Theory of self-trapping barrier for Wannier-Mott excitons in polar crystals

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An analytic theory of the self-trapping barrier for Wannier-Mott excitons is developed on the basis of the expansion of all quantities in the small parameter $m_e/m_h \ll 1$, where m_e and m_h are the electron and hole masses. The height of the self-trapping barrier is calculated and its tunnel transparency is estimated (with exponential accuracy). The results are compared with the calculations of other authors.

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Free and self-trapping states of an exciton in a polaron crystal are separated by an energy barrier[1] and can therefore coexist.[2] This phenomenon, first observed in alkali-halide crystals (AHC),[3] is at present under study for a large class of substances.[4–7] The height of a self-trapping barrier in a continual approximation is best carried out for a Frenkel exciton.[8,9] For a Wannier-Mott exciton the situation is much more complicated because it has additional degrees of freedom connected with the relative motion of the electron and hole. The difficulties are great even in models with a nondegenerate valence band, to which all the studies known to us are confined at present.

Since the electron is usually much lighter than the hole, it is natural to attempt to use the small parameter m_e/m_h to construct an analytic theory. Regardless of how applicable the asymptotic formulas obtained in this paper are to real crystals, the qualitative picture obtained can be quite instructive. As shown by variational calculations[10] (in accordance with the prediction of Ref. 11), the height W of the barrier decreases with decrease of this parameter. Consequently, the lifetime of the free exciton must also decrease.

We consider in this paper Wannier-Mott excitons in polar crystals in the continual approximation, which goes back to the Pekar theory of polarons.[12] We assume that the effective-mass approximation holds for the electron and hole, and that the crystal lattice can be regarded as a continuous polarizable medium with fixed natural frequency low enough for the adiabatic approximation to be applicable. The result is the notion[13] that a Coulomb interaction takes place between an electron and a hole located in a common potential well produced by the slowly varying polarization of the lattice. Leaving aside the question of the localized self-trapping state of such a system, we obtain the barrier height and (with exponential accuracy) the time of tunneling through it; our equations are valid in the limiting case of a large difference between the electron and hole masses. It is then possible to construct of some sort of an adiabatic approximation with the small parameter $m_e\varepsilon_0/m_h(\varepsilon_0-\varepsilon_\infty)$ and carry out the calculations almost analytically. The main results reduce to the following.

The height of the barrier (more accurately, the energy of the saddle-point state)

$$W=2.14 m_e^2\varepsilon_0 E_i/m_h^2(\varepsilon_0-\varepsilon_\infty) \tag{1}$$

is small compared with the exciton-ionization energy

$$E_i=m_e e^4/2\hbar^2\varepsilon_\infty^2.$$

The polarization potential well on the barrier has a radius of the order of the exciton Bohr radius $\hbar^2\varepsilon_\infty/m_e e^2$ and a depth $E_i m_e/m_h$. The time of tunneling through the self-trapping barrier is, accurate to a factor in front of the exponential,

$$\tau=\omega^{-1}\exp(W/\hbar\omega) \tag{2}$$

(ω is the phonon frequency). The shape of the polarization well and the wave function on the optimal tunneling paths are similar to those in the saddle-point state. The expressions obtained for W and τ are valid subject to the condition

$$\hbar\omega \ll W,$$

which is thus the adiabaticity criterion for our problem.

1. SADDLE POINT STATE

In the adiabatic approximation the total energy of the system (Wannier-Mott exciton in a polar crystal) is of the form[14]

$$\mathscr{E}[\varphi(\mathbf{r})]=\min_{\psi}\langle\psi^*|-\frac{\hbar^2\Delta_e}{2m_e}-\frac{\hbar^2\Delta_h}{2m_h}-\frac{e^2}{\varepsilon_\infty|\mathbf{r}_e-\mathbf{r}_h|}+e\varphi(\mathbf{r}_h)-e\varphi(\mathbf{r}_e)|\psi\rangle+\frac{1}{8\pi\tilde{\varepsilon}}\int(\nabla\varphi)^2\,d^3r, \tag{3}$$

where $\tilde{\varepsilon}=(\varepsilon_\infty^{-1}-\varepsilon_0^{-1})^{-1}$ and $\varphi(\mathbf{r})$ is the electrostatic-induction potential. It is more convenient to seek the free, self-trapping, and saddle-point states as the stationary points of the functional[10]

$$J[\psi(\mathbf{r}_e,\mathbf{r}_h)]=\langle\psi^*|-\frac{\hbar^2\Delta_e}{2m_e}-\frac{\hbar^2\Delta_h}{2m_h}-\frac{e^2}{\varepsilon_\infty|\mathbf{r}_e-\mathbf{r}_h|}|\psi\rangle-\frac{1}{8\pi\tilde{\varepsilon}}\int(\nabla\varphi)^2\,d^3r, \tag{4}$$

where $\varphi(\mathbf{r})$ is defined by the expression

$$\varphi(\mathbf{r})=e\int\left(\frac{1}{|\mathbf{r}-\mathbf{r}_h|}-\frac{1}{|\mathbf{r}-\mathbf{r}_e|}\right)\psi^2(\mathbf{r}_e,\mathbf{r}_h)\,d^3r_e\,d^3r_h. \tag{5}$$

The values of the functional (4) at the stationary points give the energies of the corresponding states.

The entire analysis that follows is based on an approximation which we shall call the model of a "rigid" exciton. Namely, we assume throughout that the relative motion of the electron and hole are described by the same hydrogenlike wave function as in the case of a free exciton. This approach

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is certainly applicable to the self-trapping state but, as will be shown, for the saddle-point state and for all the states on the optimal path for tunneling through the barrier the distortion of the inner structure of the exciton and its influence on the energies of the state is small in the parameter $m_e/m_h \ll 1$.

We transform right away to new measurement units, namely the length $\hbar^2\varepsilon_\infty/m_e e^2$ (the Bohr radius of the exciton at $m_e \ll m_h$) and the energy $m_e e^4/\hbar^2\varepsilon_\infty\tilde{\varepsilon}$ (the exciton Rydberg multiplied by $2\varepsilon_\infty/\tilde{\varepsilon}$).

The motion of the rigid exciton is described by the wave function $\psi(r)$ of the mass center, which coincide in the limit $m_e \ll m_h$ with the hole. The charge density is given by

$$\rho(\mathbf{r})=\rho_h+\rho_e=\left[\psi^2(\mathbf{r})-\int\chi^2(\mathbf{r}-\mathbf{r}')\psi^2(\mathbf{r}')\,d^3r'\right]\equiv\hat{\rho}\psi^2(\mathbf{r}), \quad (6)$$

where $\chi(r)=\pi^{-1/2}e^{-r}$ is the wave function of the ground state of the relative motion of the free electron, and the potential (5) is equal to

$$\varphi(\mathbf{r})=e\int\frac{1}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}')\,d^3r'\equiv e\hat{K}\rho(\mathbf{r})=e\hat{K}\hat{\rho}\psi^2(\mathbf{r}). \quad (7)$$

The identities (6) and (7) define the linear operators $\hat{\rho}$ and $\hat{K}$.

Using as the origin the free-exciton energy, we obtain from (4) a functional that contains only one parameter

$$\mathcal{J}[\psi(\mathbf{r})]=\int\left[\frac{(\nabla\psi)^2}{2M}-\frac{1}{2}\psi^2\hat{\rho}\hat{K}\hat{\rho}\psi^2\right]d^3r, \quad M=\frac{m_h\varepsilon_\infty}{m_e\tilde{\varepsilon}}. \quad (8)$$

The stationary points of this functional define the free, self-trapping, and saddle-point states in the rigid-exciton model, while the values of $\tilde{J}[\psi(\mathbf{r})]$ at these points define the energy of the states relative to the free exciton. In the present section we obtain the wave function $\psi(\mathbf{r})$ of the mass center and the energy W of the saddle-point state in the limit of large values of the parameter M.

Variation of the functional (8) with respect to ψ yields the nonlinear "Schrödinger equation"

$$-\Delta\psi(\mathbf{r})/2M+V(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r}), \quad (9)$$

where

$$V(\mathbf{r})=-\hat{\rho}\hat{K}\hat{\rho}\psi^2(\mathbf{r}), \quad (10)$$

and E is a Lagrange multiplier chosen to obtain normalization to unity and called hereafter the Schrödinger energy. In the case of a spherically symmetrical internal-motion wave function $\chi(r)$ we can assume, without loss of generality, that $\chi(r)$ is also spherically symmetrical.

The "potential energy" (10) has a property that will be useful later, namely it decreases rapidly over distances that are large compared with the exciton size. This property, due in final analysis to the exciton electroneutrality, is possessed also by a wave function that falls off slowly at large r, for in this case

$$\hat{\rho}\psi^2\approx-{}^1/_2\Delta\psi^2, \quad V(r)=-\hat{\rho}\hat{K}\hat{\rho}\psi^2\approx-\pi\Delta\psi^2.$$

We assume now that the polarization well binds the exciton weakly, i.e., that the Schrödinger energy E in the region $r\sim 1$ of the well is small compared with the characteristic potential energy $V(r)$ and the kinetic energy M^{-1}. In this case, owing to the rapid decrease of $V(r)$ in Eq. (9), it is possible to single out two overlapping distance regions: a central region $r \ll (M|E|)^{-1/2}$ in which the right-hand side of $E\psi(r)$ can be neglected, and a peripheral region $r \gg 1$, where the term $V(r)\psi(r)$ is negligibly small.

We turn first to the peripheral region. Equation (9) has then a solution that decreases at infinity for $V\equiv 0$, in the form

$$\psi(r)\propto r^{-1}\exp\left[-(2M|E|)^{1/2}r\right].$$

In the normalization integral, the contribution of the region $r \lesssim 1$ is negligibly small, therefore the normalization coefficient is uniquely connected with E. As a result we have

$$\psi(r)=\pi^{-1/2}(M|E|/2)^{1/4}r^{-1}\exp\left[-(2M|E|)^{1/2}r\right], \quad r\gg 1. \quad (11)$$

In the central region Eq. (9) without the right hand side is reduced by the substitution

$$\psi(r)=M^{-1/2}\Phi(r) \quad (12)$$

to the equation

$$-{}^1/_2\Delta\Phi-\Phi\hat{\rho}\hat{K}\hat{\rho}\Phi^2=0, \quad (13)$$

which contains no parameters. The required solution is uniquely determined by the condition that it decrease at infinity [in the intermediate region $1 \ll r \ll (M|E|)^{-1/2}$ Eq. (12) must be compatible with (11)]. This function has no singularities and decreases at infinity like r^{-1}. Equation (9) was solved by us by an iteration method. We used the iteration function

$$\Phi=\sum_{i=0}^{4}A_i\left(1+\frac{r^2}{R^2}\right)^{-(1/2+i)} \quad (14)$$

with six variation parameters, for which we obtained the values $R=3.253$; $A_0=0.1929$; $A_1=0.1005$; $A_2=0.1311$; $A_3=0.2235$; $A_4=0.0005$.

All the quantities calculated in the present paper are expressed in terms of two constants obtained from the function Φ:

$$E_0=2\pi^2[\lim_{r\to\infty}(r\Phi)]^4\approx 3.1,$$
$$W_0=\frac{1}{4}\int(\nabla\Phi)^2\,d^3r=\frac{1}{2}\int\Phi^2\hat{\rho}\hat{K}\hat{\rho}\Phi^2\,d^3r\approx 1.07. \quad (15)$$

The constant E_0 determines the Schrödinger energy in the saddle-state point, since the solutions obtained in the central and peripheral regions should coincide at $1 \ll r \ll (M|E|)^{-1/2}$. Equality is reached at

$$E=-E_0/M^3. \quad (16)$$

Calculating the potential energy $V(r)$ from (10), we can use for ψ expression (12), which is valid in the neutral region, and obtain

$$V(r)=-M^{-1}\hat{\rho}\hat{K}\hat{\rho}\Phi^2. \quad (17)$$

The function $V(r)$ decreases like r^{-4} at $r \ll 1$ and is of the order of M^{-1} at $r\sim 1$. We see thus that the Schrödinger energy is indeed small, as assumed.

The total energy of the system [the value of the functional (8)] in the saddle-state point can be written in the form

$$W=T+U/2,$$

where

$$T \equiv \frac{1}{2M}\int (\nabla\psi)^2\, d^3r, \quad U \equiv \int V(r)\psi^2\, d^3r$$

are the mean values of the kinetic and potential energies of the rigid exciton. The energy is concentrated in the region $r \lesssim 1$. Taking the corresponding expression (12) for the wave function, we obtain up to terms of higher order in M^{-1}

$$T=-U=2W_0M^{-2},$$

whence

$$W=W_0M^{-2}. \tag{18}$$

Let us describe once more the obtained qualitative picture of the saddle-point state. The polarization potential well turns out to be shallow (radius ~ 1, depth $\sim M^{-1}$). The wave function has two spatial scales: internal, over which is concentrated the energy of the system (the exciton has a low probability M^{-1} of being in this region), and external $r \sim M$, which characterizes the decrease of $\psi(r)$ at infinity and ensures satisfaction of the condition $\int \psi^2 d^3r = 1$.

2. TUNNELING

A theory of tunnel self-trapping, based on a quasiclassical approximation, was developed by Iordanskiĭ and Rashba[15] for electrons interacting with acoustic or unpolarized optical lattice vibrations. We shall proceed in analogy with Ref. 15 and consider the interaction of a rigid exciton with polarization optical phonons. The applicability of this model will be discussed later.

We introduce, as usual, an imaginary time $\tau = it$ measured in reciprocal phonon frequency ω^{-1} (the energy and length units were introduced in the preceding section). The quasiclassical tunneling probability is defined by the quantity $\exp(-SS_0)$, where $S_0 = m_e e^4/\hbar^3\omega\varepsilon_\infty\tilde{\varepsilon}$ is a dimensionless parameter assumed to be large, and S is the value of the functional

$$S[\varphi] = \int\left\{\frac{1}{8\pi}\int[(\nabla\dot{\varphi})^2+(\nabla\varphi)^2]d^3r + \min_{\psi}\int\left[\frac{(\nabla\psi)^2}{2M}+\varphi\rho|\psi|^2\right]d^3r\right\}d\tau$$

at its saddle point relative to $\varphi(\tau,\mathbf{r})$.[1)] After eliminating the phonon coordinates $\varphi(\tau,\mathbf{r})$ the problem reduces to finding the saddle point of the functional

$$\tilde{S}[\psi(\mathbf{r},\tau)] = \frac{1}{2}\int\left[\frac{|\nabla\psi|^2}{2M}-\psi^2(\mathbf{r},\tau)\hat{\rho}\hat{K}\hat{\rho}\int_{-\infty}^{+\infty}\frac{e^{-|\tau-\tau'|}}{2}\psi^2(\mathbf{r}',\tau')\,d\tau'\right]d^3r\,d\tau. \tag{19}$$

The integration with respect to τ in (19) is from $-\infty$ to $+\infty$. The point $\tau = 0$ is regarded as the end point of the tunneling described by the segment $-\infty < \tau \leqslant 0$. The function $\psi(\tau)$ is continued into the region of positive τ in even fashion.

Variation of $\tilde{S}$ with respect to ψ leads to the Euler equation

$$-\Delta\psi(\mathbf{r},\tau)/M+V(\mathbf{r},\tau)\psi(\mathbf{r},\tau)=E(\tau)\psi(\mathbf{r},\tau), \tag{20}$$

where

$$V(\mathbf{r},\tau)=-\hat{\rho}\hat{K}\hat{\rho}\int_{-\infty}^{+\infty}\psi^2(\mathbf{r},\tau)\frac{e^{-|\tau-\tau'|}}{2}d\tau'. \tag{21}$$

Equation (20) is a Schrödinger equation at each instant of time. Since there is no bound state in an insufficiently deep well, we have $\psi(\mathbf{r})\equiv 0$ (more accurately, $\psi(\mathbf{r})$ is normalized to the volume of the crystal) at $|\tau| > \tau_0$, where τ_0 is the instant of time at which a bound state appears in the $V(\mathbf{r},\tau)$ well ($E(\pm\tau) = 0$).

We assume now that $\tau_0 \ll 1$, i.e., the bound state exists only during a brief concluding stage of the tunneling [as can be seen from (21), the characteristic time of phonon-well formation is $\tau \sim 1$]. In this case the coordinate dependence of $V(\mathbf{r},\tau)$ becomes separated in first-order approximation from the time dependence:

$$V(\mathbf{r},\tau)\approx -\frac{e^{-|\tau|}}{2}\hat{\rho}\hat{K}\hat{\rho}\int_{-\tau_0}^{\tau_0}\psi^2(\mathbf{r},\tau')\,d\tau'. \tag{22}$$

This expression gives grounds for assuming that $V(\mathbf{r},\tau)$ differs little from $V(\mathbf{r},\pm\tau_0)$ in the entire region $-\tau_0 < \tau < \tau_0$, and the state is weakly bound.

Weakly bound states have the following property of importance to us. At small changes of the potential-well depth the coordinate dependence of the wave function remains practically constant within the well, but the shift of the state energy E alters the decrease of $\psi(\mathbf{r})$ at large distances. Normalization yields for $\psi(\mathbf{r})$ at small $\mathbf{r}$ a common factor that depends on the energy E, which determines at small E all the changes of the wave function in the central region.

In the calculation of the potential energy (21) only the central region of r is important, just as in the case of the saddle state. Therefore, just as $\psi(\mathbf{r})$ in the central region, $V(\mathbf{r})$ should be constant accurate to a time dependent common factor; this can be expressed as

$$\left.\begin{aligned}\psi(\mathbf{r},\tau)&=A(\tau)\Phi(\mathbf{r}),\\ V(\mathbf{r},\tau)&=[1+\alpha(\tau)]V_0(\mathbf{r})\end{aligned}\right\} \quad r\lesssim 1, \tag{23}$$

where $V_0(\mathbf{r})$ is the potential energy at $\tau = \pm\tau_0$; $0 < \alpha(\tau) \ll 1$ at $|\tau| < \tau_0$. At the points $\tau = \pm\tau_0$ the functions $E(\tau)$, $A(\tau)$, and $\alpha(\tau)$ vanish.

To obtain $V_0(\mathbf{r})$ and $\Phi(\mathbf{r})$ we substitute (23) in (21). At $|\tau| < \tau_0 \ll 1$ we obtain

$$[1+\alpha(\tau)]V_0(\mathbf{r})\approx-\hat{\rho}\hat{K}\hat{\rho}\Phi^2(\mathbf{r})\int_{-\infty}^{+\infty}\frac{e^{-|\tau-\tau'|}}{2}A^2(\tau')\,d\tau'. \tag{24}$$

To determine the coordinate dependences, the principal approximation in τ_0 is sufficient, so that in the region $|\tau| < \tau_0$ we can neglect $\alpha(\tau)$ in the left-hand side of (24) and replace $\exp(-|\tau-\tau'|)$ by unity in the right-hand side. Without loss of generality, we can write here

$$\frac{1}{2}\int_{-\tau_0}^{\tau_0}A^2(\tau)\,d\tau = \frac{1}{M}$$

(this condition will hereafter be satisfied automatically) and obtain for the connection between $V_0(\mathbf{r})$ and $\Phi(\mathbf{r})$ an expression similar to (10):

$$V_0(\mathbf{r})=-M^{-1}\hat{\rho}\hat{K}\hat{\rho}\Phi^2(\mathbf{r}). \tag{25}$$

Substituting this expression in place of $V(\mathbf{r},\tau)$ in (20) and neg-

lecting as usual in the central region the term $E\psi$, we obtain for $\Phi(r)$ Eq. (13), which describes the wave function of the saddle state in the central region. Thus, the function $\Phi(r)$ coincides with that obtained in the preceding section and is characterized by the same constants E_0 and W_0 [Eq. (15)]. The function $V_0(r)$ is given by (17).

To explain the temporal picture of the tunneling we obtain first the connection between $A(\tau)$ and $\alpha(\tau)$. The quantity $A(t)$ is connected with the Schrödinger energy $E(\tau)$ by a relation that follows from the matching of the expressions for $\psi(\tau)$ in the central (23) and peripheral (11) regions: $A^2(\tau) = (M|E|/E_0)^{1/2}$. The change dE of the Schrödinger energy following a small change $V_0(r)d\alpha$ of the well can be obtained from (20) by stationary perturbation theory. Taking (25) and (15) into account we have

$$dE = d\alpha\langle\psi|V_0(r)|\psi\rangle = 2W_0M^{-1}A^2d\alpha = 2W_0(|E|/E_0M)^{1/2}d\alpha,$$

whence

$$E(\tau) = \frac{W_0^2}{ME_0}\alpha^2(\tau), \quad A^2(\tau) = \frac{W_0}{E_0}\alpha(\tau). \tag{26}$$

To determine $\alpha(\tau)$ we substitute in (24) the expressions obtained for Φ and V_0. After canceling $V_0(r)$ we obtain the integral equation

$$1+\alpha(\tau) = \frac{W_0M}{2E}\int_{-\tau_0}^{\tau_0} e^{-|\tau-\tau'|}\alpha(\tau')d\tau'. \tag{27}$$

Differentiating this equation twice with respect to τ we obtain the differential equation

$$\alpha'' = 1+(1-W_0M/E_0)\alpha,$$

from which we get at $M \gg 1$

$$\alpha = \text{const}\cos(\tau[W_0M/E_0]^{1/2}).$$

The proportionality coefficient is determined by substitution in (27), and as a result we have

$$\alpha(\tau) = (E_0/W_0M)^{1/4}\cos[\tau(W_0M/E_0)^{1/2}], \quad \tau_0 = {}^1/_2\pi(E_0/W_0M)^{1/2}. \tag{27a}$$

At $-\tau_0 < \tau \leqslant 0$ the wave function takes according to (26) and (27a) the form

$$\psi(r,\tau) = \begin{cases} \left(\frac{W_0}{E_0M}\right)^{1/4}\{\cos[\tau(W_0M/E_0)^{1/2}]\}^{1/2}\Phi(r), & r \ll M \\ \pi^{-1/2}\left(\frac{M|E(\tau)|}{2}\right)^{1/4}\exp[-(2M|E(\tau)|)^{1/2}r], & r \gg 1 \end{cases}, \tag{28}$$

$$E(\tau) = -\frac{W_0}{M^2}\cos^2\left[\tau\left(\frac{W_0M}{E_0}\right)^{1/2}\right].$$

We see that the assumption that τ_0 is small holds, so that in the temporal picture of the tunneling there are two scales, the time $\tau \sim 1$ of formation of the polarization well, and the interval $\tau \sim M^{-1/2} \ll 1$ during which the bound state exists in this well. The state is weakly bound at all times, since the Schrödinger energy is of the order of M^{-2} while the well has a depth M^{-1}.

We note that, as expected, at the end of the tunneling path the total energy is zero (the lattice polarization energy W_0M^{-2} is cancelled by the binding energy $E(0) = -W_0M^{-2}$ of the exciton in the well).

It remains to calculate the value of the action along the obtained optimal trajectory. Substituting (28) in (19) we obtain

$$S = W_0M^{-2} = W,$$

i.e., the extremal action is directly expressed in terms of the energy of the saddle state. The lifetime of the free exciton is estimated with exponential accuracy (in ordinary units) at

$$\tau_{\text{f.e.}} \sim \omega^{-1}\exp(W/\hbar\omega). \tag{29}$$

3. ADIABATIC APPROXIMATION

We begin the discussion of the applicability of the approximations made with the rigid-exciton approximation, by estimating the corrections to the calculated quantities in powers of the parameter m_e/m_h.

We have seen above that both in the saddle state and on the entire tunneling path the polarization well has a radius of the order of the exciton radius and a depth small, in the parameter m_e/m_h, compared with the internal energy E_i of the exciton. Such a well deforms slightly the exciton it contains, and the relative change of the wave function $\chi(\mathbf{r}_e - \mathbf{r}_h)$ of the internal motion, and hence of the operator $\hat{\rho}$ [see (7)], is of the order of m_e/m_h. This leads to small corrections in Eq. (18) for the wave function in the central region, and these alter Φ by $\sim m_e/m_h$. Of the same order is the relative change of the mean values of the kinetic T and potential U energies of the exciton in the polarization well and, in final analysis, of the total energy W of the saddle state. To estimate the corrections to the Schrödinger energy E we note that outside the well the "non-rigidity" of the exciton does not manifest itself in any way, so that the mass-center wave-function expression (11), the matching of which to (12) determines E, remains in force. This means that the corrections to E are of the order of $(m_e/m_h)E$ rather than $(m_e/m_h)W$, as might seem because of the relation $E = T - U$. Thus the estimates presented show that the corrections to all the calculated quantities are small in the parameter m_e/m_h, i.e., the rigid-exciton approximation yields the principal terms of the expansions for all the quantities in terms of the adiabatic small parameter m_e/m_h.

We examine now the restrictions imposed by the requirement that the lattice motions be slow compared with those of the electrons. In our case the internal energy of the exciton is high and the adiabaticity condition reduces in fact to smallness of the phonon energy $\hbar\omega$ compared with the binding energy of the exciton in the polarization well E (the Schrödinger energy).

On tunneling through the self-trapping barrier, the characteristic energy E is of the order of the energy W of the saddle state,[2] so that the adiabaticity condition takes the form

$$\hbar\omega \ll W = 1.07m_e^3e^4\varepsilon/\hbar^2m_h^3\varepsilon_\infty^3. \tag{30}$$

Since the exponential that determines the tunneling rate is

$$\exp(-W/\hbar\omega),$$

the condition (30) coincides with the condition that the tunneling be quasiclassical and in fact with the very condition that a self-trapping barrier exist.

We consider now the saddle state. It has a rigorous meaning so long as the phonon energy is lower than the Schrödinger energy in this state:

$$\hbar\omega \ll E_s = E_0 m_e^4 e^4 \tilde{\varepsilon}^2/\hbar^2 m_h^3 \varepsilon_\infty^4. \qquad (31)$$

When this condition is violated, the concept of saddle state loses an exact meaning, but this does not mean, generally speaking, vanishing of the self-trapping barrier. The restriction on the phonon frequency is stronger than (30), since $E \sim W/M \ll W$ (see Sec. 2). This raises the question of the barrier height in the case

$$E_s \ll \hbar\omega \ll W,$$

when the barrier exists but the saddle state has strictly speaking no meaning. In this case, since "on that side" of the barrier the binding energy E increases rapidly with increasing potential-well depth to states that are still close enough to the saddle state, the adiabaticity condition begins to be satisfied. The self-energy of the polarization well changes little in these states compared with the saddle state, so that the total energy[3] is $\mathscr{E} \approx W - \hbar\omega$. Thus, in the case considered the "trans-barrier" states with total energy $\mathscr{E} < W - \hbar\omega$ are described by the adiabatic approximation.

This allows us to conclude that in the case $E_s \ll \hbar\omega \ll W$, despite the absence of a true saddle state, expression (2) for the barrier height remains valid. The value of W is only smeared out and is lowered by a small amount of the order of $\hbar\omega$. It must be emphasized in this connection that $\hbar\omega$ is in general the usual scale of the corrections to the principal terms of the adiabatic approximation (see, e.g., Ref. 12).

4. DISCUSSION

To conclude, we compare our results (see the Introduction) with other results known to us. The work of Nasu and Toyozawa,[17] who calculated both the barrier height and the tunneling time, is based on exceedingly rough approximations. Their paper contains no explicit analytic expressions for the final results, so that comparison with their results is difficult.

Pekar *et al.*,[10] who determined the barrier height by a direct variational method, did not trace the asymptotic behavior as $m_e/m_h \to 0$. The equations in Ref. 10 show that the three-parameter Gaussian trial function used there yields for the barrier height the asymptotic expression

$$W = \frac{16}{25}\left(\frac{15}{2}\right)^{1/3}\left[\frac{m_e\varepsilon_0}{m_h(\varepsilon_0-\varepsilon_\infty)}\right]^{5/3}\left(\frac{\varepsilon_0-\varepsilon_\infty}{\varepsilon_0}\right)E_i, \qquad (32)$$

which differs from (1). The weaker dependence, compared with ours, on the adiabatic parameter $M = (m_h/m_e)[(\varepsilon_0-\varepsilon_\infty)/\varepsilon_0]$ is due the fact that the trial function of Ref. 10 does not reflect the fact that the wave function of the exciton mass center has two scales (see Sec. 1). At $M > 5$ our asymptotic expression yield a lower barrier height than Eq. (25). At the same time, the results of Ref. 10 show (see Fig. 1) that the asymptotic relation (25) is very remote. For example, at $\varepsilon_\infty = \tilde{\varepsilon}$ the asymptotic (25) reaches an accuracy of

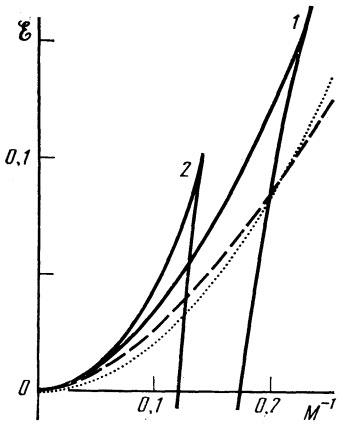

FIG. 1. Value of the functional $\mathscr{E}$ [see (3)] reckoned from the free-exciton energy in units of $m_e e^4/\hbar^2\varepsilon_\infty\tilde{\varepsilon}$, as a function of the parameter $M^{-1} = m_e\tilde{\varepsilon}/m_h\varepsilon_\infty$. Curves 1 and 2 were calculated from the variational equations of Ref. 10 at $\tilde{\varepsilon}/\varepsilon_\infty = 1$ and $\tilde{\varepsilon}/\varepsilon_\infty = 4$, respectively (the upper curve describes the saddle state, and the lower the self-trapping state). Dashed line—asymptotic plot of $\mathscr{E}(M^{-1})$ calculated from the equations of Ref. 10. Dotted line—exact asymptotic form of $\mathscr{E}(M^{-1})$.

10% only at $m_e/m_h < 50$. There are apparently no grounds whatever to regard the region of applicability of the exact asymptotic relation (1) as wide. This situation seems quite natural in light of the fact that the very existence of the self-trapping barrier calls for a large carrier-mass difference.[10,13]

Since the valence band of real AHC is degenerate,[6] comparison with experiment is meaningless. Furthermore, the band parameters of these crystals are far from well known. It is instructive, for example, that at the published values of m_e and m_h of those AHC in which self-trapping was reliably observed, there is no self-trapping minimum at all according to the theory with a nondegenerate valence band (the plots of Ref. 10).

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[1)] In full agreement with classical mechanics (see, e.g., Ref. 16, where in the general case only the principle of stationary (not necessarily least) action is valid.

[2)] During the initial state of the trapping, when there is no bound state or else its binding energy is low, the adiabatic approximation is, of course, not valid. This is of importance, however, only for the calculation of the coefficient in front of the exponential.

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