Self-localization of electron pairs in disordered systems[1)]

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It is shown that in disordered atomic structures (glasses) self-localization of pairs of like carriers (electrons or holes) should be possible, with a negative effective correlation energy that can be appreciable ($\lesssim 1$ eV). The effective attraction between the carriers in the pairs is due to the anomalously high local susceptibility of the disordered atomic system, i.e., to the existence of a *sui-generis* critical potential with anomalously small quasielastic constants for the atoms of the substance. Besides the usual one-well potentials, there are also two-well atomic potentials in the disordered system. The interrelation and microscopic nature of two important features of glasses, previously postulated on an empirical basis, are thus explained, namely the existence in them of two-well atomic potentials and the presence of localized carrier pairs with negative effective energy. Some novel effects are predicted on the basis of the proposed theory.

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1. INTRODUCTION

We demonstrate here the possibility of realizing a new phenomenon—self-localization of electrons and hole pairs (SLEP) in amorphous nonmetallic matter. The self-localization of the electron and hole pairs corresponds to strong local effective attraction between carriers of like sign.

The presence of electron pairs in the mobility gap (MG) of nonmetallic glasses was postulated in Ref. 5 on the basis of empirical data. The main focus was on the observed coexistence of diamagnetism and pinning of the chemical potential ζ by the electron subsystem, i.e., the fact that ζ is practically insensitive to a change in the impurity density (see, e.g., Ref. 6). In the traditional models of single-electron state density $g^{(1)}(E)$ in the MG, the presence of diamagnetism is incompatible with the pinning of ζ. Thus, in the model of Mott and of Cohen-Fritzsche-Ovshinsky,[7] in which $g^{(1)}(E)$ is appreciable near the center of the MG [e.g., $g^{(1)}(E_0) \sim 10^{19}$ cm^{-3} eV^{-1}], one should expect a noticeable paramagnetism. In the Mott-Davis model,[6] however, in which there is a true gap, i.e., $g^{(1)}(E_0) = 0$, there is no paramagnetism, but the pinning of ζ cannot be explained. It was in this connection that Anderson[5] postulated the possibility of formation, on any normal interatomic bond in glass, of electron pairs with an effective correlation energy $U < 0$ and with a zero total spin; the energy spectrum of the pairs is in fact identified with the observed spectrum in the MG. The density of these pair states is assumed to be high enough for pinning of ζ to be realized (see also Refs. 8 and 9). It was implied in Ref. 5 that the effective correlation energy could be negative because of the reaction of the atomic subsystem to the population of any normal valence bond of the glass by the electron pair of the term, and it was necessary to assume that $|U|$ is large, $|U| \lesssim 1$ eV. At the same time, certain models of quantum-chemical character were proposed, in which it was assumed that an electron pair with $U < 0$ and with large $|U| \lesssim 1$ eV can be produced as a localized charge carrier only on a specific defect (broken valence bond etc.) when the short-range order in the glass is disturbed (see, e.g., Ref. 6). Further investigations have revealed, however, a number of problems raised by such models (see, e.g., Ref. 10 and 11).

We note that in the case of carriers in a solid, the usual polaron effect, which corresponds to relatively small harmonic displacements of the atoms, is insufficient for the production of electron (hole) pairs with large binding energy $|U|$. Indeed, as a rule the characteristic polaron binding energy, with a largest scale of the order of 0.1 eV, cannot compete with the energy of the Coulomb repulsion of the like carriers on a valence bond, $U_c \sim 0.3$–0.5 eV (see, e.g., Ref. 6), and at any rate cannot ensure large $|U| = -U \lesssim 1$ eV. Thus, the problem of verifying the very existence of local pairing of carriers of like sign with large $|U| = -U \lesssim 1$ eV in ideal glass (far from defects) remained open.

We shall deal below precisely with a new approach to the solution of this problem and with the onset of a similar phenomenon, namely SLEP. The model described below and the SLEP theory connect the electron (hole) pairs in the MG with the specific structure of the glass itself, which constitutes a continuous random network (CRN) of atoms with a definite short-range order (see Refs. 6 and 12). This theory, consequently, differs radically from the aforementioned "defect" models of electron pairs.

2. QUALITATIVE CONSIDERATIONS AND FORMULATION OF THE PROBLEM

The main idea concerning the nature of the SLEP is the following. A finite density (< 1) of atoms (and/or groups of large numbers of atoms) can exist in the system under consideration, and an appreciable displacement of these atoms ($x_0 \to x = x_0 + \delta x$ at $|\delta x| \lesssim a$) is connected with an anomalously small change $\delta V(x)$ of the CRN potential energy

$$\delta V(x) = V(x) - V(x_0) \ll k^{(0)} a^2, \quad k^{(0)} \approx M\omega_D{}^2 \sim 10\text{–}30 \text{ eV/Å}^2 .$$

These atomic potentials are called critical for reasons that will be made clear subsequently. At the same time,

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in its own characteristic scale (~1 eV), the corresponding change $\delta E(x) \equiv E(x) - E(x_0)$ of the energy of the single-electron term of the localized "extra" electron or hole (relative to the assembled aggregate of valence bonds) is generally speaking not small. In the upshot there can be realized self-localization of the carrier, i.e., population of a term with simultaneous appreciable shift of the atom in the critical potential, with a large energy gain $\Delta E^{(1)}$. The population of the term by a second carrier of the same sign can be accompanied by an appreciable increase in the displacement of the atom and by a corresponding energy gain at a total energy change $\Delta E^{(2)}$. Self-localization of electron and hole pairs is realized if the effective correlation energy of the localized pair in the region of a structure with a given single-electron term is

$$U \equiv \Delta E^{(2)} - 2\Delta E^{(1)} < 0, \tag{2.1}$$

where $2\Delta E^{(1)}$ describes the energy gained by self-localization of each of the carriers in the spatially separated regions with the same single-electron terms.

The change of the total energy of the system $E_t(j, x)$ upon localization of one ($j = 1$) or two ($j = 2$) carriers of like sign and following a displacement δx of the atom in the localization region can be written in the form

$$\begin{aligned} \Delta E^{(1)}(x) &= E_t(j=1, x) - E_t(j=1, x_0) = \delta E(x) + \delta V(x), \\ \Delta E^{(2)}(x) &= E_t(j=2, x) - E_t(j=2, x_0) = \delta E(x) + \delta E'(x) + \delta V(x). \end{aligned} \tag{2.2}$$

Here

$$V(x) = E_t(j=0, x), \quad E(x) = E_t(j=1, x) - E_t(j=0, x),$$
$$E'(x) = E_t(j=2, x) - E_t(j=1, x), \quad \delta E'(x) = E'(x) - E'(x_0),$$

where $\delta E'(x) = \delta E(x) + U_c(X)$, where $U_c(x)$ is defined as the energy of the effective repulsion between the carriers. The energy gained upon self-localization of one carrier or a pair of carriers is described now by the relations

$$\begin{aligned} \Delta E^{(1)} &\equiv \Delta E^{(1)}(x_1) = \delta V(x_1) + \delta E(x_1), \\ \Delta E^{(2)} &\equiv \Delta E^{(2)}(x_2) = \delta V(x_2) + 2\delta E(x_2) + U_c(x_2). \end{aligned} \tag{2.3}$$

Here x_j are the equilibrium values of x, which minimize $\Delta E^{(j)}(x)$; $\Delta E^{(j)}(x_j) \equiv \min\{\Delta E^{(j)}(x_j)\}$, $j = 1, 2$. It will be shown that SLEP criterion (2.1) can be realized at sufficiently large values of $x_2 - x_1 = \delta x_2 - \delta x_1$, when $V(x)$ corresponds to the critical potential.

The rest of the problem consists of determining the forms of $\delta V(x)$ and $\delta E(x)$, and finding subsequently the conditions for the realization of the criterion (2.1). To this end we consider in greater detail the situation for covalent glass, in which an appreciable fraction of all the CRN atoms have the lowest coordination number $z = 2$. The model of such a glass is as system of atoms coupled by covalent bonds in disordered chains (rings) and with weak van der Waals bonds between the chains and the rings.

3. CRITICAL ATOMIC POTENTIALS

The simplest model for $\delta V(x)$ can be obtained by separating in a chain (ring) an atom whose neighbors in the considered structure can actually be regarded as having physical positions that are fixed [see (3.11) below]. What is kept in mind in this connection is that in amorphous semiconductors a considerable majority of the atoms, as usual, oscillate harmonically in single-well potentials.[6] Actually, the atom and its two neighbors can form either a linear fragment or a non-one-dimensional fragment with a finite angle between the bonds at the "site" of the considered atom. The qualitative character of $\delta V(x)$ is the same in both cases, and for simplicity we shall refer hereafter to the linear fragment (−1, 0, 1) of Fig. 1.

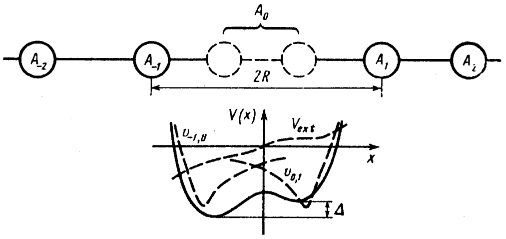

FIG. 1. Fragment of atomic chain and two-well potential.

We take $V(x)$ to be the effective potential of the inner atom 0, i.e., the change of the potential energy of the system caused by its linear displacements x. It turns out that this potential has the following distinguishing features. First, there exists a critical length $2R = 2R_c$ of the fragment such that at $R < R_c$ the potential $V(x)$ is mainly single-well, and is two-well at $R > R_c$. Second, in a certain range of the parameters that determine the form of $V(x)$, the quasi-elastic constants $k_i \equiv d^2V/dx^2|_{x_i}$ at the minimum points x_i of the potential are anomalously small, $k_i \ll k^{(0)}$; in this sense, such a potential is critical.

To verify the foregoing, we represent $V(x)$ in the form

$$V(r_0) = v_{-1,0}(r_{-1,0}) + v_{0,1}(r_{0,1}) + V_{ext}(r_0) \equiv V_0(x) + V_{ext}(x), \quad r_{ij} \equiv r_i - r_j, \tag{3.1}$$

where $v_{-1,0}$, $v_{0,1}$, and v_{ext} are respectively the potential energies of the atom 0 in the field of the two nearest atoms −1 and 1 and in the random field of the remaining atoms; r_i are the independent linear coordinates of the atoms ($i = -1, 0, 1$; $r_0 = x$). The energy $V_{ext}(x)$ is determined by the relatively weaker bonds (van der Waals, etc.) so that $|V_{ext}| \ll |V_0|$ in the considered region of lengths r_{ij}. We choose the origin of x at the minimum of the single-well potential $dV/dx = 0$ at $x = x_0 \equiv 0$. Then, at a given fragment length $2R = r_{-1,1}$ it is convenient to introduce the parameters

$$\tau = -\frac{r_{-1}+r_1}{2}, \quad \eta = \frac{r_{-1}-r_1}{2} + R_c \equiv R_c - R. \tag{3.2}$$

The first of them characterizes the asymmetry of the "arms" $r_{-1,0} = r_{-1}$ and $r_{0,1} = r_1$ of the fragment (at $x = 0$), and the second the difference of its length from critical. The critical length is determined from the condition $d^2V/dx^2 = 0$ at $x = 0, \eta = 0$. Taking this definition into account, the potential

$$V(x) = v_{-1,0}(R_c - \eta + \tau + x) + v_{0,1}(R_c - \eta - \tau - x) + V_{ext}(x) \tag{3.3}$$

can be represented at small $|x|$ and $|\eta|$ by the expansion

$$V(x)-V(0)\equiv\delta V(x)\cong A_2x^2+A_3x^3+A_4x^4,$$
$$A_2=A\eta,\quad A=\frac{1}{2!}[v_{-1,0}^{(3)}(R_c+\tau)+v_{0,1}^{(3)}\ (R_c-\tau)],\tag{3.4}$$
$$A_3=\frac{1}{3!}V^{(3)}(0),\quad A_4=\frac{1}{4!}V^{(4)}(0),\quad V^{(n)}(0)\equiv\frac{d^n}{dx^n}V(x)|_{x=0}$$

at

$$v_{-1,0}^{(2)}(R_c+\tau)+v_{0,1}^{(2)}\ (R_c-\tau)+V_{ext}^{(2)}=0,$$
$$v_{i,j}^{(n)}(R)\equiv\frac{d^n}{dR^n}v_{i,j}(R),\quad V_{ext}^{(n)}\equiv\frac{d^n}{dx^n}V_{ext}(x)|_{x=0}.\tag{3.5}$$

We assume further that $A_4>0$ in accordance with the limited character of the displacements of the atom 0, and assume for the sake of argument $A_3>0$. Then the extrema

$$x_0=0,\quad x_{1,2}=\frac{3A_3}{8A_4}\left[-1\pm\left(1-\frac{\eta}{\eta_0}\right)^{1/2}\right],\quad \eta_0\equiv\frac{9}{32}\frac{A_3^2}{AA_4},\tag{3.6}$$

correspond either to a single minimum of the potential (3.4) at $\eta>\eta_0$, or to two minima separated by a barrier at $\eta<\eta_0$, i.e., the potential $V(x)$ can be either single-well or two-well.

As follows from general considerations and is seen directly from Fig. 1, at sufficiently large $\eta=R_c-R>\eta_0$ the potential $V(x)$ has a single minimum at the point $x_0\equiv0$ (this allows us to conclude that $A>0$). With increasing R, a second well is produced at $0<\eta<\eta_0$, with a minimum at the point x_2 (to the left of x_0), and a barrier with a vertex is produced at the point x_1. The depth of the new well increases with increasing η and exceeds the depth of the previous well at a certain $\eta(>0)$; at the same time, the barrier shifts to the right. At $\eta<0$ the point x_0 represents the vertex of the barrier, and the point $x_1(>x_0)$ is the bottom of the shallower right-hand well. With further decrease of $\eta<0$ the arrangement of the extrema remains unchanged. The foregoing critical properties of $V(x)$ are determined by the following relations:

$$k_0=2A\eta\quad\text{at}\quad\eta>\eta_0,$$
$$k_0=2A\eta,\quad k_2=4A\eta_0\left[1-\frac{\eta}{\eta_0}+\left(1-\frac{\eta}{\eta_0}\right)^{1/2}\right]\quad\text{at}\quad0<\eta<\eta_0,\tag{3.7}$$
$$k_{1,2}=4A\eta_0\left[1-\frac{\eta}{\eta_0}\mp\left(1-\frac{\eta}{\eta_0}\right)^{1/2}\right]\quad\text{at}\quad\eta<0.$$

It is seen from (3.7) that, generally speaking, the critical properties are possessed by the shallower well of the two-well potential at the instant of the well appearance, or by the well of the single-well potential as $\eta\to0$. However, if η_0 is small enough, the critical properties are possessed by both wells of the two-well potential.

It is convenient next to use the characteristic atomic radius γ^{-1} ($\lesssim$ 1 Å) to make all the lengths dimensionless, so that A, A_3, and A_4 are energy parameters, and replace the k_i in (3.7) by $k_i\gamma^{-2}$.

We turn now to the important case of small $\eta_0\ll1$. The smallness of $\eta_0\ll1$ is due to the smallness of $|\tau|\ll1$ and of $|V_{ext}/V_0|\ll1$. Indeed, the equilibrium value $\tau_0=\tau_0(R,V_{ext})$ of the parameter τ is determined by the equation

$$^1/_6A_+^{(4)}(R)\tau_0^3+{}^1/_2A_-^{(3)}(R)\tau_0^2+A_+^{(2)}(R)\tau_0+A_-^{(1)}(R)+V_{ext}^{(1)}=0,\quad|\eta|\ll1,\tag{3.8}$$
$$A_\pm^{(n)}(R)\equiv\frac{d^n}{dR^n}[v_{-1,0}(R)\pm v_{0,1}(R)],$$

which follows from the relation that determines the origin of x ($V^{(1)}(x)|_{x=0}=0$) when expanded in terms of τ. It is seen from (3.8) that $|\tau_0|\ll1$ when $|V_{ext}/V_0|\ll1$ and when $v_{-1,0}$ and $v_{0,1}$ (i.e., the atoms −1 and 1) are equal or differ little. At $|\tau_0|\ll1$ we have

$$A_3=Bt,\quad A_4=\frac{1}{4!}[A_+^{(4)}(R)+A_-^{(5)}(R)\tau_0]\approx\frac{1}{2}B,\quad B\equiv\frac{1}{12}A_+^{(4)}(R),$$
$$t\equiv2(\tau_0+t'),\quad t'\equiv[A_-^{(3)}(R)+V_{ext}^{(3)}]/A_+^{(4)}(R),\tag{3.9}$$

so that A_3 and η_0 are small at small $|\tau_0|$, whereas B and A_4 do not contain such a small quantity. The functions $R_c=R_c(V_{ext})$ and $\tau_0(R,V_{ext})$ are then defined by the relations $R_c=R_c^{(0)}+\delta R_c$, $R_c^{(0)}\equiv R_c(V_{ext}=0)$ as well as by the equations that follow for $R_c^{(0)}$ and δR_c from the conditions

$$V^{(1)}(x=0,R,V_{ext})=0\quad\text{и}\quad V^2(x=0,R=R_c,V_{ext})=0.$$

As a result we have

$$\left|\frac{\delta R_c}{R_c^{(0)}}\right|\leqslant0\left(\left|\frac{V_{ext}}{V_0}\right|\right)\ll1,\tag{3.10}$$

so that $R_c\approx R_c^{(0)}$. The critical length of an isolated diatomic molecule is $R_c^{(0)}=r_0+p_0\gamma^{-1}$, $p_0\lesssim1$, where the equilibrium length of such a molecule is $r_0\approx a$ with $|r_0-a|\ll a$ (e.g., in the case of paired Morse potentials $p_0=\ln2$).

In accord with the foregoing, expression (3.4) takes at $|\eta|\ll1$ and $|\tau_0|\ll1$ the form

$$\delta V(x)\approx A\eta x^2+Btx^3+Cx^4,\quad C={}^1/_2B,\tag{3.11}$$

where the quantities $A(>0)$ and $C(>0)$ fluctuate relatively little and can be regarded as constants of the material. As is easily seen, $A\sim M\omega_D^2\gamma^{-2}\sim$ 10–30 eV and $C\lesssim A$.

Within the framework of the described model, the existence of two-well and critical atomic potentials and of characteristic parameters R_c and η in glass is due to the fluctuations of the lengths R and of the fields $V_{ext}(x)$. [The contribution of the polaron-like local relaxation of the configuration near the atom in a critical potential well to the parameters η, R_c, $V_0(x)$ etc.,[6,12], determined by the shift δ of the potential well, is small at the usually small $|\delta/A|\ll10^{-2}$ and at the actual η, $1\gg|\eta|\gg|\delta/A|$.] Actually, in an equilibrium isolated triatomic molecule of the type considered, the central atom would be characterized usually by an effective single-well potential $V_0(x)$. In a nonequilibrium (metastable) system, however, such as an amorphous structure, a qualitatively different situation arises, inasmuch as R and $V_{ext}(x)$ are random quantities. The probability distribution of R for individual atoms (with $z=2$) can apparently be characterized, on an empirical basis (see, e.g., Ref. 6), by a noticeable albeit relatively small width

$$\Delta R\equiv R_{max}-R_{min}\sim0{,}1\overline{R},\quad 1\gg\Delta R/\overline{R}\gg|V_{ext}/V_0|,$$

the mean value being $\overline{R}\approx a$ with $|\overline{R}-a|\ll\Delta R$. Here R_c is close to $R_c^{(0)}$ with $|\delta R_c|\ll\Delta R$. From the foregoing relations between R_c, $\bar{R}$, and ΔR we can conclude that it is possible to have both $R_c - \bar{R} < (1/2)\Delta R$ and $(1/2)\Delta R < R_c - \bar{R} (< \bar{R})$. Two-well and critical potentials correspond to a noticeable fraction (< 1) of all the R (i.e., η and t) for the considered atoms precisely in the case when R_c lies within the width ΔR of the distribution density for R, i.e., $R_c - \bar{R} \lesssim \Delta R/2$. The same can take place for atomic groups of a definite type both in the cases noted above and in the alternate cases.

We shall need later [see (4.13)] the density $c_a(\tilde{\eta})$ of the regions of the critical potentials at $|\eta| \leqslant \tilde{\eta} = \text{const} \ll 1$, which is determined by the probability distributions for the random quantity η. The distribution for η is determined directly by the distribution for R, and, as can be seen, the mean value $\bar{\eta}$ of η can be small ($|\bar{\eta}| < \Delta\eta$) while the width $\Delta\eta \equiv \eta_{\max} - \eta_{\min}$ can be comparable with unity, $|\eta_{\min}| < 1$ and $\Delta\eta \lesssim 1$. The distribution density $N(\eta)$ for η in the region of its width, $|\eta - \bar{\eta}| \lesssim (1/2)\Delta\eta$, can be approximated in the usual manner by the practically uniform $N^{(0)}(\eta)$,

$$N(\eta) \approx N^{(0)}(\eta) = (\Delta\eta)^{-1}\theta(R_c - R_{min} - \eta\gamma^{-1})\,\theta(\eta\gamma^{-1} + R_{max} - R_c)$$

[$\theta(x)$ is the step function]. In the region of importance to us subsequently, $\tilde{\eta} \gg \eta_0(t) = (9/16)Bt^2/A$, we can estimate $c_a(\tilde{\eta})$ in the form

$$c_a(\tilde{\eta}) = \int_{-\tilde{\eta}}^{\tilde{\eta}} N(\eta)\,d\eta \approx \int_{-\tilde{\eta}}^{\tilde{\eta}} N^{(0)}(\eta)\,d\eta \lessapprox \tilde{\eta}/\Delta\eta. \tag{3.12}$$

Generaly speaking, the distribution density for t can also be estimated by recognizing that the energy difference Δ between the minima of the two-well potential are described at $|\eta| > \eta_0$ within the framework of Eqs. (3.4)–(3.7) by the expression ($|\eta| \ll 1$, $|t| \ll 1$)

$$\Delta \approx \Delta_0 |t|\,|\eta|^{3/2}, \quad \Delta_0 = A(A/B)^{1/2} \gg A. \tag{3.13}$$

The possibility of estimating the distribution of Δ from the empirical data is established in this case by the following considerations. It is known, (see, e.g., Refs. 13 and 6) that an experimental investigation of the low-temperature anomalies of the thermal and ultrasonic properties of glasses has led to the hypothesis that of two-well potentials exist for an appreciable fraction of the atoms of a medium with almost uniform distribution for Δ in a certain interval $0 \lesssim \Delta \lesssim \Delta_c$, $\Delta_c \lesssim 0.1$ eV. We assume that the model developed above reveals the essential factor of the nature of the two-well potentials postulated in Ref. 13, and establishes the presence of critical potentials in glasses. Expressions (3.4) and (3.11) for $V(x)$ and the characteristic parameters such as R, R_c, and η, as well as relations of the type (3.6) and (3.7), can have a more general character than the concrete model considered above. When so generalized, the meaning and the dimensionality of the variable x and of the parameters R, R_c, η, and t are determined by the concrete form of the system and by the type of its motion (both translations and rotations); the role of the atom can be played by an individual atom or by a non-macroscopic atomic group. At the same time, the concrete model of $V(x)$ in linear or nonlinear quasimolecules can be adequate for a large class of glasses of the type α-Se, α-As_2Se_3, α-SiO_2, etc. (These questions will be discussed elsewhere.) We note also that since $\Delta \lesssim \Delta_c \ll C$ for phenomenological two-well potentials[13] it follows that an important role in (3.4) is played by small $|\tau_0| \ll 1$ and $|t| \ll 1$, so that we can use expression (3.13) hereafter for $\delta V(x)$ at $|\eta| \ll 1$.

4. SELF-LOCALIZATION OF ELECTRON AND HOLE PAIRS

The assembly of the bonds in an ideal covalent glass constitutes a statistical distribution (over the energies, lengths, angles, etc.) of ordinary two-electron valence bonds between the CRN atoms (these bonds can have a certain asymmetry). The electron (or hole) that is "external" with respect to this assembly of bonds can be set in correspondence in the MG with the term E in the tail of the conduction or valence band. These terms correspond to states that are localized on ν-atomic regions (ν-center bonds, quasimolecules) at a suitable $\nu \geqslant \nu_{\min} \geqslant 2$. In the simplest considered CRN model these states are localized mainly on ν-atom quasimolecules in individual chains, and the value of $\nu_{\min}$ is determined by the type of the quasimolecular state. Thus, $\nu_{\min} = 2$ for the states of the binding (B) or antibinding (AB) types, but $\nu_{\min} = 3$ for states of the nonbinding type, etc. The dependence of the term $E(x)$ on the position x of one of the boundary atoms of the quasimolecule (the atom 0 in Fig. 1) can be described by a relation of the form

$$E(x) = E_{\nu\alpha}(x) = Q_{\nu\alpha} f_{\nu\alpha}(x, \Lambda). \tag{4.1}$$

Here $Q_{\nu\alpha}(>0)$ is the energy parameter of the bond between the indicated atom of the ν-atom quasimolecule and the carrier with the term $E = E(0)$, so that $f_{\nu\alpha}(x, \Lambda) \gtrless 0$ at $|f_{\nu\alpha}(x, \Lambda)| \lesssim 1$ for the essential values $|x| \lesssim 1$; the index α corresponds to the type of the quasimolecular state. The parameter $\Lambda (\neq 0)$ in a disordered system describes the fluctuations of the term energies at different quasimolecules for given ν and α. The expected scale of these fluctuations is of the order of the scale w_α of the fall-off of the state density in the tail of the corresponding α-th band (for example, $w_\alpha \sim 0.1$ eV in covalent glasses). The energy $E(x)$ increases or decreases, depending on the type (α) of the state and on the sign of $x (\gtrless 0)$. Thus, for AB or B states we can write approximately at $\nu = 2$ (Ref. 14)

$$f_{\nu\alpha}(x) = f_{2(AB,\,B)}(x) \approx \pm[\Lambda + e^{-2x}]^{1/2},$$

$$Q_{\nu\alpha} = Q_{2(AB,B)} \approx \beta \exp(-r_{-1,0}^{(0)}), \quad r_{-1,0}^{(0)} \equiv r_{-1,0}(x=0).$$

Here β is of the order of the atomic energy, $\beta \gtrsim 10$ eV, and usually $Q_2 \equiv Q(a) \gtrsim 1$ eV at $r_{-1,0}^{(0)} \approx a\gamma$. In this case the term $E_{AB}(x)$ increases and $E_B(x)$ decreases with increasing $x > 0$. The parameter Λ may be determined, in particular, by the influence of the neighboring atoms of the chain and by the corresponding fluctuations of parameters of the type $\exp(-r_{-2,-1})$ (see Fig. 1).

The value of ν determines the characteristic radius r_ν of the electronic states, i.e., $Q_{\nu\alpha} = Q_{\nu\alpha}(r_\nu)$. It is natural to assume that

$$Q \equiv Q_{\nu\alpha}(r_\nu) \ll Q_\alpha(a), \quad r_\nu \gg a,$$

and therefore one can expect appreciable values of $|\delta E(x)|$ for localized states with $r_\nu \approx a$ at large $|x| \lesssim 1$.

When one ($j=1$) or two ($j=2$) carriers ("extra" electrons or holes) become localized on a definite quasimolecule, the energy of the system, depending on the configuration variable x, can be written, just as in the absence of carriers ($j=0$), in the form [see (2.3)]

$$\begin{aligned}\Phi_j(x)&=\delta V(x+s_j)+j\delta E(x+s_j)+U_c(x+s_j)\delta_{j,2}\\&\approx a_jx^4+b_jx^2+h_jx+U_c(x)\delta_{j,2}+\text{const};\end{aligned}\tag{4.2}$$

here and elsewhere, unless otherwise stipulated, the indices ν and α of the parameters are left out for brevity. The coefficients a_j, b_j, and h_j are obtained by expanding the total energy $j\delta E(x)+\delta V(x)$ in powers of x, including terms proportional to x^4, as well as by changing the origin $x\to x+s_j$, so as to exclude the cubic terms

$$\begin{gathered}s_j=\tilde{B}_j/4\tilde{C}_j,\quad a_j=\tilde{C}_j,\quad b_j=\tilde{A}_j-3\tilde{B}_j^2/8\tilde{C}_j,\\h_j=jQ^{(1)}-2b_js_j-4a_js_j^3,\\\tilde{A}_j=A\eta+jQ^{(2)},\quad \tilde{B}_j=Bt+jQ^{(3)},\quad \tilde{C}_j=C+jQ^{(4)},\\Q^{(n)}=\frac{Q}{n!}\frac{d^n}{dx^n}f(x,\Lambda)|_{x=0},\quad n=1,2,3,4;\quad |\eta|\ll 1,\quad |t|\ll 1,\end{gathered}\tag{4.3}$$

and usually $|Q^{(n)}|\lesssim Q$ and $|s_j|<1$. Indeed, the following inequalities hold

$$Q=Q(r_\nu)\leqslant Q(a)\ll A\tag{4.4}$$

and it is really possible to have $Q(a)<C$, since $C\lesssim A$ and the usual scales are $Q(a)\gtrsim 1$ eV and $A\gtrsim 10$ eV. At $|\eta|\ll 1$ and at (4.4) the atomic potential remains critical also if one or two carriers are trapped in a given region of the system, since b_j, a_j, and h_j ($j=1,2$) differ from b_0, a_0, and h_0 by values of the order of $Q\ll A$, and consequently $|b_j|\ll A$. Next, we approximate $U_c(x)$ for simplicity by the x-independent characteristic quantity $U_c\equiv U_c(r_\nu)$, which decreases with increasing r_ν, $U_c(r_\nu)\ll U_c(a)$ at $r_\nu\gg a$, inasmuch as in the SLEP region (4.9) (see below) the influence of the $U_c(x)$ dependence on the results of minimization of the functional $\Delta E^{(2)}(x)$ is small to the extent that $U_c(x_2)/2Q\ll 1$ is small, where x_2 is determined at $U_c(x)\approx U_c$.

Taking (4.2) and the foregoing into account, the SLEP criterion (2.1) becomes

$$U=\Phi_2(x_2)+\Phi_0(x_0)-2\Phi_1(x_1)<0,\tag{4.5}$$

where x_j is that value of x which minimizes $\Phi_j(x)$. The expression for $\Phi_j(x)$ is transformed into

$$\begin{gathered}\Phi_j(y)=\frac{b_j^2}{4a_j}\varphi_j^{(\pm)}(y),\quad \varphi_j^{(\pm)}(x)\equiv x^4\pm 2x^2-\chi_jx,\\\chi_j=-\frac{h_j}{a_j}\left(\frac{2a_j}{|b_j|}\right)^{3/2},\quad y=x\left(\frac{2a_j}{|b_j|}\right)^{1/2},\end{gathered}\tag{4.6}$$

where the sign in front of the term $2x^2$ coincides with the sign of b_j. In the upshot it turns out to be sufficient to obtain the general single-parameter function $\varphi_j^{(\pm)}\min\{\varphi_j^{(\pm)}(x,\chi)\}$. The results of its numerical calculation (accurate to ~10%) can be approximated by the relations

$$\varphi_j^{(\pm)}(\chi)=-\frac{\chi^2}{2|\chi|^{2/3}+p_\pm},\quad p_\pm=6\mp 2.\tag{4.6a}$$

A quantitative analysis of the criterion (4.5), based on expressions (4.6), and an estimate of the correlation energy U encounter no difficulties in principle, but are quite cumbersome. The main result, however, can be obtained also on the basis of the qualitative considerations that follow.

We note first that in the considered cases the real asymmetry of the initial potential $\Phi_0(x)$ is small to the extent that $|t|\ll 1$ is small, and is characterized by an energy $\Delta(\geqslant 0)$ that is actually small in the sense of the inequalities

$$\Delta\lesssim\Delta_c\ll Q(a)\ll A,\tag{4.7}$$

since $\Delta_c\lesssim 0.1$ eV ($\Delta_c\lesssim|V_{\text{ext}}|\sim 0.1$ eV; cf. Ref. 13, where $\Delta_c\sim T_g\lesssim 0.1$ eV and T_g is the vitrification temperature).

We consider first the case $\delta h_j=|h_j-h_0|\ll|h_0|$, i.e., $jQ\ll|h_0|$, which corresponds to a considerable asymmetry of the initial potential $\Phi_0(x)$, or to a relatively weak interaction of the carriers with the CRN. Regarding this interaction as a small perturbation, $|\delta h_j|\ll|h_0|$, we obtain

$$|\Phi_2(x_2)+\Phi_0(x_0)-2\Phi_1(x_1)|\sim(Q/h_0)^2|\Phi_0(x_0)|\ll U_c$$

for the usual $|\phi_0(x_0)|\sim\Delta<U_c$. Thus, the SLEP criterion is not satisfied in this case.

In the other limiting case, $Q\gg|h_0|$, corresponding to a real small asymmetry of the initial potential $\Phi_0(x)$, the quantity $\Phi_0(x_0)$ in (4.5) can be neglected. The potential $\Phi_j(x)$ turns out to be biharmonic as $b_0\to 0$ in the essential region of x, and minimization of the expression $\Phi_j(x)\approx a_jx^4-jQx$ ($j=1,2$) at $a_j\approx a_0$ transforms the criterion (4.5) into a relation of the form

$$U=U_c-p_1Q(Q/a_0)^{1/3}\equiv U^-<0,\quad 0<p_1\leqslant 1,\tag{4.8}$$

i.e., into the inequality

$$p_1Q(Q/a_0)^{1/3}>U_c.\tag{4.9}$$

Thus, in the region of a biharmonic potential the energy $U=U^-$, and the equilibrium displacements x_j do not depend on the random quantity $b_0(\eta,t)$ at

$$|b_0|=\pm b_0<b_\pm'\equiv\frac{2}{p_\pm}Q^{2/3}a_0^{1/3}$$

(accurate to a small correction of the order of $|\eta|\ll 1$); the values of $|x_j(b_0\to 0)|\equiv x_j^{(0)}$ and $|U^-|$ are appreciable in the sense that $|U^-|\lesssim Q\lesssim Q(a)$ and $x_2^{(0)}\lesssim 1$, i.e., $|U^-|\lesssim 1$ eV and $x_2^{(0)}\gamma^{-1}\lesssim 1$ Å. However, the condition (4.9) can hold also in the region of large b_0 satisfying the inequalities

$$\frac{4Q^2}{p_\pm U_c}\equiv b_\pm''>|b_0|=\pm b_0>b_\pm'\equiv\frac{2}{p_\pm}Q^{2/3}a_0^{1/3},\tag{4.10}$$

which agree with (4.9). The inequalities (4.10) mean the SLEP can be realized also in a certain corresponding part of the region of the harmonic displacements: the right-hand side of the inequality (4.9) is the condition that the harmonic displacements $|x_h|\sim|h_j/b_0|$ do not go outside the region $x_b\sim|b_0|/a_0$; its left-hand side, on the other hand, expresses the SLEP criterion in the harmonic approximation. Indeed, in the region of harmonic displacements $|b_0|=\pm b_0>b_\pm'$ the contribution $\delta b_j\equiv|b_j-b_0|$ to the coefficient of x^2 in $\Phi_j(x)$ is relatively small, $|\delta b_j/b_0|<(Q/A)^{1/3}<1$, and can be neglected in a qualitative analysis. In the region $b_\pm'<|b_0|=\pm b_0<b_\pm''$ the effective correlation energy is

$$U=U(b_0)=U_c-Q|x_2(b_0)|\approx U_c-4Q^2/p_\pm|b_0|<0,\tag{4.11}$$

so that $|U(b_0)|<|U^-|$, and $|U|$ decreases monotonically (at a given r_ν), with increasing $|b_0| < b_\pm''$. Thus, the correlation energy $U(b_0) < 0$ describes the SLEP due to an effect of the polaron type in the case of harmonic displacements of the atom (atom group) in the corresponding well of the critical potential, whereas U^- describes the SLEP for essentially anharmonic displacements. The interpolation formulas for $U(b_0)$ and $x_2(b_0)$ at all $|b_0| = \pm b_0$ can be obtained by replacing $\pm b_0$ in (4.11) by $\pm b_0 + 2b_\pm'/p_1$. In particular, at $|b_0| \ll b_\pm'$, this replacement is equivalent to taking into account, by perturbation theory, the harmonic component of the potential as a small increment to the biharmonic component.

The inequality (4.9) plays the role of the necessary condition of the realizability of a SLEP in a given substance, and the parameters of the critical potentials capable of taking part in the SLEP should, in accord with the foregoing, satisfy the relations

$$|b_0| = \pm b_0 \leqslant 4p_2Q^2/p_\pm U_c \quad \text{and } |h_0| \leqslant p_3Q; \quad p_2 \leqslant 1, \quad p_3 \leqslant 1. \tag{4.12}$$

A more detailed quantitative analysis based on the approximations (4.6) leads to the same results and refines somewhat the values of the dimensionless numerical constants p_1, p_2, and p_3.

The conditions (4.12) determine implicitly the restrictions imposed on the basic parameters η and t of the critical potentials that generate the SLEP. To make this determination explicit, it is necessary to use expressions (4.3) for b_0 and h_0. The spectrum of the permissible values of the parameters is then represented by certain region in the (η, t) plane, shown schematically in Fig. 2, which must in addition be bounded on the right by the condition $|t| < t_c$. The existence of an effective boundary t_c of the distribution of the random quantity t corresponds to the parameter Δ_c mentioned in Sec. 3 and to the correlated small quantities $\Delta_c C^{-1} \ll 1$ and $t \ll 1$. If, as should apparently be the case, the relations between the parameters of the systems are such that

$$t_c \leqslant t_1 = (8p_2/p_\pm)U_cQ^{-1},$$

then the part of the (η, t) plane of interest to us can be approximated by the rectangular region

$$t \leqslant t_c(\ll 1), \quad |\eta| \leqslant \min\left\{\frac{1}{2}\Delta\eta, \eta_\pm''\right\} = \eta_\pm'' \equiv \frac{4p_2}{p_\pm}\frac{Q^2}{U_cA} \tag{4.13}$$

at (4.9) and $\Delta(t_c, \eta_{\min}) \sim \Delta_c$; $\eta_\pm'' \gg t_c^2$. Indeed, $\eta_\pm'' \ll 1$ [say $\eta_\pm'' \lesssim 10^{-2}-10^{-1}$ in covalent glasses at (4.9)], in accord with the general formulation of the problem which implies that the SLEP cannot be realized far from the critical potentials, i.e., $Q_2/2A \ll U_c$, in the polaron effect. As a result, we are left with the condition

$$|\eta| = \pm\eta \leqslant \eta_\pm'' = \frac{4p_2}{p_\pm}\frac{Q^2}{U_cA}(\ll 1), \quad p_2 \leqslant 1. \tag{4.14}$$

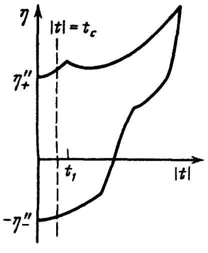

FIG. 2. Domain of the values of the parameters η and t of the critical potentials that generate the SLEP.

We note, however, that if we consider only the region in which the SLEP is determined by anharmonic displacements and is characterized by the largest (at the given r_ν) value $|U| = |U^-| \equiv |U^-(r_\nu)|$, then it is necessary to satisfy the condition $|b_0| = \pm b_0 < b_\pm'$, i.e., the condition

$$|\eta| = \pm\eta < \eta_\pm' = \frac{2}{p_\pm}Q^{2/3}a_0^{1/3}A^{-1},$$

given in Refs. 2 and 3. This stronger restriction agrees with (4.14) if (4.9) is valid; in this case we have also $\eta_\pm' \gg t^2$.

We note also in connection with the foregoing that in the presented relations we have

$$Q \equiv Q(r_\nu) \leqslant Q(a) \text{ and } U_c \equiv U_c(r_\nu) \leqslant U_c(a)$$

for a given $r_\nu \geqslant a$, so that

$$|U^-| \equiv |U^-(r_\nu)| \leqslant |U^-(a)|, \quad b_\pm \equiv b_\pm(r_\nu) \leqslant b_\pm(a)$$

and $\eta_\pm \equiv \eta_\pm(r_\nu) \leqslant \eta_\pm(a)$. If SLEP [the criterion (4.9)] takes place on a quasimolecule with $r_\nu \approx a$, this phenomenon is not realized or else can be all the more realized at $r_\nu \gg a$, respectively, when $U_c(r_\nu)/Q(r_\nu)\,|x_2(b_0, r_\nu)|$ increases or decreases with increasing r_ν at a given $b_0 = \pm b_0 < b_\pm''(r_\nu)$. However, even in the case when the SLEP phenomenon does take place at $r_\nu \gg a$, it is characterized by small $|U^-(r_\nu)| \ll |U^-(a)|$ at real $|U^-(a)| \lesssim 1$ eV; in this case, the fraction of the corresponding critical potentials that are suitable for SLEP is small to the extent that $Q(r_\nu)$ is small (see below).

5. SPECTRAL CHARACTERISTICS OF SLEP

In this section we deal with the spectral characteristics of SLEP in the MG of ideal glass. In fact, the SLEP alters the spectrum of the electron subsystem as a whole, inasmuch as the terms corresponding to the quasimolecules are lowered $(2E \to 2E + U)$. We start from the bare (in the absence of SLEP) single-particle density

$$g^{(1)}(E) = \sum_\alpha g_\alpha^{(1)}(E)$$

in the MG, e.g., at (see Ref. 6)

$$g_\alpha^{(1)}(E) \approx g_\alpha^{(1)}(E_\alpha)\exp\left\{-\left|\frac{E_\alpha - E}{w_\alpha}\right|^{\mu_\alpha}\right\}, \quad \frac{1}{2} \lesssim \mu_\alpha \lesssim 2. \tag{5.1}$$

The index α denotes now the type of the band, namely conduction ($\alpha = 1$) or valence ($\alpha = 2$), with the corresponding mobility thresholds $E_1 = E_c$ and $E_2 = E_v$. Since the considered bare terms E are situated in the MG, we have for them $q_\alpha(E) \equiv (-)^\alpha(E - E_\alpha) > 0$. It can usually be assumed, as will be done hereafter, that there is practically no correlation between the localization regions of the bare terms in the MG and the critical potentials.

In the considered disordered system, characterized by an appropriate parameter Λ, the term E in the MG corresponds generally speaking to a set of quasimolecular states that corresponds to a certain set ν at $\alpha = 1$ or $\alpha = 2$. If it is assumed that the given value E corresponds to practically one value $\nu \approx \nu_E$, which determines the characteristic radius $r_\nu \approx r_E$ of the state (see, e.g., Ref. 15), then we can put approximately

$$Q_{\nu\alpha} \approx Q_\alpha(r_E), \quad U_{c\nu\alpha} \approx U_{c\alpha}(r_E)$$

etc. It is such cases that we have in mind mainly from now on.2)

In the systems considered, we have $U < 0$ only on selected regions (bonds), whose density is relatively small, $c_a[\eta''(a)] \ll 1$, whereas on the other regions we have $U > 0$. The density $\rho_\alpha(U, E)$ of the distribution determines here the relative density $\rho_\alpha(U, E)dUdE$ of the terms with energies in the interval $(E, E + dE)$ of the bare spectrum, and with pair correlation energies in the interval $(U, U + dU)$. We can represent $\rho_\alpha(U, E)$ in the usual manner in the form

$$\rho_\alpha(U, E) = y_\alpha(U|E) g_\alpha^{(1)}(E),$$

where $y_\alpha(U|E)$ is the density of the conditional probability that the term with the bare energy E changes by an amount $U/2(2E - 2E + U, U \gtrless 0)$. The distributions $\rho_\alpha(U, E)$ and $y_\alpha(U, E)$ determines the main spectral characteristics of the SLEP. Thus, the SLEP efficiency

$$\xi_\alpha(E) = \int_{-\infty}^{0} y_\alpha(U|E)\,dU \tag{5.2}$$

is the probability that a state with bare energy E in the tail of the α-th band has a correlation energy $U < 0$. The density of such paired states is

$$c_\alpha^{(2)} = \int_{-\infty}^{\infty} \xi_\alpha(E) \bar{g}_\alpha^{(1)}(E)\,dE, \quad \bar{g}_\alpha^{(1)}(E) = g_\alpha^{(1)}(E)\,\theta[q_\alpha(E)],$$
$$\theta(x) = \{1 \text{ at } x > 0;\ 0 \text{ at } x < 0\}. \tag{5.3}$$

The effective density (per carrier) of the paired states is

$$g_\alpha^{(2)} = \bar{g}_\alpha^{(2)}(E) = \int_{-\infty}^{\infty} dU \int_{-\infty}^{\infty} dE' \rho_\alpha(U, E')\,\delta\left(E - E' + (-)^\alpha \frac{U}{2}\right) \theta[q_\alpha(E')]. \tag{5.4}$$

On the whole, the MG spectrum is a superposition of the spectra of paired ($j = 2$) and single-particle ($j = 1$) states

$$g(E) = g^{(1)}(E) + g^{(2)}(E), \quad g^{(j)}(E) = \sum_\alpha g_\alpha^{(j)}(E),$$

and the total density of the j-particle states in the MG is

$$c^{(j)} = \sum_\alpha c_\alpha^{(j)}$$

with

$$c_\alpha^{(j)} = \int_{-\infty}^{\infty} \bar{g}_\alpha^{(j)}(E)\,dE. \tag{5.5}$$

The distribution density $y_\alpha(U|E)$ can be expressed by means of the relation

$$y_\alpha(U|E) = \sum_{+,-} N\{\eta(U; \alpha, E, \pm)\} \left| \frac{d\eta(U; \alpha, E, \pm)}{dU} \right| \tag{5.6}$$

in terms of the distribution density $N(\eta)$ of the parameter η. Here $\eta = \eta(U; \alpha, E, \pm)$ is the inverse of the function $U = U(\eta; \alpha, E, \pm)$ that connects the correlation energy U with the critical parameter η at given fixed values of α and E; the indices plus (for $\eta > 0$) and minus (for $\eta < 0$), over which the summation is carried out, take into account the fact that the expressions $U = U(\eta; \alpha, E)$ are somewhat different at $\eta > 0$ and $\eta < 0$ (see Sec. 4). In accord with the discussion in Secs. 3 and 4, in the region $|\eta| \ll \Delta\eta$ that is essential for the SLEP we can assume $N(\eta) \leq (\Delta\eta)^{-1}$, so that the problem reduces to a determination of the functions $d\eta(U; \alpha, E, \pm)/dU$ and to calculation of the spectral characteristics (5.1)–(5.5) with their aid. We use next the expression

$$y_\alpha(U|E) \lesssim \frac{4}{A\Delta\eta}\left(\frac{1}{p_+} + \frac{1}{p_-}\right) \frac{Q_\alpha^2(|E_\alpha - E|)}{\{U - U_{c\alpha}(|E_\alpha - E|)\}^2}, \tag{5.7}$$

which can be easily obtained from (5.6) by using the aforementioned interpolation relation $U = U(\eta; \alpha, E, \pm)$ [see the discussion that follows (4.11) and (3.12)].

In the calculation of $g_\alpha^2(E)$ we note that the function $\rho_\alpha(U, E')$ in the integrand decreases rapidly towards the interior of the MG, because of the decrease of $g_\alpha^{(1)}E'$ at $|E_\alpha - E'| > w_\alpha$. Near the edge of the MG the behavior of $\rho_\alpha(U, E')$ is determined by the relation

$$|Q_\alpha(|E_\alpha - E'|)/\{U - U_{c\alpha}(|E_\alpha - E'|)\}|,$$

which for all finite $U \neq 0$ vanishes as $E' \to E_\alpha$ together with $Q_\alpha(|E' - E_\alpha|)$. Therefore the function $\rho_\alpha(U, E')$ in the integrand of (5.4) has a sharp maximum at a certain $|E' - E_\alpha| = \delta_\alpha$. (The corresponding strip in which $r_{E,\alpha} \gg a$ has a width close to δ_α; see Ref. 6.) Integrating in (5.4) with respect to U and recognizing that $|U_\alpha| = -U_\alpha \leqslant |U_\alpha^-|$, we easily see that for the integral in $G_\alpha^{(2)}(E)$,

$$g_\alpha^{(2)}(E) \lessapprox \left(\frac{1}{p_+} + \frac{1}{p_-}\right) \frac{1}{A\Delta\eta} \left| \int_{E}^{\bar{E}_\alpha} g_\alpha^{(1)}(E') \left\{ \frac{Q_\alpha(|E_\alpha - E'|)}{E - E' - {}^1\!/_2 U_{c\alpha}(|E_\alpha - E'|)} \right\}^2 dE' \right|, \tag{5.8}$$
$$\bar{E}_\alpha \equiv \min\left\{(-)^{\alpha+1}\left[E_2, E + (-)^\alpha \frac{U_\alpha^-}{2}\right]\right\}(-)^{\alpha+1},$$

there can be realized in principle two cases:

$$\delta_\alpha w_\alpha^{-1} \lessapprox 1 \text{ and } \delta_\alpha w_\alpha^{-1} \gg 1. \tag{5.9}$$

In the first case of (5.9) the influence of the SLEP on the properties of the system can be quite substantial, whereas in the second case of (5.9) it is much weaker or completely absent. We therefore discuss here only the first case of (5.9) which, from the described point of view, can indeed be realized, e.g., at

$$Q_\alpha(|E' - E_\alpha|) \propto |E' - E_\alpha|^n, \quad n = n(|E' - E_\alpha|) > 0.$$

Expression (5.7) corresponds to the presence in the MG of asymmetrical bands of paired states with densities $g_\alpha^{(2)}(E)$, when the SLEP is realized for both bands, i.e., $c_1^{(2)}$ and $c_2^{(2)}$ are appreciable, or for one such band, when the SLEP is realized for only one band, e.g., $c_1^{(2)} \neq 0$ and $c_2^{(2)} = 0$ (Fig. 3). The paired bands can overlap [at $(1/2)|U_1^- + U_2^-| > E_1 - E_2$] or even become inverted. We note that if the initial atomic state is identical for the terms E' of both bands, one can expect the quantities $Q_\alpha(|E_\alpha - E'|)$, U_α^-, etc. to be close or of the same order as the values for $\alpha = 1$ and $\alpha = 2$. If the

SLEP phenomenon is realized in this case, it does so for both bands (this is possibly the situation in chalcogenide glasses).

The concrete form of the bands $g_\alpha^{(2)}(E)$ might be found from (5.7) given the functions $g_\alpha^{(1)}(E)$, $Q_\alpha(|E_\alpha - E'|)$, and $U_{c\alpha}(|E_\alpha - E'|)$. Since, however, these functions are still not fully known even for the most investigated glasses, we confine ourselves here only to the rough approximation

$$g_\alpha^{(2)}(E) \leqslant \left(\frac{1}{p_+}+\frac{1}{p_-}\right)\frac{w_\alpha}{A\Delta\eta} g_\alpha^{(1)}(E_\alpha)\left\{\frac{Q_\alpha(|E_\alpha-E_\alpha|)}{E-E_\alpha-{}^1/_2U_{c\alpha}(|E_\alpha-E_\alpha|)}\right\}^2$$

$$|E_\alpha - E| \gtrsim w_\alpha, \text{at } E_\alpha \approx \min\{|E_\alpha+(-)^\alpha\delta_\alpha|;\ E_\alpha+(-)^\alpha U_\alpha^-(a)/2|\}, \tag{5.10}$$

which is obtained when account is taken of the relatively weak (in the w_α scale) change of the factor in the curly brackets of the integrand of (5.8). More explicit expressions for $g_\alpha^{(2)}(E)$ can be obtained for different kinds of models, in particular for the model with

$$y_\alpha(U|E) \approx \xi_\alpha(E)\delta(U-U_\alpha^-)+\Delta y_\alpha(U|E), \tag{5.11}$$

where Δy_α takes into account the influence of the SLEP in the harmonic region of the displacements, whereas in the anharmonic region we have $U = U_\alpha^-$, as was obtained, e.g., in Refs. 8 and 9 for cases when $\Delta y_\alpha = 0$.

The approximation (5.10), as well as the model (5.11), shows that in the interior of the MG we have $g_\alpha^{(2)}(E) \gg g_\alpha^{(1)}(E)$, since $g_\alpha^{(1)}(\bar{E}\alpha) \gg g_\alpha^{(1)}(E)$ [say, at $|U_\alpha^-(a)| > (3 \text{ to } 5)w_\alpha$ and $g_\alpha^{(1)}(E)$ of the form (5.11)]. Thus, in the interior of the MG the total state density $g(E)$ is determined in the presence of SLEP and at sufficiently large $|U_\alpha^-(a)|$ by the paired states. The density of the paired states in the MG can be estimated in accord with the (5.5) and (5.7) at[3]

$$c_\alpha^{(2} \leqslant \frac{4}{A\Delta\eta}\left(\frac{1}{p_+}+\frac{1}{p_-}\right)\int_{-\infty}^{0} dU \int_{-\infty}^{\infty} \bar{g}_\alpha^{(1)}(E)\frac{Q_\alpha^2(|E'-E_\alpha|)}{[U-U_{c\alpha}(|E'-E_\alpha|)]^2}dE'$$

$$\sim \frac{1}{A\Delta\eta}\frac{Q_\alpha^2(\delta_\alpha)}{|U_\alpha^-(\delta_\alpha)-U_{c\alpha}(\delta_\alpha)|}c_\alpha^{(1)}, \tag{5.12}$$

$$U_\alpha^-(\delta_\alpha) \equiv U_\alpha^-(r_{E'}\,|\,|E'-E_\alpha|=\delta_\alpha)$$

etc. For tentative estimates we can bear in mind the values of the quantites

$$Q_\alpha(|E'-E_\alpha|\gtrsim\delta_\alpha)\gtrsim 1\text{ eV},\quad w_\alpha\sim 0.1\text{ eV},\quad g_\alpha^{(1)}(E_\alpha)\sim 10^{-1}-10^{-2}\text{ eV}^{-1},$$
$$U_{c\alpha}(|E'-E_\alpha|\gtrsim\delta_\alpha)\sim 0.3-0.5\text{ eV},\ A\sim 10-30\text{ eV},$$

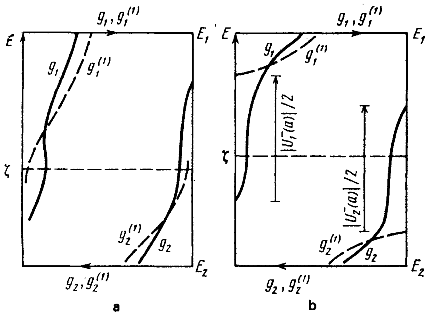

FIG. 3. Electronic state density in GM of an ideal crystal in the presence of SLEP for the following models: a) of Mott and Davis; b) of Mott and Cohen-Fritzsche-Ovshinsky; the dashed lines show the bare densities.

as well as

$$|U_\alpha^-(|E'-E_\alpha|\gtrsim\delta_\alpha)| \sim |U_\alpha^-(r_{E'}\approx a)| \sim 1\text{ eV}$$

(e.g., for chalcogenide glasses in accordance with the results of Sec. 4). In this case, e.g.,

$$g_\alpha^{(2)}\left(\frac{|U_\alpha^-|}{2}\right) \leqslant (\Delta\eta)^{-1}(10^{-1}-10^{-3})g_\alpha^{(1)}(E_\alpha),$$

$$c_\alpha^{(2)} \leqslant \frac{Q_\alpha^2 c_\alpha^{(1)}}{A|U_\alpha^-|\Delta\eta} \sim (10^{-1}-10^{-2})\frac{c_\alpha^{(1)}}{\Delta\eta}.$$

The other spectral characteristics of the SLEP can be treated similarly, using expressions (5.6) and (5.7). We note that in this case, since $\xi_\alpha(E')$ varies relatively little, it can be replaced in the corresponding integral as follows: $\xi_\alpha(E') \to \xi_\alpha^{(0)} = \text{const}$; e.g., we can write (5.3) in the form $c_\alpha^{(2)} \sim \xi_\alpha^{(0)} c_\alpha^{(1)}$ (cf. Refs. 8 and 9).

Systems characterized by a significant role of the SLEP and by the described spectra reveal substantial singularities of the thermodynamic properties. Thus, e.g., in an MG of considerable state density $g(E) \approx g^{(2)}(E)$ fixes (pins) the position of the level of the chemical potential ζ; in this case, since $g^{(1)}(\zeta) \ll g^{(2)}(\zeta)$, the paramagnetism of the glass is on the whole effectively suppressed, so that its diamagnetism may appear. A detailed analysis of these singularities is beyond the scope of the present article (a brief exposition of some of them can be found in Refs. 8 and 9).

6. CONCLUSION

Of basic importance for the foregoing analysis is the conclusion that it is possible to realize in amorphous nonmetallic structures two interrelated phenomena: 1) the existence of two-well and critical potentials for the atoms of an "ideal" glass, and 2) self-localization of the electron (hole) pairs in the mobility gap of "ideal" glass in the case of strong attraction between the electrons (holes).[4] Two-well potentials in glasses[13] and a strong local attraction between carriers in glassy semiconductors[5] were postulated earlier on the basis of empirical data. These phenomena were assumed to be unrelated, and their microscopic nature (far from the glass defects) remained unexplained.

The described model and theory of the SLEP does not connect the pair production with the defect of the glass structure (in contrast to the "defect" models of Ref. 6), and at the same time demonstrate the existence of a finite albeit small ($c^{(2)} \ll 1$) concentration of intrinsic local charged centers — pairs ($\pm 2|e|$) in the MG, which correspond to at least two types ($\alpha = 1, 2$) of single-electron "bare" states. It is this which makes the SLEP theory substantially different from the Anderson model[5] (see Sec. 1).

The results of the presented analysis allow us to predict certain new effects. Thus, high pressure and factors contributing to the relaxation of the glass structure could decrease the role of effects of two-well and critical potentials, by lowering the density of the self-localized carrier pairs and the anomalous low-temperature heat capacity, but increasing the paramagnetism or the Mott hopping conduction and other manifestations of single-particle states. At the same time, the penetration of hydrogen (e.g., in α-Si) could generate or amplify the effects connected with the presence of two-well potentials (on account of formation of hydrogen bonds), i.e., diamagnetism, anomalies of the low-temperature heat capacity, SLEP, and others.

We note also that z_0-well potentials similar to those considered, and SLEP, can apparently be realized for suitable atoms also in other structures, particularly in certain defects (such as off-center defects) in nonmetallic crystals. This may be the cause of the unusual properties of In and Ga in $Pb_{1-x}Sn_xTe$ crystals with $0 < x \leqslant 0.2$ (see, e.g., Ref. 16),5) interstitial boron in the Si crystals,[18] and hydrogen in amorphous Si (see Ref. 6).

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1) Brief expositions of the main idea and of certain results of the work were given in Refs. 1–4.

2) In the alternate cases, if the distribution for ν at a given E is essentially smooth, the qualitative picture can be expected to remain the same, but the corresponding relations turn out to be more cumbersome.

3) This estimate of $c_\alpha^{(2)}$ is more adequate than the estimate given in Refs. 2 and 3, although the difference between them should actually not be large (it is possible to exclude η_{cr} from Refs. 2 and 3 as an inessential restriction).

4) Interactions between the pairs are outside the scope of the present article.

5) An interesting model of the anomalous electric properties of $Pb_{1-x}Sn_xTe$ (In, Ga) at $0 < x \leqslant 0.2$, not connected with electron pairing, is given in Ref. 17.

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