Energy and charge trapping by localized vibrations: Electron-vibrational coupling in anharmonic lattices

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We study the time dependence of the energy redistribution between an initially localized electron and the vibrations of a one-dimensional anharmonic lattice. Numerical solutions show the periodic electron-lattice energy exchange, in contrast to the usual irreversible gradual decrease of the electronic energy. This energy trapping is shown to occur due to the appearance of localized vibrations, induced by strong enough electron-vibrational coupling in the anharmonic lattice. For these strong-coupling situations, we observed both localized (trapped) and conductive electronic charge.

The interaction between electronic and vibrational subsystems is crucial for such phenomena as electron transfer, conductivity, nonradiative decay, and energy transport. Experimentally, it is now possible to go to the space and time scales where the detailed time dependence of these processes can be seen. Very impressive examples are known for molecular systems, quantum wells and quantum wires, electron beam–thin film interaction, etc.[1-10] The main goal of the present paper is to demonstrate, in a rather simple model, that this transfer and its time dependence may be drastically changed by the appearance of localized vibrations, generated in anharmonic chains by the electron-vibrational coupling.

Consider the situation when at time $t = 0$ an electron appears, due to the phototransfer or any other process, at one of the lattice sites. It is the time evolution of this state that interests us, especially the time dependence of electron-lattice energy redistribution and of electron localization (small polaron) caused by the electron-lattice interaction.

In the tight-bonding approximation for the electron states and the linear approximation for "diagonal," on-site, vibronic coupling, the electron-vibrational Hamiltonian takes the form

$$H = \sum_n \{ -\beta(a_{n+1}^+ a_n + a_n^+ a_{n+1})$$
$$+ g a_n^+ a_n (x_{n+1} - x_{n-1} - 2R_0) \} + H(x) , \qquad (1)$$

where a_n, a_n^+ are the electronic operators on site n, β and g are the electron transfer integral and vibronic constant, x_n and R_0 are the coordinates of nth atom and equilibrium lattice constant, respectively. In Eq. (1) $H(x)$ is the Hamiltonian of free vibrations

$$H(x) = \sum_n p_n^2/2m + W(\cdots x_n \cdots) ,$$

the first term being the kinetic energy E_{kin} of the lattice atoms and the second one describing the potential of the atom-atom interaction, that may be chosen as a harmonic, Morse or Lennard-Jones type.

To treat the time evolution of the electron-vibrational system we use the Born-Oppenheimer version of the time-dependent self-consistent field (TDSCF) approximation (see Ref. 11), i.e., we write the total wave function $\Psi(r,x;t)$ as a product of electronic $\psi(r,t)$ and vibrational $\Phi(x,t)$ functions

$$\Psi(r,x;t) = \psi(r,t)\Phi(x,t) . \qquad (2)$$

Each term depends on time and can be found from the solution of the related time-dependent Schrödinger equation. The Born-Oppenheimer electronic Hamiltonian (H_{el})

$$H_{\mathrm{el}} = \sum_n \{ -\beta(a_{n+1}^+ a_n + a_n^+ a_{n+1})$$
$$+ g a_n^+ a_n (x_{n+1} - x_{n-1} - 2R_0) \} \qquad (3)$$

contains the atom coordinates x as parameters, so the electronic energy $E(x,t) = \langle \psi(r,t)|H_{\mathrm{el}}|\psi(r,t) \rangle$ depends on both t and x, the latter in turn being time dependent. The behavior of the vibrational subsystem is described by the Hamiltonian $H_{\mathrm{vib}}(x,t) = H(x) + E(t,x)$ where the x-dependent electronic energy $E(t,x)$, determined above, plays a role of a vibronic part of the potential for atom motion. Thus we start with evolving, from $t=0$ to $t=dt$, the initial electronic state for some initial values of atomic velocities and coordinates by numerical solution of the electron Hamiltonian in the tight-bonding model. Then the new potential for atom motion is found, and new velocities and coordinates are determined that are used to find out a new electronic function at $t+dt$, and so on.

We choose Lennard-Jones potentials to describe nearest-neighbor atom-atom interactions, $W(R) = \varepsilon(-\xi^6 + \xi^{12})$, $\xi = (\sigma/R)$, R is the interatomic distance, with equilibrium distance $R_0 = \sigma(2)^{1/6} = 4$ and potential depth $\varepsilon = 0.01$; typical values of β and g vary between 0.01–0.001 and 0.005–0.020 correspondingly (all values in a.u.), and the mass m of atoms has been chosen as 60 proton masses. We use a classical description of the vibrations, so the coordinates x_n and velocities v_n can be found from Newton's equations of motion. The results below are given for a linear chain, chosen long enough to avoid any boundary influence for the time scale of several characteristic chain vibrations. For $T=0$ at $t=0$ all the

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atoms have been placed at equilibrium positions with zero velocities, at $T\neq0$ sets of initial coordinates and velocities have been generated in a standard way, and the averaging has been performed over $N0$ initial sets (trajectories); for the temperatures that we considered the results do not depend on $N0$ if $N0>100$, so we used $N0=100$.

Figures 1(a) and 1(b) show the spatial and time dependence of electronic density. In regular and "frozen" chains the occupation P_0 of the site where the electron appears at $t=0$ rapidly vanishes due to spreading of the electron over all equivalent sites. If the vibronic constant g is small, vibronic coupling does not change the situation, because the vibronically induced atomic displacements are also small and evolve very slowly [the case of Fig. 1(a)]. However, with increased vibronic coupling local distortions appear simultaneously, or even before the electron completely leaves the initial site. Thus an additional vibronically induced lattice potential appears, consistent with the initial electronic distribution, that self-traps the electron. At short times before effective self-trapping the electron decay is practically independent of g, but after that the electron starts to feel the additional

potential that results in nonvanishing P_0 at long times, and in a nonuniform distribution of the electron over the chain, in sharp contrast to the case of Fig. 1(a). Figure 1(b) illustrates both the time for producing such localized polaron states at large-enough vibronic coupling, and the resulting localization of the electron, for details see Ref. 12. The electronic distribution may be considered as consisting of two components—the delocalized "zonelike" one, corresponding to the part of the electron that has escaped from the initial site before the evolving of the self-trapping potential, and the localized part, characterized by the value of P_0, that shows the amount of electron density that has remained trapped near the initial site. Features representative of both delocalized and localized states of electron in a molecular adsorbed layer on a metal surface were found and examined recently.[13]

Since coupling of the electron to the lattice causes displacements of the chain atoms, the chain gains energy from the electron. Figure 2 shows the time-dependence of the chain kinetic energy at different values of vibronic constant and transfer parameter. With increased vibronic coupling at fixed β, more energy is transferred to the vibrations from the electron. At fixed g the amount of

electron density (a)
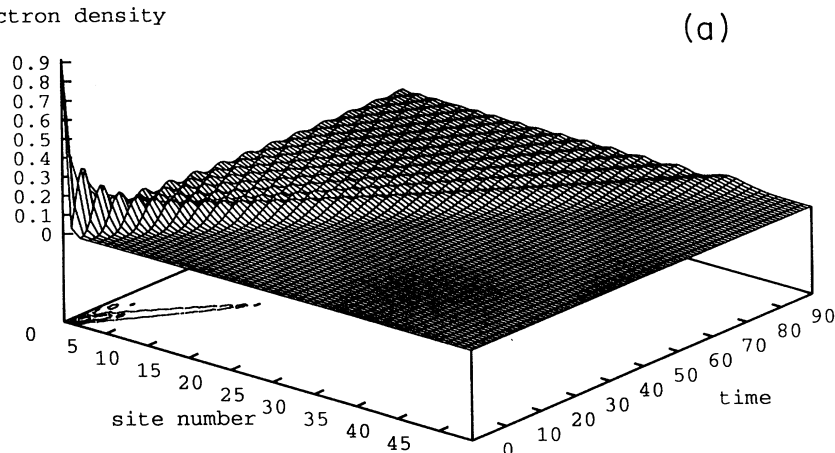
electron density (b)
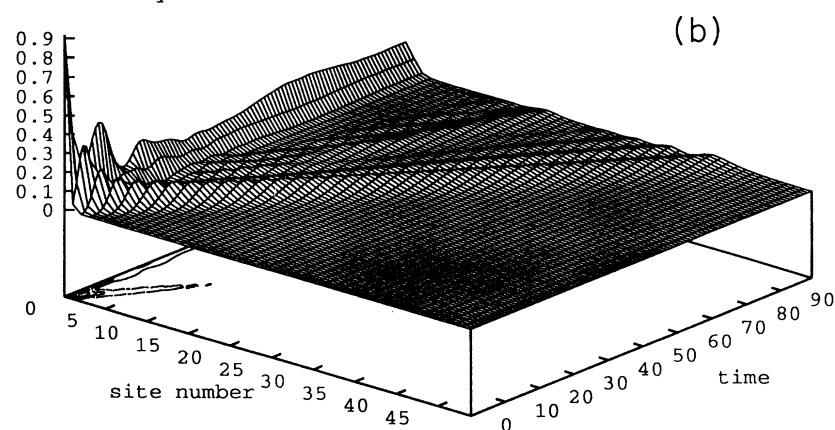

FIG. 1. (a) Spatial and time dependence of the electron density at weak coupling, $\beta=0.001$ and $g=0.005$, showing uniform spreading of the electron over the chain (in Figs. 1 and 9 at $t=0$ the electron is located on site 0, the time is measured in units 200 a.u.; due to the symmetry only the right half of the chain is shown). (b) Spatial and time dependence of the electron density at strong coupling, $\beta=0.001$ and $g=0.015$, clearly illustrating both the localized and delocalized components of the electron distribution.
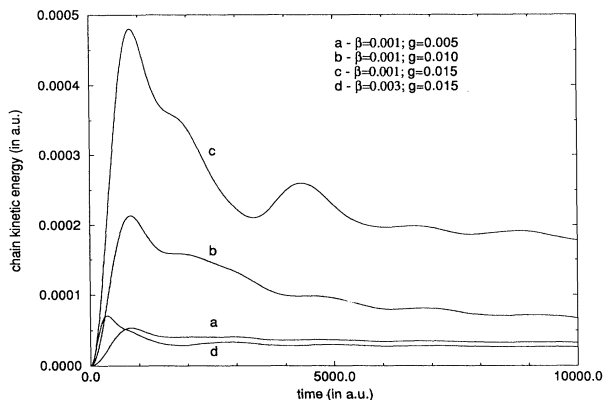
FIG. 2. Kinetic energy of the chain for different vibronic coupling and electron transfer integrals, $T = 0$.

energy transferred from the electron to the chain increases essentially with the increase of electron localization. We see that for increased g/β, localization is stronger and more energy is received by the chain. The greatest energy transfer is reached at $\beta = 0$; in this case the energy transfer in a harmonic chain is proportional to g^2. For harmonic lattices the dimensionless parameter $\alpha = g^2/2K\beta$ determines the strength of coupling where K is the interatomic harmonic force constant. At not very strong coupling one can estimate the coupling in an anharmonic lattice by the same parameter, with K_2 instead of K where K_2 is the harmonic component of the real anharmonic potential. For the Lennard-Jones potentials

$$K_2 = (d^2W/dR^2)_{R=R0}$$

$$= 6\varepsilon[-7(\sigma/R_0)^6 + 26(\sigma/R_0)^{12}]/R_0^2 \qquad (4)$$

which gives $K_2 \approx 10^{-2}$ for the parameters we use. Then cases (a) and (d) of Fig. 2 correspond to an intermediate coupling ($\alpha \approx 1$), while the curve (c) illustrates the strong-coupling case ($\alpha \approx 10$).

Due to vibronic coupling the electron generates displacements of the surrounding atoms, and the resulting wave packet, corresponding to the superposition of chain vibrational modes with different velocities and phases, evolves and spreads with time over the chain. This process is irreversible, i.e., due to the large number of active vibrational modes energy cannot be transferred back to the electron on any experimental time scale. Figures 3(a) and 3(b) give examples of the time dependence of the electron energy given by the Hamiltonian (3) with instant $x_n(t)$ found by solving the vibrational Hamiltonian. The cases (a) illustrate just such a behavior, showing that there are practically no oscillations of $E(x,t)$ for weak coupling. However, as curves b,c show, at strong vibronic coupling these oscillations appear and they damp very slowly. While these behaviors are clearest in the case of $\beta = 0$, where the electron must remain at its initial site, Fig. 3(a) shows that these trapping behaviors are also seen for $\beta \neq 0$, if the vibronic coupling is sufficiently strong. This demonstrates the process of energy going

back from the chain to electron, instead of spreading over vibrational band states. Such a process can take place only if the electron-generated displacements do not easily go away from the site where the electron is located, into the collective chain vibrations. The decrease of oscillations describes the relaxation of local excitations of the chain, and as Fig. 4 shows, the relaxation of the highly excited chain with strong vibronic coupling is much slower than at weak coupling.

The appearance of such stable mixed electron-vibrational localized polaron excitations can be of a great importance for the problem of energy redistribution and long-distance energy transfer in strong-coupled electron-vibrational systems. To find the mechanism responsible for this effect, we have repeated the same calculations of energy redistribution for a harmonic chain, whose elastic force constants correspond to the harmonic terms of Lennard-Jones potentials. One can see from Fig. 5, that the relaxation in the harmonic chain does not show any dependence upon the vibronic constant. Therefore the phenomenon is related to the anharmonicity of the system, and thus is different from the periodic, at much lower frequency, energy exchange between electron and vibrations found recently by the molecular dynamics modeling in the harmonic chain.[14] Note that the temperature increase causes stronger damping, however, as Figs. 6(a) and 6(b) show, these oscillations are still much more pronounced than in the harmonic case.
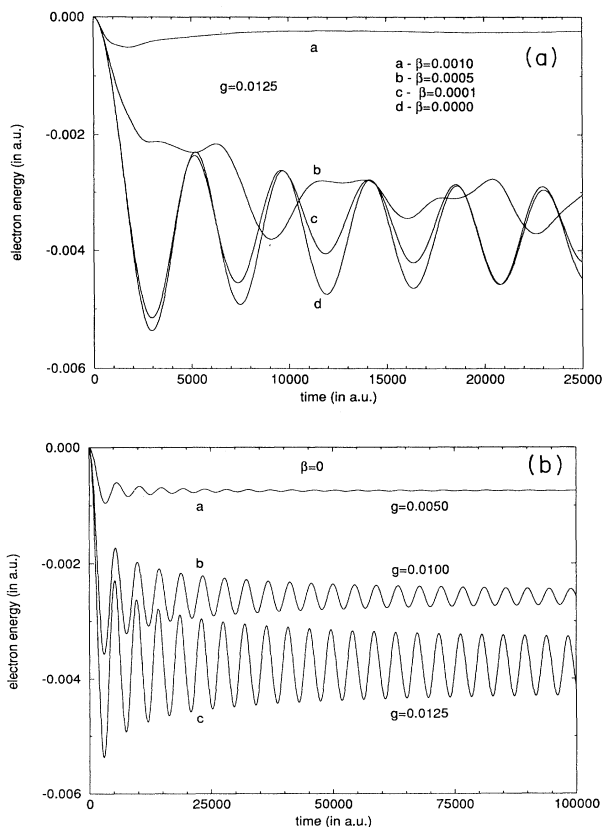

FIG. 3. Electronic energies at different couplings and transfer integrals, $T = 0$.
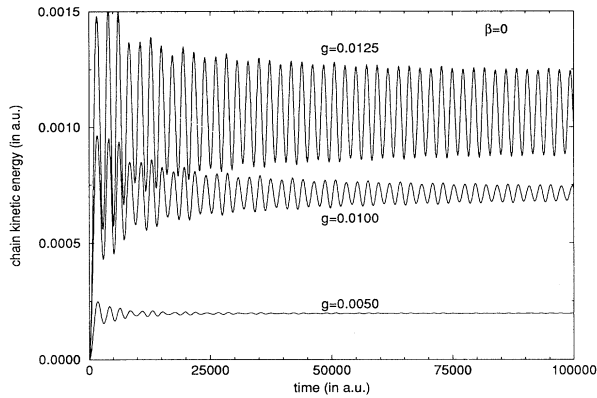
FIG. 4. Chain kinetic energy at different coupling, for fully localized electron, $\beta=0$, $T=0$.

For this localization behavior we have suggested a trapping mechanism that is based on the idea that the electron-vibrational coupling causes vibrational mode localization. The vibronic coupling changes the equilibrium interatomic distances; then, due to anharmonicity the harmonic and anharmonic chain force constants are changed also, and this can result in the appearance of local modes. In this picture the electron and local vibrations are always localized in the same area; thus it can lead to slow damping of the energy exchange between the electron and these local vibrations. Note the nonmonotonic dependence of this phenomenon on the vibronic constant. The stronger the coupling is, the more localized the electron; the more it is localized the larger are the local displacement that it causes, the larger the displacements are the greater are the changes of lattice force constants—as a result the threshold behavior with increase of g is realized, clearly seen in Figs. 3 and 4.

Let us estimate the magnitude of this effect. At strong vibronic coupling the electronic energy $E(x,t)$ is almost linear in the atomic displacements, so the harmonic constant of the renormalized interatomic potential is equal to the parameter K_2, given by Eq. (4) with R_0 replaced by the new equilibrium positions. As Fig. 7 shows the vib-
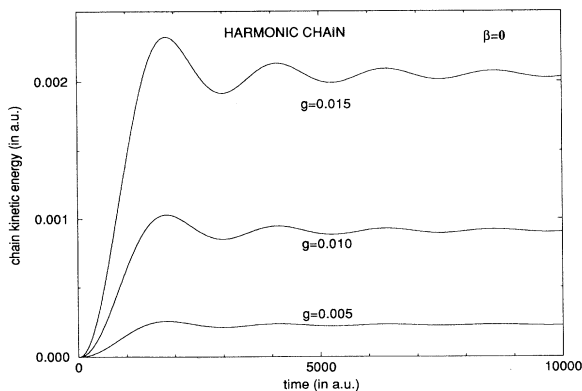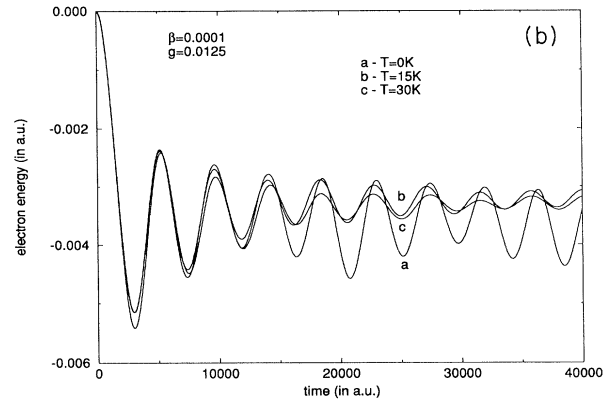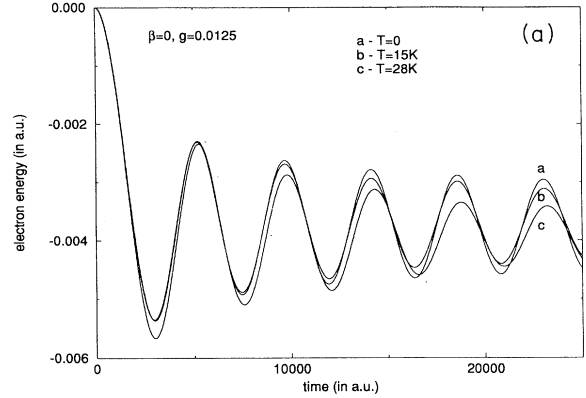

FIG. 6. Temperature damping of the electron energy oscillations.

ronically induced renormalization of the harmonic force constant can be rather efficient (our calculations show that the atomic displacements ~ 0.1 are typical for the situations under consideration), and the relative change of the local harmonic constant, $\gamma = K_2'/K_2$, may greatly differ from 1. Due to the symmetry the vibronically in-
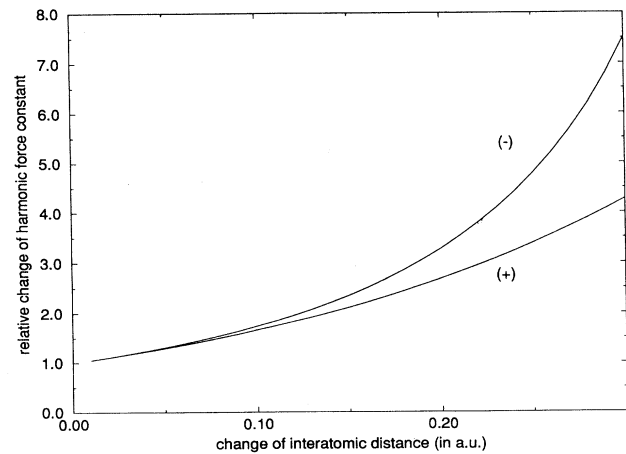

FIG. 5. Kinetic energy of harmonic chain at $\beta=0$, and different coupling, $T=0$.

FIG. 7. Dependence of the harmonic (quadratic) force constant K_2 of anharmonic chain upon the forced change of interatomic distance. The y axis shows the value of ratio K_2'/K_2 [curve $(-)$] or $(K_2'/K_2)^{-1}$ [curve $(+)$] depending upon a decrease or increase of the bond length.
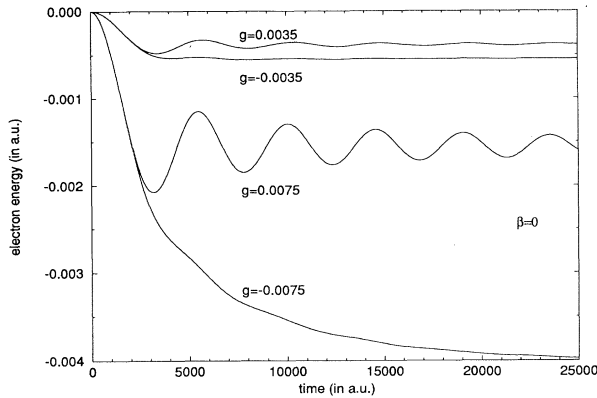
FIG. 8. Dependence of energy redistribution between the electron and chain upon the sign of vibronic constant, $T = 0$.

duced change of the lattice force constant influences only the even vibrations around the initially occupied site 0. The chief interactions are between the site 0 and its two neighbors. Following Refs. 18 and 19 one can write the equation

$$(\gamma - 1)\omega_D^{2*}[G(2) - G(0)]/4 = 1 \tag{5}$$

that determines the vibrational spectra of the chain with locally changed harmonic constant. In Eq. (5) $\omega_D = 2(K_2/m)^{1/2}$ is the maximal, Debye, frequency of the chain, and vibrational Green functions G have the form

$$G(n) = (1/N) \sum_{l=-N/2}^{N/2} \exp(2\pi i l n / N) / [\omega_0^2(2\pi l / N) - \omega^2] , \tag{6}$$

ω_0 being the frequencies of an ideal chain. In a monoatomic lattice there can be two types of local vibrations, i.e., quasilocal ones, appearing inside the continuum spectra of the acoustic band, and local vibrations with frequencies above ω_D. For the latter, which show stiffening of the lattice force constant and are more decoupled from the rest of the vibrations, the Green function has the form ($z = \omega/\omega_D$)

$$G(n) = -(-1)^n[2z^2 - 1 - 2z(z^2 - 1)^{1/2}]^{|n|}/\omega_D^2 z(z^2 - 1)^{1/2} \tag{7}$$

and, inserting (7) into (5) one finds

$$(\omega/\omega_D)^2 = \gamma^2/[4(\gamma - 1)] . \tag{8}$$

chain kinetic energy
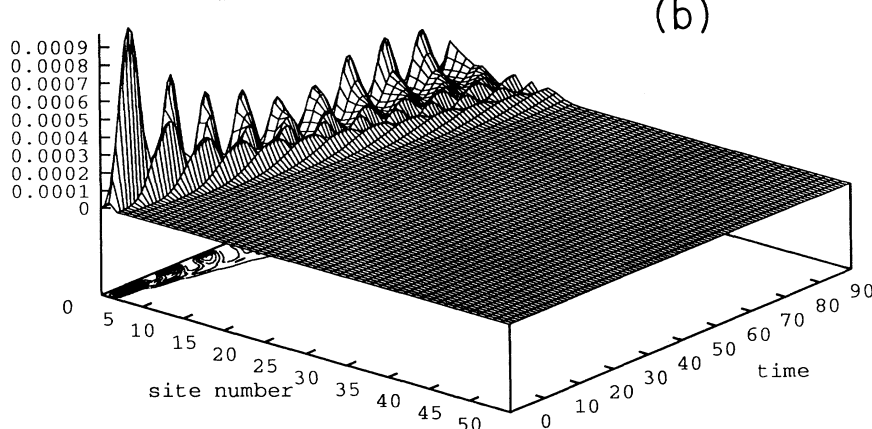
(a)

chain kinetic energy

(b)
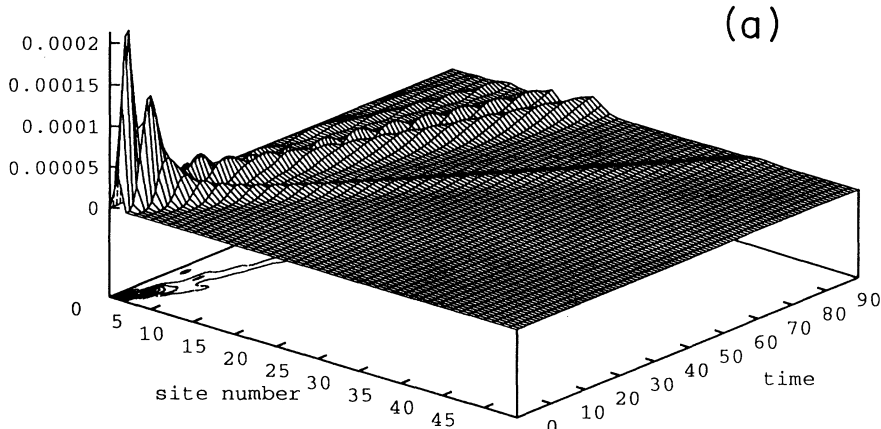
FIG. 9. (a) Spatial and time dependence of the chain kinetic energy (in a.u.) for $\beta = 0.001$ and $g = 0.015$, showing free vibration traveling over the chain. (b) Spatial and time dependence of the chain kinetic energy (in a.u.) for $\beta = 0.0001$ and $g = 0.015$, illustrating the energy trapping.

The last equation shows that for the appearance of the local vibrations with $\omega > \omega_D$ the condition

$$\gamma > 2 \qquad (9)$$

must be fulfilled. It is known[15,16] that for local vibrations around site 0, the corresponding displacements of surrounding atoms fall off as γ^{-n}, where n is the neighbor number, so at large γ the vibrations are strongly localized indeed.

Figure 7 shows that the change of K_2 depends upon the sign of vibronic constant. Positive values of g cause the increase of effective local frequency. As a result the vibronic effects have to decrease because the stiffer lattice resists the vibronic-induced rearrangements more efficiently. When g is positive a second effect can be seen: oscillations in the energy transfer between lattice and electron due to the appearance of a local mode of frequency above ω_D. These effects are illustrated in Fig. 8, which demonstrates the fast monotonic decrease of the electron energy for the vibronic constant $g < 0$, while for the vibronic constant of the same absolute value, but different, positive, sign, the electron energy loss is smaller and shows oscillations.

As Fig. 7 shows the criterion (9) is very likely fulfilled (note that in anharmonic chains this criterion for the local vibration appearance is even softer), and so the vibronic coupling can generate vibration modes localized in the vicinity of electron location. To check that, we have performed calculations of the spatial dependence of the chain kinetic energy as a function of time [Figs. 9(a) and 9(b)]. If the coupling is not strong enough, the usual picture of the vibrational excitations leaving the region, where they have been generated, and spreading over the chain, can be seen [Fig. 9(a)]. On the other hand, Fig. 9(b) clearly illustrates two main features of the trapping situation at strong coupling: (a) the chain energy is localized near the initially occupied site and spreads over the chain very slowly, (b) the oscillations in the chain energy, caused by the energy backfeeding of the electron, are well pronounced. These results strongly support the key role

of the localized vibrations.

However, it is known that intrinsic localized modes may be generated in anharmonic lattices at a high-enough level of excitation.[17-21] Thus one can suppose that, beside the mechanism suggested above, in a situation under consideration the electron-vibrational interaction can generate, at strong-enough coupling, such a localized vibrational excitation, and then a periodic exchange of energy between the electron and that mode (with which the electron interacts most efficiently), takes place. To check that we have calculated the relaxation behavior of highly excited local vibrations in the same anharmonic chain, but without vibronic coupling. This requires solving the chain equations of motion with initial velocities and coordinates, corresponding to the highest peak in the time dependence of chain energy in Fig. 4, cases of larger chain energies have been considered also. The results demonstrate that the vibrations damp very quickly, thus the energy trapping by vibrational solitons is insufficient for the model under consideration. The main reasons for that perhaps are that (a) the breathing-type localized vibrations centered around the site of the initial electronic state are unstable (in contrast to the breathing type modes centered at the midpoint between adjacent sites, which are stable)[17,20,21] and (b) in monoatomic chains with realistic potentials these modes usually do not occur.[22]

In conclusion, we have shown the possibility of the long-lived periodic exchange of the energy between initially localized electron and lattice vibrations. Our calculations give evidence that this effect is due to the appearance of localized vibrations, generated by strong vibronic coupling in anharmonic lattices, and that this can result in long-lived charge localization.

[1]P. F. Bagwell, A. Kumar, and R. Lake, in *Quantum Effect Physics, Electronic and Applications*, edited by K. Ismail, T. Ikoma, and H. I. Smith, Institute of Physics Conference Series No. 127 (Institute of Physics, Bristol, 1992), p. 45.

[2]A. Nakano, R. K. Kalia, and P. Vashishta, Appl. Phys. Lett. **62**, 3470 (1993).

[3]M. A. Stroscio, K. W. Kim, G. J. Iarfate, M. Dutta, and H. Grubin, Philos. Mag. Lett. **65**, 173 (1992).

[4]M. Mihailidi, Q. Xing, K. M. Yoo, and R. R. Alfano, Phys. Rev. B **49**, 3207 (1994).

[5]E. S. Peterson, B. J. Schwartz, and C. B. Harris, J. Chem. Phys. **99**, 1693 (1993).

[6]M. Michaud, P. Cloutier, and L. Sanche, Phys. Rev. B **44**, 10 485 (1991); L. Sanche, in *Ultrafast Reaction Dynamics and Solvent Effects*, edited by Y. Gauduel and R. J. Rossky, AIP Conf. Proc. 298 (AIP, New York, 1994), p. 499.

[7]D. Kuszner and N. Schwentner, J. Chem. Phys. **98**, 6965 (1993).

[8]N. Schwentner, M. E. Fajardo, and V. A. Apkarian, Chem. Phys. Lett. **154**, 237 (1989).

[9]G. Stock and W. Domcke, Chem. Phys. **124**, 227 (1988).

[10]R. B. Barnett, U. Landman, and A. Nitzan, J. Chem. Phys. **90**, 4413 (1989); **91**, 5567 (1989).

[11]R. B. Gerber and M. A. Ratner, Adv. Chem. Phys. **70**, 97 (1988); J. Phys. Chem. **92**, 2087 (1988).

[12]B. G. Vekhter and M. A. Ratner, J. Chem. Phys. **101**, 9710 (1994).

[13]C. B. Harris, Bull. Am. Phys. Soc. **39**, 1230 (1994).

[14]G. Kopidakis, C. M. Soukoulis, and E. N. Economou, Phys. Rev. B **49**, 7036 (1994).

[15]A. A. Maradudin, *Theoretical and Experimental Aspects of the Effects of Point Defects and Disorder on the Vibrations of Crystals* (Academic, New York, 1966).

[16]G. S. Zavt, *Theory of Crystal Lattice Vibrations* (Tartu State University, 1966) (in Russian).

[17]K. W. Sandusky, J. B. Page, and K. E. Smith, Phys. Rev. B **46**,

6161 (1992).

[18]S. R. Bickman, A. J. Sievers, and S. Takeno, Phys. Rev. B **45**, 10 344 (1992).

[19]S. R. Bickman, S. A. Kiselev, and A. J. Sievers, Phys. Rev. B **47**, 14 206 (1993).

[20]K. W. Sandusky and J. B. Page, Phys. Rev. B **50**, 866 (1994).

[21]J. B. Page, Phys. Rev. B **41**, 7835 (1990).

[22]S. A. Kiselev, S. R. Bickham, and A. J. Sievers, Phys. Rev. B **48**, 13 508 (1993).