Energy transfer between the local centers with allowance for interaction of excitations with the lattice

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A change in the population of the electronic levels of the local centers due to the transfer of excitation in the case of a weak electron-phonon interaction causes a slow change in the equilibrium state of the lattice atoms. This leads to energy fluctuations of the electronic levels, affecting appreciably the kinetics of the excitation transfer, which may lead to its localization.

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Energy transfer between local centers has been studied in many papers.[1] The dipole-dipole interaction (or higher-multipole interaction) has been analyzed according to the perturbation theory in all theoretical papers in which the interaction of excitations with the lattice was taken into account. There are situations, however, in which the conditions of its applicability are not satisfied. In this paper we solve without using the perturbation theory the problem of the time-dependent evolution of the state of two centers, one of which was in the excited state at the initial moment of time and the other was in the ground state (the temperature is assumed to be zero degrees). We shall start with the Hamiltonian

$$\begin{aligned}\frac{1}{\hbar}H = {} & \epsilon_1 a_1^+ a_1 + \epsilon_2 a_2^+ a_2 + \epsilon_1 c_1^+ c_1 + \epsilon_2 c_2^+ c_2 + \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}\lambda} b^+_{\mathbf{k}\lambda} b_{\mathbf{k}\lambda} \\ & + \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}\lambda} a_2^+ a_2 (b_{\mathbf{k}\lambda} u^*_{\mathbf{k}\lambda} l^{i\mathbf{k}\mathbf{R}_a} + \text{h.c.}) + \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}\lambda} c_2^+ c_2 (b_{\mathbf{k}\lambda} u^*_{\mathbf{k}\lambda} l^{i\mathbf{k}\mathbf{R}_c} + \text{h.c.}) \\ & + V (a_1^+ a_2 + a_2^+ a_1)(c_1^+ c_2 + c_2^+ c_1), \end{aligned} \tag{1}$$

where ϵ_1 and ϵ_2 are the energies of the ground state and the excited state, a_1 and a_2 are the electron operators corresponding to the first center, c_1 and c_2 are the electron operators corresponding to the second center, $\mathbf{R}_a$ and $\mathbf{R}_c$ are the coordinates of the centers, $b_{\mathbf{k}\lambda}$ are phonon operators, $\omega_{\mathbf{k}\omega}$ are phonon frequencies, and V is the matrix element of the dipole-dipole interaction. We shall seek a solution of the Schrödinger equation $i\hbar\dot{\Psi} = H\Psi$ in the form

$$\Psi = \left(\prod_{\mathbf{k}\lambda} \exp(- g_{\mathbf{k}\lambda} b^+_{\mathbf{k}\lambda} + g^*_{\mathbf{k}\lambda} b_{\mathbf{k}\lambda}) \right)(a_1 a_2^+ c_1^+ + a_2 a_1^+ c_2^+) |0\rangle , \tag{2}$$

where $g_{\mathbf{k}\lambda}$, a_1, and a_2 are complex functions of time t. Since the electron subsystem, by definition, was in the $a_2^+ c_1^+ |0\rangle$ state at the initial moment of time and the in-

teraction V is such that it couples it only with the $a_1^+c_2^+|0\rangle$ state, the $a_2^+c_2^+|0\rangle$ and $a_1^+c_1^+|0\rangle$ states are not affected in any way and are therefore missing in Eq. (2). We shall insert (2) into the Schrödinger equation. Multiplying both sides of the equation by $\langle 0|c_1a_2\Pi_{k\lambda}\exp(g_{k\lambda}b_{k\lambda}^+ - g_{k\lambda}^*b_{k\lambda})$, $\langle 0|c_2a_1\Pi_{k\lambda}\exp(g_{k\lambda}b_{k\lambda}^+ - g_{k\lambda}^*b_{k\lambda})$, and $\langle 0|b_{k\lambda}(a_1^*c_1a_2 + a_2c_2a_1)\Pi_{k\lambda}\exp(g_{k\lambda}b_{k\lambda}^+ - g_{k\lambda}^*b_{k\lambda})$, we obtain a system of equations for $g_{k\lambda}$, a_1, and a_2

$$i\dot{a}_1\left[1 + \frac{1}{2}\sum_{k\lambda}(\dot{g}_{k\lambda}g_{k\lambda}^* - \dot{g}_{k\lambda}^*g_{k\lambda})\right] = \left[\epsilon_1 + \epsilon_2 - \sum_{k\lambda}(\omega_{k\lambda}u_{k\lambda}^*g_{g\lambda}\, l^{ikR_a} + \text{h.c.}\right]a_1 + Va_2,$$

$$i\dot{a}_2\left[1 + \frac{1}{2}\sum_{k\lambda}(\dot{g}_{k\lambda}g_{k\lambda}^* - \dot{g}_{k\lambda}^*g_{k\lambda})\right] = \left[\epsilon_1 + \epsilon_2 - \sum_{k\lambda}(\omega_{k\lambda}u_{k\lambda}^*g_{k\lambda}\, l^{ikR_c} + \text{h.c.}\right]a_2 + Va_1,$$

$$i\dot{g}_{k\lambda} = \omega_{k\lambda}g_{k\lambda} - \omega_{k\lambda}n_su_{k\lambda}, \tag{3}$$

where

$$n_s = n_{2c}\, l^{-ikR_c} + n_{2a}\, l^{-ikR_a}, \quad n_{2c} = \langle\Psi|c_2^+c_2|\Psi\rangle = |a_2|^2,$$

$$n_{2a} = \langle\Psi|a_2^+a_2|\Psi\rangle = |a_1|^2.$$

As shown below, the rate of variation of n_s is given by max (V, f_e), where $f_e = \Sigma_{k\lambda}\omega_{k\lambda}|u_{k\lambda}|^2[1 - \cos k(\mathbf{R}_a - \mathbf{R}_c)]$, and ω_D is the Debye frequency. We can therefore confine ourselves to a quasi-static solution of the third equation in (3), $g_{k\lambda} = n_su_{k\lambda}$, correct to within terms $|V|\omega_D \ll 1, (f_e/\omega_D) \ll 1$. Inserting this expression into the first two equations in (3), we find, within the indicated error limits,

$$\begin{aligned} i\dot{a}_1 &= (\epsilon_1 + \epsilon_2 - 2fn_{2a} - 2f'n_{2c})a_1 + Va_2, \\ i\dot{a}_2 &= (\epsilon_1 + \epsilon_2 - 2fn_{2c} - 2f'n_{2a})a_2 + Va_1, \end{aligned} \tag{4}$$

where

$$f = \sum_{k\lambda}\omega_{k\lambda}|u_{k\lambda}|^2 \qquad f' = \sum_{k\lambda}\omega_{k\lambda}|u_{k\lambda}|^2\cos k(\mathbf{R}_a - \mathbf{R}_c).$$

The f constant is the Stokes energy shift (or the Huang-Reese factor). The f' constant describes the shift of the level of one atom under the influence of a strain produced by by another atom. Since $n_{2a} + n_{2c} = |a_1|^2 + |a_2|^2 = 1$, incorporation of f' leads to the renormalization $f \to f - f' \equiv f_e$.

We introduce the variables $n = |a_2|^2 - |a_1|^2$, $p = a_1a_2^* + a_1^*a_2$, and $r = ia_1a_2^* - ia_1^*a_2$. Differentiating these variables and using Eq. (4), we find

$$\begin{aligned} \dot{n} &= -2Vr, \\ \dot{p} &= -2f_enr, \\ \dot{r} &= 2Vn + 2f_enp. \end{aligned} \tag{5}$$

We shall assume that the impurity ($n_{2a} = |a_1|^2 = 1, n_{2c} = |a_2|^2 = 0$) is excited at the initial moment of time. Accordingly, we shall determine the integration constants C. Eliminating p and r in (5), we find

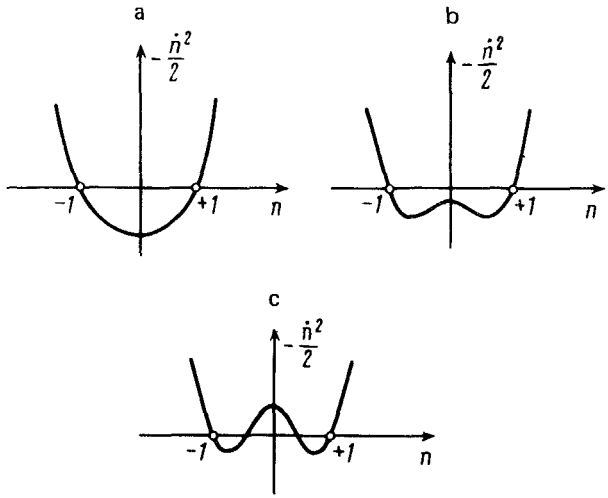

FIG. 1. The shape of the effective potential when (a) $a_{fe}<\sqrt{2}\,|V|$, (b) $\sqrt{2}\,|V|<2|V|$, and (c) $f_e>2|V|$.

$$\frac{\dot{n}^2}{2}+(2V^2-f_e^2)\,n^2+\frac{1}{2}f_e^2\,n^4+C=0, \tag{6}$$

consistent with the equation of state for a classical particle in the given charge image. Its shape, which depends on the relationship between the parameters f_e and V, is shown in Fig. 1. It can be seen that at $f_e<2|V|$ the excitation at one center is transferred to another center (from the point $n=-1$ to the point $n=1$) after a certain time. This situation changes if $f_e\geqslant 2|V|$ (Fig. 1c). The solution of Eq. (6) is (see Ref. 2)

$$n^2(t)=1-\frac{4V^2}{f_e^2}\,\mathrm{Sn}^2 f_e t,$$

where Sn x is an elliptic sine which depends on the parameter $\lambda=2|V|/f_e$ as well as on the indicated argument. At $\lambda\ll 1$ Sn $x=\sin x$ the oscillations are low-amplitude harmonic oscillations. Thus the electron-phonon interaction, which is weak in the usual sense of the word ($f_e\ll\omega_D$), nonetheless, localizes the excitation at one lattice site if $f_e>2|V|$.

The population fluctuations discussed above have a real physical meaning if their period is much smaller than the excitation lifetime. These conditions are satisfied for a ruby, for example, at low temperatures (see Ref. 2 and the literature cited therein).

The interaction discussed by us reveals interesting systematic features of the excitation propagation in a crystal. After taking the constant f into account, we have instead of (4), the following expression ($\varepsilon=\epsilon_2$, $\epsilon_1=0$, and n is the number of the lattice site):

$$i\dot{a}_n = (\epsilon - 2f|a_n|^2)a_n + \sum_m V_{nm}a_m .$$

This gives a nonlinear Schrödinger equation with an anisotropic mass for the states with a large radius. We shall confine ourselves to a one-dimensional case and take into account the interaction V of only the nearest neighbors. We shall seek a solution of Eq. (7) in the form $a_n = \varphi(an - st)l^{-iE_k t + ikan}$. Inserting α_n in Eq. (7), we find $s = -2Va \sin ka$ and a one-dimensional Schrodinger equation for $\varphi(x)$, which, as in known,[3] has the solution $\varphi(x) = (\sqrt{\kappa a/2})(1/\mathrm{ch}\kappa x)$. In our case $\kappa = \kappa_k = -(f/2a\, V \cos ka)$, $E_k = \epsilon + (2 + (\kappa_k a)^2)V \cos ka$, and a is the lattice constant. We see from the expression for κ_k that the interaction f, however weak, plays a key role for the states with $ka = \pi/2$, which are always microscopic. In the case $f > 2|V|$, however, all the exciton states are soliton-like and microscopic. The region $ka \approx \pi/2$ is clearly identifiable because the effective mass of the exciton, which was determined from the second derivative of the spectrum obtained at $f = 0$, becomes infinite. Even a weak interaction, therefore, leads to a localization.

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