi} \simeq 0$ and $\eta_{\rm max} \simeq \eta_{\rm eff}(\varepsilon_d^{(0)}, \bar{\xi})$ for an actual $F(\eta, \xi)$ steeply decreasing around $\bar{\eta} \simeq 1$ and $\bar{\xi} \simeq 0$. In fact, $dF(\eta, \bar{\xi})/d\eta > 0$ while $d\phi_{2e}(\varepsilon_d^{(0)}; \eta, \bar{\xi})/d\eta < 0$ as $2E \equiv E_{2e}(\varepsilon_d^{(0)}; \eta, \bar{\xi})$ increases with $\eta$ and $d\bar{\phi}_2/dE < 0$, so $\eta_{\rm max}$ is found from $E_{2e}(\varepsilon_d^{(0)}; \eta, \bar{\xi}) = 2\zeta$. For most soft modes which are quasiharmonic, Eqs. (4.14) give rise to

$$\eta_{\rm max}^{(e)}(\varepsilon_d^{(0)}; \zeta) \simeq \eta_{\rm eff}^{(e)}(\varepsilon_d^{(0)}; \zeta)$$

$$= (Q_d^{(e)})^2/A(E_g + U_d^{(e)}), \quad (5.26)$$

for the mentioned characteristic values of $\varepsilon_d^{(0)}$ and $\zeta$, which, from the calculations (see below), are $\varepsilon_d^{(0)} \simeq E_c$ and $\zeta \simeq \bar{E} = E_g/2$. The related estimates of $c_{\rm ST(e)}^{(2)}$ and $c_{2e}$ are

$$c_{2e} \approx g_0^{(e)}(E_c)F(\eta_{\rm eff}^{(e)}, 0)\phi_{2e}(\eta_{\rm eff}^{(e)}, 0; E_c)\frac{\Delta E_{\rm eff}}{E_g}$$

$$\approx 0.1 g_{2e}(E_{\rm eff}) \leq 10^{-4} \leq c_{\rm ST(e)}^{(2)} \leq g_{2e}(E_{\rm eff}) \quad (5.27)$$

with $\Delta E_{\rm eff} \leq \delta E$, $\phi_{2e}(\eta_{\rm eff}^{(e)}, 0; E_c)\Delta E_{\rm eff}/E_g \approx 0.1$, and $g_{2e}(E_{\rm eff}) \approx g_L \approx 10^{-3}$ at $E_{\rm eff} = E_2(E_c; \eta_{\rm eff}^{(e)}, \bar{\xi}) \approx \bar{E}$. In fact, the integrand $g_{2e}(E)\bar{\phi}_{2e}(E)$ in Eq. (5.16) exhibits a pronounced maximum at $E_{\rm max} \approx E_{\rm eff}$, since $dg_{2e}(E)/dE > 0$ while $d\bar{\phi}_{2e}(E)/dE < 0$, with $\bar{\phi}_{2e}(E_{\rm eff}) \leq 0.5$ and $\Delta E_{\rm eff}/E_g \leq 0.5$.

The substrate anharmonicity and hybridization lead to relatively small deviation of $\eta_{\rm max}(\varepsilon_d^{(0)}, \zeta)$ from $\eta_{\rm eff}(\varepsilon_d^{(0)}, \zeta)$ at $\varepsilon_d^{(0)} = E_c$ and $\zeta = \bar{E}$.

As follows from the above, the main contributions to $c_2^{(e)}$ come from a small spot in the sector $A$ of $(\eta, \xi)$, which corresponds to soft-mode equilibrium displacements $x_2^{(e)}(\eta_{\rm max}^{(e)}, \xi_{\rm eff} = 0) \approx 1$ and is marked in Fig. 11. The situation for hole states is similar. Thus negative-$U$ centers are largely formed due to two-band self-trapping at large soft-mode displacements $x_2 \approx 1$ and strong hybridization of the defect states with the nonparent band states.

Solving Eq. (5.10) numerically gives rise to

$$\zeta = \bar{E} + \Delta\zeta \simeq \bar{E} = E_g/2 \quad (5.28)$$

with $\Delta\zeta/E_g \approx 0.1 \ll \bar{E}$ (Fig. 13), so that

$$\eta_{\rm eff} = \eta_{\rm eff}(\varepsilon_d^{(0)} = E_c, \zeta = \bar{E}) \simeq Q_d^2/AE_g, \quad (5.29)$$

with accuracy to corrections $\sim \Delta/E_g \ll 1$, $w_t/E_g \ll 1$, and $U_d/E_g \ll 1$, just as assumed in Eq. (5.11). The above calculations are self-consistent, if the most important $\varepsilon_d^{(0)}$ are close to the parent band edge. Indeed, the integrand $g_0^{(e)}(\varepsilon_d^{(0)})\psi_e(\varepsilon_d^{(0)})$ in Eq. (5.16) exhibits a rather sharp maximum at $\varepsilon_d^{(0)} \simeq E_c$, since, e.g., $dg_0^{(e)}(\varepsilon_d^{(0)})/d\varepsilon_d^{(0)} > 0$ while $d\psi_e(\varepsilon_d^{(0)})/d\varepsilon_d^{(0)} < 0$ in the gap. The resulting pair correlation energy

$$U_{\rm eff}^{(e,h)} \simeq U^{(e,h)}(\varepsilon_d^{(0)} = E_{c,v}; \eta = \eta_{\rm eff}^{(e,h)}; \xi = 0)$$

$$\simeq U_m^{(e,h)} \simeq -E_g/2 \quad (5.30)$$

is characteristic of most negative-$U$ centers, as long as $E_g/2 \gg U_d^{(e,h)}$. It is worth adding that $|U_{\text{eff}}|$ varies with increasing band-tail width and the width of $F(\eta, \xi)$, but the variations are relatively small as the width remain of the same scale.

With Eqs. (5.28)–(5.30), the relations (4.19) and (4.20) still hold so the discrete levels

$$E_\nu = E_c - \nu|W_1| \quad \text{or} \quad E_\nu = E_v + \nu|W_1| \qquad (5.31)$$

with $\nu = 1, 2, 3$ and $E_g/4 \leq |W_1| < E_g/3$, $|W_1| - E_g/4 \ll E_g$, are characteristic of the gap spectrum and coexist with the continuum spectrum DOS $g(E) \simeq g_2(E)$ around $E = \bar{E}$. In other words, coexistence of continuum features and discrete levels, which is found in experiments to characterize most negative-$U$ centers in the mobility gap of glassy semiconductors (see, e.g., Refs. 9 and 20) can also be established in the theory under discussion, in a rather natural way.

## VI. CONCLUSIONS

A consistent theory of two-band self-trapping of electrons (holes) in semiconductors is presented in detail, in which negative-$U$ centers in the interband (mobility) gap are formed as singlet electron (hole) pairs self-trapped in substrate atomic soft configurations. The latter appear to be characteristic of glasses, and possibly of some types of defects in crystalline lattices, and exhibit anharmonicity, each in a single soft motion mode. Both the softness of the configuration (motion mode) and the hybridization of the bare electron (hole) state with extended states of the nonparent band are essential for formation of the self-trapped states and negative-$U$ centers. The hybridization significantly changes the soft substrate configurations, introducing extra anharmonic features in the related atomic dynamics, i.e., giving rise to an additional softness and adding or subtracting one minimum in their adiabatic potentials. The resulting electron (hole) pair correlation energy $U$ is basically negative and for most negative-$U$ centers comparable in magnitude to the gap width, $|U| \approx E_g/2$. The dependence of $U(\eta)$ on the

configuration softness ($\eta$) is nonmonotonic and exhibits a deep minimum with large magnitude $|U_m| \simeq E_g/2$ characteristic of the negative-$U$ centers. For the latter, the DOS is rather high, $g_2(E) \leq 10^{-3}$, and determines the position of the low-temperature Fermi level $\zeta$ near the midgap $\bar{E} = E_g/2$. The related low-temperature concentration of negative-$U$ centers is relatively high, $c_2 \leq 10^{-4}$, corresponding to a low electron spin resonance (ESR) signal and to the Fermi level pinning observed in glassy semiconductors. The high susceptibility of soft configurations and related negative-$U$ centers to external fields like hydrostatic pressure in the semiconductors in question gives rise to significant effects, which are predicted to be considerable even at not very high pressures $p \approx 10^4$–$10^5$ bar and still finite gap width, and will be discussed elsewhere (see Refs. 9 and 28).

The earlier models of negative-$U$ centers in glassy semiconductors are characterized either by a continuum gap spectrum and high DOS $g_2(\bar{E}) \sim 10^{-2}$ and $c_2 \sim 10^{-3}$ (see Ref. 11) or by quasidiscrete levels $\approx E_c - \nu E_g/4$ at $\nu = 1, 2, 3$ in the gap with a much lower $c_2 \leq 10^{-5}$.[14,15] The theory under consideration, as well as the earlier theory of negative-$U$ centers in soft configurations,[9] establishes the coexistence of both continuum features of the gap and discrete levels $E_\nu \approx E_c - \nu\varepsilon_0$ at $E_g/4 \leq \varepsilon_0 < E_g/3$ in the gap, as observed in thermal equilibrium and nonequilibrium phenomena in glassy semiconductors. In this connection, the earlier models of negative-$U$ centers in glassy semiconductors[11,14,15] may be considered as limiting cases of the theory in question with $g_2(\bar{E}) \leq 10^{-3}$ and $c_2 \leq 10^{-4}$.

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