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Self-trapping in quasi-one-dimensional solids

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Electronic excitations in highly anisotropic quasi-one-dimensional solids are often regarded as being in a one-dimensional system. Here we determine the degree of anisotropy that is required to justify treating an excess carrier in this manner. In particular, we consider the adiabatic ground-state eigenfunctions for an excess electron in an electronically anisotropic solid in which the electron-lattice interaction is short ranged. In this circumstance an excess carrier in a one-dimensional system always self-traps to form a finite-radius (generally, large) polaron. On the other hand, in a three-dimensional system, an excess carrier will either self-trap to form a severely localized (small) polaron or it will not self-trap at all. We determine that the one-dimensional behavior typically requires the ratio of the electronic transfer integral for the easy direction to that for the transverse directions to be at least two orders of magnitude. Thus, estimated electronic anisotropies in many quasi-one-dimensional systems are not sufficient for these systems to be regarded as one dimensional with regard to self-trapping.

I. INTRODUCTION

Charge carriers in quasi-one-dimensional systems are frequently regarded as being self-trapped to form one-dimensional polarons. As was shown some time ago,[1] self-trapping in a truly one-dimensional system differs qualitatively from that in systems of higher dimensionality. In particular, a charge carrier in a one-dimensional system will always self-trap to form a polaron. Furthermore, this polaron expands in spatial extent continuously as the ratio of the intersite transfer energy to the electron-lattice coupling energy is increased. Quite distinct from this, in a three-dimensional system self-trapping is dichotomous. The charge carrier either self-traps to form a severely localized *small* polaron or it does not self-trap at all. Thus, in approaching the question of self-trapping in real anisotropic materials one must develop a criterion for one-dimensionality. Here we employ an adiabatic approach to this problem.

It is found that one-dimensional behavior will prevail if the binding energy associated with a one-dimensional polaron exceeds one-half the electronic bandwidth associated with electronic motion transverse to the quasi-one-dimensional chain. The binding energy of a one-dimensional molecular-crystal-model polaron is $E_p = W/12(a/L)^2$,[2] where W is the one-dimensional electronic bandwidth, L is the polaron half-length, and a is the intersite separation. This generally yields quite modest estimates of the large (one-dimensional) polaron binding energy: at very most ~ 0.1 eV. Thus, for one-dimensional polaron theory to be applied to quasi-one-dimensional systems such as *trans*-polyactelene, the transverse contribution to the electronic bandwidth must be comparably small. This corresponds to an anisotropy of electronic transfer integrals of at least 2 orders of magnitude. Failing to meet this criterion means that the charge carrier will not form a large one-dimensional polaron. Rather, it will remain as a quasifree particle which will move, albeit tenuously, transverse to the quasi-one-dimensional chain.

Band structure calculations yield estimates of the anisotropy of only 10 to 100 in various quasi-one-dimensional solids.[3,4] Accepting these estimates implies that one-dimensional polarons will not form in these quasi-one-dimensional solids.

II. ADIABATIC CALCULATION

We begin with the tight-binding eigenvalue expression for an electron in a solid:

$$(E - E_{\mathbf{g}})a_{\mathbf{g}} = -\hat{\sum_{\mathbf{h}}} J_{\mathbf{g},\mathbf{g}+\mathbf{h}} a_{\mathbf{g}+\mathbf{h}} \; . \tag{1}$$

Here E is the eigenvalue of the system, $E_{\mathbf{g}}$ is the energy of the system with the electron confined to site $\mathbf{g}$, and $J_{\mathbf{g},\mathbf{g}+\mathbf{h}}$ is the electronic transfer integral linking site $\mathbf{g}$ with site $\mathbf{g}+\mathbf{h}$. The amplitude for the electron's occupancy of site $\mathbf{g}$ ($\mathbf{g}+\mathbf{h}$) is denoted by $a_{\mathbf{g}}$ ($a_{\mathbf{g}+\mathbf{h}}$). As indicated by the circumflex over the $\mathbf{h}$ summation, the summation only extends to adjacent sites in each direction.

For definiteness, we consider a molecular solid in which the site index $\mathbf{g}$ refers to a molecule. Each molecule is associated with a single deformation parameter $x_{\mathbf{g}}$ which refers to the deviation of atoms of the molecule from their (carrier-free) equilibrium positions. Then, with a short-range linear electron-lattice interaction, the energy of an electron confined to the $\mathbf{g}$th equivalent molecule of the molecular crystal is given by

$$\epsilon_{\mathbf{g}} = -F x_{\mathbf{g}} \; , \tag{2}$$

where F is the electron-lattice force.

We assume that the electron can adjust to the instantaneous atomic positions. In particular, we employ the adiabatic approach and seek the eigenstates of the system which minimize the sum of the electron energy and the vibrational potential energy. That is, we neglect the vibrational kinetic energy and minimize the energy eigenvalue E with respect to atomic displacements. In analogy with the procedure of Ref. (2), the energy minimization condition is found to be

$$\sum_{\mathbf{g}'}(\partial E_{\mathbf{g}'}/\partial x_{\mathbf{g}})\,|a_{\mathbf{g}'}|^2=0\ , \tag{3}$$

for all $\mathbf{g}$. Within the adiabatic approach,

$$E_{\mathbf{g}}=\epsilon_{\mathbf{g}}+(k/2)\sum_{\mathbf{g}}x_{\mathbf{g}}^2\ , \tag{4}$$

where k is the stiffness constant associated with the molecular deformations. Inserting Eq. (4) into Eq. (3) we then obtain the minimization condition

$$x_{\mathbf{g}}=F\,|a_{\mathbf{g}}|^2/k\ . \tag{5}$$

Inserting the minimizing values of the deformation parameters from Eq. (4) into Eq. (1), we obtain the nonlinear eigenvalue equations which characterize self-trapping in a molecular crystal:

$$\left[E-(F^2/2k)\sum_{\mathbf{g}'}|a_{\mathbf{g}'}|^4+(F^2/k)\,|a_{\mathbf{g}}|^2\right]a_{\mathbf{g}}=-\hat{\sum_{\mathbf{h}}}J_{\mathbf{g},\mathbf{g}+\mathbf{h}}a_{\mathbf{g}+\mathbf{h}}\ . \tag{6}$$

Multiplying this Eq. (6) by $a_{\mathbf{g}}^*$ and summing over $\mathbf{g}$ we obtain an expression for the adiabatic ground-state energy:

$$E=-\sum_{\mathbf{g}}\hat{\sum_{\mathbf{h}}}J_{\mathbf{h}}a_{\mathbf{g}}^*a_{\mathbf{g}+\mathbf{h}}-(F^2/2k)\sum_{\mathbf{g}}|a_{\mathbf{g}}|^4\ . \tag{7}$$

We now consider an anisotropic solid with easy transfer in the x direction. The x direction is associated with the nearest-neighbor transfer integral J_1 and intersite separation a. Transverse to the x direction, in the y and z directions, the transfer is associated with the transfer integral J_t and the intersite separation b. Equation (7) may then be rewritten as

$$\begin{aligned}E=&-J_l\sum_{\mathbf{g}}a_{\mathbf{g}}^*(a_{\mathbf{g}+\mathbf{i}a}+a_{\mathbf{g}-\mathbf{i}a})\\&-J_t\sum_{\mathbf{g}}a_{\mathbf{g}}^*[(a_{\mathbf{g}+\mathbf{j}b}+a_{\mathbf{g}-\mathbf{j}b})+(a_{\mathbf{g}+\mathbf{k}b}+a_{\mathbf{g}-\mathbf{k}b})\\&-(F^2/2k)\sum_{\mathbf{g}}|a_{\mathbf{g}}|^4\ .\end{aligned} \tag{8}$$

Passing to the continuum limit, the ground-state energy is rewritten as:

$$\begin{aligned}E=&(-J_la^2/2)\int d\mathbf{r}\,\psi^*(\mathbf{r})\partial^2\psi(\mathbf{r})/\partial x^2\\&+(-J_tb^2/2)\int d\mathbf{r}\,\psi^*(\mathbf{r})\partial^2\psi(\mathbf{r})/\partial y^2\\&+(-J_tb^2/2)\int d\mathbf{r}\,\psi^*(\mathbf{r})\partial^2\psi(\mathbf{r})/\partial z^2\\&-(2J_l+4J_t)-(F^2/2k)\int d\mathbf{r}\,|\psi(\mathbf{r})|^4\ .\end{aligned} \tag{9}$$

Dropping the constant term $(2J_l+4J_t)$ and integrating the kinetic energy terms by parts yields

$$\begin{aligned}E=&(J_la^2/2)\int d\mathbf{r}\,|\partial\psi(\mathbf{r})/\partial x|^2\\&+(J_tb^2/2)\int d\mathbf{r}\,|\partial\psi(\mathbf{r})/\partial y|^2\\&+(J_tb^2/2)\int dr\,|\partial\psi(\mathbf{r})/\partial z|^2\\&-(F^2/2k)\int dr\,|\psi(\mathbf{r})|^4\ .\end{aligned} \tag{10}$$

If $\psi(\mathbf{r})$ were the exact ground-state eigenfunction, E would be the ground-state energy. However, we do not have an explicit expression for $\psi(\mathbf{r})$. Thus we may attempt to get a qualitative understanding of the effects of anisotropy by doing a variational calculation presuming that the ground-state eigenfunction is spatially separable. Denoting the longitudinal extent of the wave function by R_1 and the transverse extent of the wave function by R_t, the ground-state energy will be of the form

$$E=T_l/R_l^2+2T_t/R_t^2-E_b/R_lR_t^2\ . \tag{11}$$

Here T_l and T_t are, respectively, the kinetic energies for extension in the longitudinal and transverse directions: $T_l\approx 2J_l$ and $T_t\approx 2J_t$. E_b is the small-polaron binding energy $F^2/2k$. The longitudinal and transverse spatial extents, R_l and R_t, are measured in units of the cutoff distances appropriate to a discrete lattice. These cutoffs arise because the continuum approach loses its validity for very small transverse and longitudinal decay lengths. Namely, the energy contributions saturate when the eigenfunction's spatial extents fall much below an intersite separation. Thus R_l and R_t are dimensionless quantities that are constrained to be greater than or equal to unity.

Three dimensionality then corresponds to R_l and R_t both exceeding unity. Two dimensionality corresponds to R_l being unity and R_t being greater than unity: severe localization in one dimension. One dimensionality corresponds to R_t being unity and R_l being greater than unity: severe localization in two dimensions. Severe localization at a single site, small-polaron formation, is represented by $R_l=R_t=1$.

A system's ground state corresponds to the minimum of the energy with respect to the two spatial extents R_l and R_t. We are, therefore, interested in the behavior of the function $E(R_l,R_t)$. The energy as a function of the radius R has been previously found for idealized three-, two-, and one-dimensional systems.[1] The present result, Eq. (11), reduces to the idealized cases in the appropriate limits. Namely, the three-dimensional isotropic $(T_l=T_t)$ results are found for $E(R,R)$ as a function of R. The two-dimensional results are found from $E(1,R_t)$ as a function of R_t. The one-dimensional results are found from $E(R_l,1)$ as a function of R_l.

We now study the stability of the one-dimensional solution in an anisotropic system. Namely, the energy minimum which exists in the idealized one-dimensional case $T_t=0$ is at $R_l=2T_l/E_b$ and $R_t=1$. We examine the stability of this minimum as the transverse transfer energy T_t is increased. For this purpose we write down the first derivative of the energy with respect to R_t:

$$\partial E/\partial R_t=(-4T_t+2E_b/R_l)R_t^{-3}\ . \tag{12}$$

We note that the first derivative of the energy with respect to R_t is not generally zero at $R_l=2T_l/E_b$ and

$R_t=1$. Rather, because of the $R_t=1$ cutoff, the one-dimensional minimum occurs when $\partial E/\partial R_t$ is positive at this point. That is, we have a one-dimensional minimum when

$$-4T_t+2E_b/(2T_l/E_b)=-4T_t+E_b^2/T_l>0 . \qquad (13)$$

In other words, the stability condition for a one-dimensional polaron is

$$E_b^2>4T_lT_t . \qquad (14)$$

This is the condition for *dynamic* stability—the condition that the large polaron exist.

We can reexpress it in terms of the binding energy of the large one-dimensional polaron $E_{b,1}$ calculated in Ref. (2). In our terms, $E_{b,1}=E_b^2/6T_l$. This is the amount that the energy of a large polaron on a one-dimensional chain lies below the energy of a one-dimensional free particle. The dynamic stability condition is then

$$E_{b,1}>2T_t/3 . \qquad (15)$$

However, $E_{b,1}$ is *not* the binding energy for a *quasi*-one-dimensional system. Rather, the binding energy in a quasi-one-dimensional system is $E_{b,1}-2T_t$. The added energy contribution $-2T_t$ is the kinetic energy associated with confining the particle to a chain [See Eq. (11) when $R_t=1$]. Thus, energetic stability, relative to the three-dimensional free state, requires

$$E_{b,1}>2T_t . \qquad (16)$$

Thus, the condition for energetic stability, Eq. (16), is stronger than that for dynamic stability, Eq. (15).

Hence, as T_t is increased from zero the system will first find it energetically favorable for the polaron to decompose such that the electron becomes unbound and extends over all three dimensions. The minimum corresponding to the formation of the one-dimensional polaron is then no longer an absolute minimum. With a further increase of T_t the one-dimensional polaron ceases to be dynamically stable. That is, there is then no longer an energy minima associated with the one-dimensional polaron.

III. NUMERICAL ESTIMATES

Here we contemplate whether the anisotropy of various quasi-one-dimensional systems is sufficient to justify treating them as one-dimensional systems with regards to self-trapping. For this purpose it is useful to use Eqs. (37) and (41) of Ref. 2 to express the binding energy of the one-dimensional polaron in terms of its half-length, L, and J_l. We have

$$E_{b,1}=(J_l/3)(a/L)^2 . \qquad (17)$$

Note that the one-dimensional bandwidth W is $4J_l$. The condition for energetic stability of the one-dimensional polaron with respect to the three-dimensional free carrier is then

$$(J_l/3)(a/L)^2>4J_t . \qquad (18)$$

Thus, the ratio of the transverse to longitudinal transfer integrals, J_l/J_t, must exceed $12(L/a)^2$ for the energetic stability of the one-dimensional polaron. With polaron sizes such that L/a is comparable to five, say, this requires a 3-order-of-magnitude anisotropy of the transfer integrals. Various electronic structure calculations provide anisotropy estimates considerably below this.[3,4] Thus, acceptance of these estimates would lead us to conclude that a large one-dimensional polaron formation will not occur in the materials in question.

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