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Energy localization and delocalization in a nonlinear chain on a substrate

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The dynamics of a linear chain of atoms with a central heavy atom is shown to be significantly affected by the presence of an external periodic potential representing a substrate. The system exhibits several dynamical phases, some of which are consequences of the existence of the substrate. The phases differ in the degree of energy localization and in other dynamical properties. It is shown that, unlike in a chain that is not subject to an external potential, energy localization is possible for heavy to light mass ratios that are of order one. Possible chemical applications are briefly mentioned.

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The phenomenon of energy localization in nonlinear systems is of intrinsic interest as well as of applicability in various fields of science and engineering (e.g., vibrations of large structures). In the realm of chemical physics intramolecular vibrational redistribution (IVR) has received a great deal of attention both as a basic intramolecular process and as a possible means to control intramolecular reactions. The aim in controlled intramolecular reactions is to keep a bond excited (a localized vibrational excitation) long enough, e.g., with respect to Rice-Ramsberger-Kassel-Marcus [1] lifetimes to allow for bond selective chemistry [2]. Recently some evidence for possible bond selectivity has been presented [3]. As mentioned, the problem of energy localization is of rather general nature; the results below are conveniently described in the language of the dynamics of a linear molecule. IVR in such molecules was studied almost exclusively in the gas phase. The consequences of placing a molecule in an external potential which may represent a substrate form the subject of the present study.

The pioneering work of Fermi, Pasta, and Ulam [4] demonstrated that a system of coupled nonlinear oscillators need not be ergodic. A large body of research followed this observation [5]. An important application is the problem of spreading of vibrational energy in molecules [6–10]. A significant result in the latter domain is due to Lopez and Marcus (LM [11]) who studied the dynamics of energy transfer in a linear chain composed of a small number of coupled "atoms," all of which, with the exception of the central "heavy atom," were identical. A small initial energy imparted to the leftmost atom was shown to result in an eventual average (over time) equality of the energy on both sides of the heavy atom whereas in a range of high enough initial energies (imparted to that atom)—very small energy transfer to the right side was observed. The transition to energy localization in LM-like systems has been studied only when the heavy to light atom mass ratio is relatively large. When the chain resides on a substrate, some major qualitative as well as quantitative changes in the dynamics occur. In this paper, we present a numerical and analytical study of the role of an external potential (the substrate) on the energy transfer along a chain. As the initial energy supplied to the chain is tuned one observes four regimes: complete transfer (I), almost no transfer (II), chaos and transfer (III), and dissociation or diffusion of the chain (IV). The first transition, between (I) and (II) can be mapped on the discrete nonlinear Schrödinger equation [12–15].

Consider the following (dimensionless) equation of motion of an odd number, N, of atoms, interacting by Morse potentials and residing on a "substrate:"

$$\ddot{\xi}_1+\pi\sin(2\pi\xi_1)=\frac{\gamma}{\beta}\{\exp[-\beta(\xi_2-\xi_1)] -\exp[-2\beta(\xi_2-\xi_1)]\}\ , \tag{1a}$$

$$\ddot{\xi}_i+\pi\sin(2\pi\xi_i)=\frac{\gamma}{\beta}\{\exp[-\beta(\xi_{i+1}-\xi_i)] -\exp[-2\beta(\xi_{i+1}-\xi_i)]\} -\frac{\gamma}{\beta}\{\exp[-\beta(\xi_i-\xi_{i-1})] -\exp[-2\beta(\xi_i-\xi_{i-1})]\}\ , \tag{1b}$$

$$\ddot{\xi}_N+\pi\sin(2\pi\xi_N)=\frac{\gamma}{\beta}\{\exp[-\beta(\xi_N-\xi_{N-1})] -\exp[2\beta(\xi_N-\xi_{N-1})]\}\ . \tag{1c}$$

Here ξ_i are the coordinates of the atoms normalized by the periodicity of the substrate, a; κ is the ratio of the mass of the ith atom to that of the any light atom [i.e., $\kappa(N+1)/2=\kappa,\kappa_i=1$ for $i\neq(N+1)/2$], β is a dimensionless interaction strength parameter and γ is a dimensionless measure of the strength of the potential. Define the left-side energy as

$$E_L=\sum_{i=1}^{(N+1)/2}\tfrac{1}{2}\dot{\xi}_i^2+\tfrac{1}{2}[1-\cos(2\pi\xi_i)]$$
$$+\sum_{i=1}^{(N+1)/2-1}\frac{\gamma}{\beta}\{\exp[-2\beta(\xi_{i+1}-\xi_i)]$$
$$-2\exp[-\beta(\xi_{i+1}-\xi_i)]-1\}\ , \qquad (2)$$

with a similar definition of the right-side energy, E_R. Clearly, the total energy $E_L+E_R+\frac{1}{2}\kappa\xi_{(N+1)/2}^2$ is conserved. When the amplitudes of the vibrations are not too large, Eqs. (1) can be simplified [16] by omitting fourth order terms in the ξ_i's and nonlinear terms in $\xi_{(N+1)/2}$ (since the amplitude of vibration of the heavy atom is very small [16]). A multiple scale expansion method [16] can be used to show that the amplitude corresponding to $\xi_{(N+1)/2}$ is $O(\epsilon^2)$ while the other amplitudes are $O(\epsilon)$. This simplification describes properly the transition from the "normal" mode to the "local" mode behavior and it is corroborated by numerical simulations of Eqs. (1). For instance, for the $N=3$ chain one obtains

$$\ddot{\xi}_1+\Omega^2\xi_1+\alpha_2\xi_1^2+\alpha_3\xi_1^3=\gamma\xi_2\ , \qquad (3a)$$

$$\ddot{\xi}_2+(\Omega^2+\gamma)\xi_2=\gamma(\xi_1+\xi_3)\ , \qquad (3b)$$

$$\ddot{\xi}_3+\Omega^2\xi_3-\alpha_2\xi_3^2+\alpha_3\xi_3^3=\gamma\xi_2\ . \qquad (3c)$$

Numerical results for $N>3$ demonstrate that the essential qualitative features obtained for $N=3$ hold at least up to $N=15$ and that Eqs. (3) and their generalization to large N describe properly the first transition. As mentioned, the validity of the simplification leading to Eqs. (3) can be assessed in the framework of a multiple scale expansion [16]. In deriving Eqs. (3) we have defined $\Omega^2=\omega^2+\gamma$, $\alpha_2=\frac{3}{2}\gamma\beta$, $\alpha_3=\frac{7}{6}\gamma\beta^2-\frac{1}{3}\omega_0^4$, and $\omega_0^2=2\pi^2$. The latter frequency represents the effect of the substrate and it has a major role in controlling the energy transfer. Note that α_3 is negative for small values of $\gamma\beta^2$, whereas α_2 is always positive. The multiple scale expansion technique [16] and other methods all produce the same *reduced* equations of motion from Eqs. (3). A simple way to obtain these equations is to assume the following ansatz:

$$\xi_1=a(\tau)\exp(\iota\Omega t)+a^*(\tau)\exp(-\iota\Omega t)\ , \qquad (4a)$$

$$\xi_2=b(\tau)\exp(\iota\Omega t)+b^*(\tau)\exp(-\iota\Omega t)\ , \qquad (4b)$$

$$\xi_3=c(\tau)\exp(\iota\Omega t)+c^*(\tau)\exp(-\iota\Omega t)\ . \qquad (4c)$$

Here $\tau\equiv t/\kappa$, i.e., τ is a "long" time scale and $1/\Omega$ is a "short" one and x^* denotes the complex conjugate of x. Upon substituting this ansatz into the equation of motion, Eqs. (3), and reading off the leading contributions corresponding to the frequency Ω one obtains [assuming again that $b(\tau)$, which corresponds to the heavy atom, is a slow function of τ]:

$$2\iota\Omega\dot{a}=h|a|^2a+g(a+c)\ , \qquad (5a)$$

$$2\iota\Omega\dot{c}=h|c|^2c+g(a+c)\ , \qquad (5b)$$

where $h=(4\alpha_2^2/\Omega^2)-3\alpha_3$ and $g=\gamma^2/(-\kappa\Omega^2+\Omega^2+\gamma)$. Define $|a|^2+|c|^2=E$. It is easy to see that E is a constant of motion of Eqs. (5). These equations constitute a particular case of the well known self-trapping equation, which has been widely studied, e.g., in Refs. [12–14]. Define the amplitudes A and C by $a=A\exp[-\iota(g+hE)x]$ and $c=C\exp[-\iota(g+hE)x]$ where $x\equiv\tau/2\Omega$. This transformation is similar to those invoked in Refs. [12–14]. Clearly, $E=|A|^2+|C|^2=\text{const}$. Next define the parametrization: $A=R\cos(\Theta)\exp(\iota\phi)$ and $C=R\sin(\Theta\exp(\iota\psi)$. Using these definitions it follows from Eqs. (5) that the phase difference $\chi=\phi-\psi$ and the angle $\mu\equiv2\Theta$ satisfy the equations:

$$\chi_y=\epsilon\cos(\mu)+\cos(\chi)\cot(\mu)\ , \qquad (6a)$$

$$\mu_y=\sin(\chi)\ , \qquad (6b)$$

where $y\equiv2g\chi,\epsilon=E/E_c$, and the critical energy is defined by $E_c\equiv-2g/h>0$. A detailed analysis of the consequences of Eqs. (6) is presented elsewhere [16]. Following this analysis, the chain of atoms undergoes a dynamical phase transition at $\epsilon=1$, which alters the extent of energy transfer from one side of the chain to the other. The transition may be realized only for an appropriate set of initial conditions. Here we discuss only the case which corresponds to the LM initial conditions $\chi=\pi/2$, and $\Theta=0$, i.e., the initial state in which all atoms assume their equilibrium positions and only the leftmost atom has nonvanishing kinetic energy. This solution can be obtained from Eqs. (6) by assuming that χ is a function of μ at all times. A straightforward manipulation then yields [for $\chi(0)=\pi/2$ and $\mu(0)=0$] $\cos\chi=-(\epsilon/2)\sin(\mu)$ and $\ddot{z}_y+(\epsilon^2/4)\sin(z)=0$, where $z=2\mu$, which is the well known equation for a pendulum. We wish to reiterate that other initial conditions do not correspond to this simplification. This equation (for the pendulum) is known to possess two kinds of solutions. Given the above initial conditions the solution is a rotation for $\epsilon<2$. In this case μ is unbounded and there is clearly complete energy transfer. When $\epsilon>2$ the solution is a vibration and μ is bounded. In the latter case only partial energy transfer occurs.

The transition energy at which there is a transition between the two kinds of solutions, and which corresponds to $\epsilon=2$, is $E=2E_c$, i.e., $-4\Omega_g/h=-4\gamma^2\Omega^2/[h(-\kappa\Omega^2+\Omega^2+\gamma)]$. The latter relation defines a critical mass ratio κ_c, below which the transition cannot occur: $\kappa_c=1+\gamma/\Omega^2$. Recall that $\Omega^2=\omega_0^2+\gamma$, where ω_0^2 represents the effect of the substrate. In the absence of a substrate, i.e., when $\omega_0=0$, the critical energy is given by $2E_c=4\gamma^2/h(-\kappa+2)$. It is easy to check that $E_c^0/E_c\rightarrow\omega_0^4$ as $\omega_0\rightarrow\infty$, i.e., the presence of substrate decreases the value of the critical energy above which there is localization. This conclusion is of possible practical importance since it means that the substrate weakens the condition of the heavy to light atom mass ratio for energy localization to occur: in practice this ratio does not have to be much larger than unity. The aforementioned conclusion holds for $N > 3$ as well.

Next we present some results of numerical simulations of Eqs. (1). Figure (1) presents the power spectra corresponding to ξ_1 and ξ_2 below the transition point E_c. The

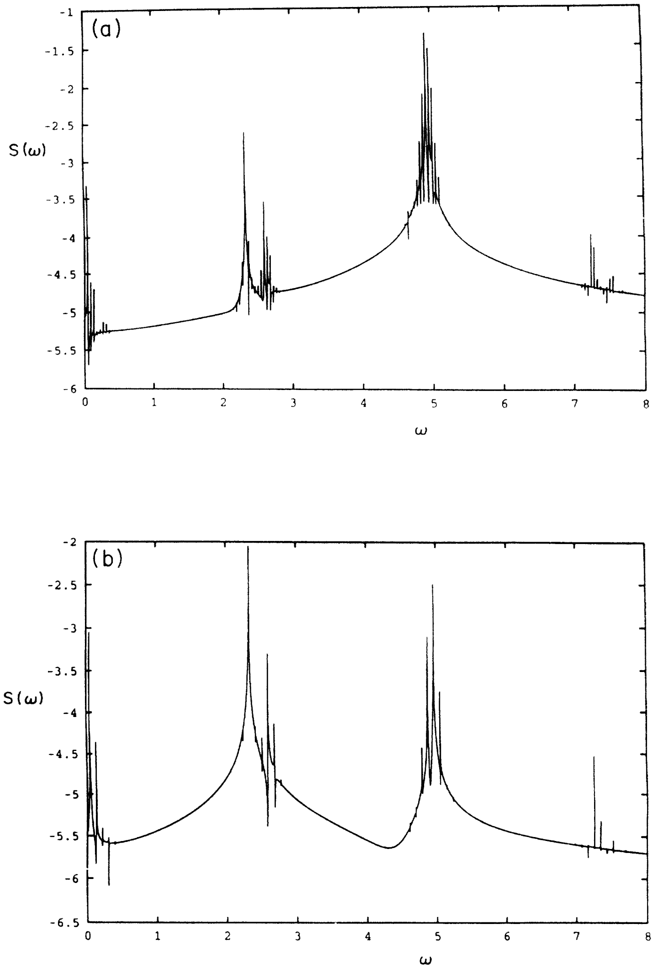

FIG. 1. Power spectra of the displacements of (a) the leftmost atom and (b) the heavy atom for N = 3. The other parameters are $v_0=0.45$, $\kappa=5$, $\gamma=5$, and $\beta=1$. Note the small frequency $\Delta\omega$ in the spectra.

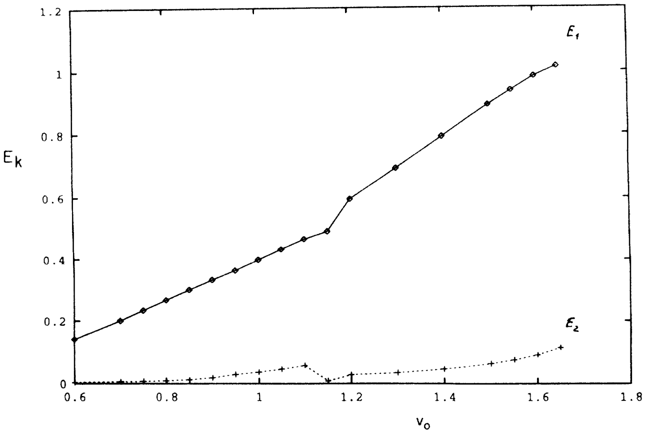

FIG. 2. Single atom kinetic energies versus v_0 (see text) for $N=3$. Squares: the leftmost atom; crosses: heavy atom. The other parameters are $\kappa=5$, $\gamma=5$, and $\beta=1$.

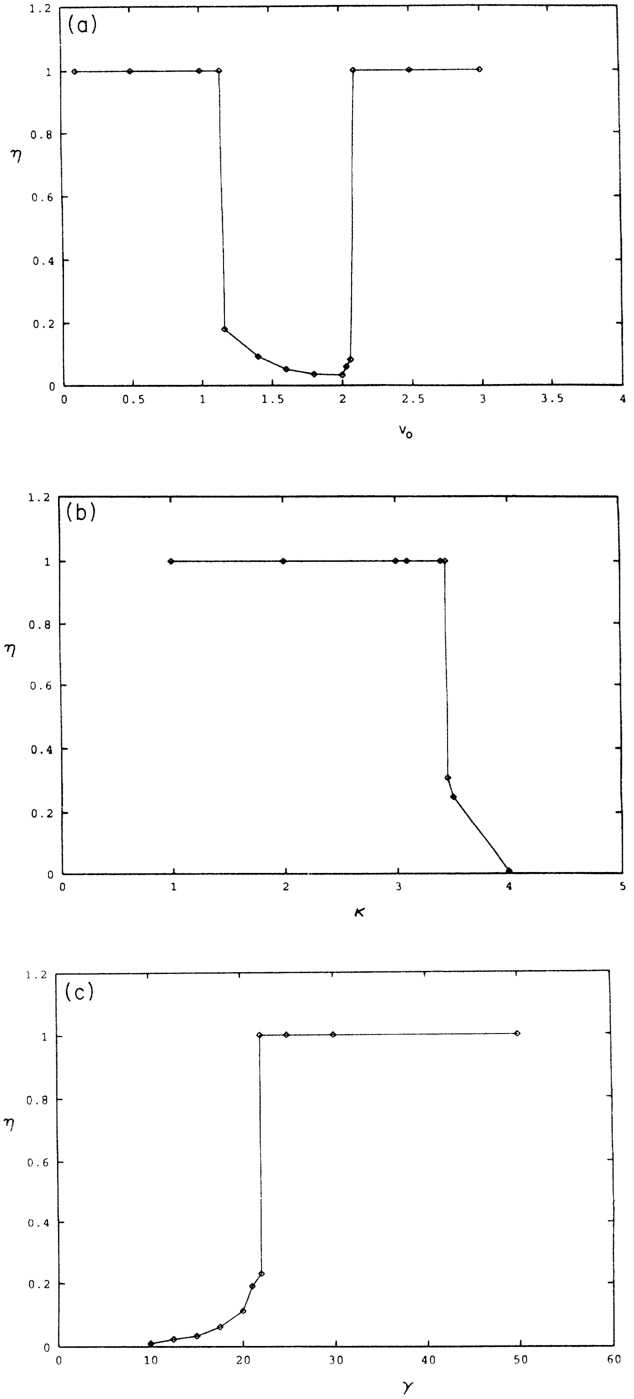

FIG. 3. The energy transfer coefficient $\eta=E_R/E_L$ for $N=5$ as a function of (a) v_0 with $\gamma=15$, $\beta=1$, and $\kappa=5$. (b) κ with $\gamma=15$, $\beta=1$, and $v_0=1.8$. (c) γ with $\kappa=5$, $\beta=1$, and $v_0=1.8$.

initial conditions are the same as in LM. As expected on the basis of linear theory and weakly nonlinear analysis, the power spectra exhibit three major peaks corresponding to the linear eigenmodes: ω_1 and ω_3 correspond to the symmetric and antisymmetric modes, respectively, and ω_2 corresponds to low frequency motion of the heavy atom. The modulation frequency $\Delta\omega=\omega_3-\omega_1$ satisfies $\Delta\omega \propto \sqrt{1-\epsilon}$ for $\epsilon<1$, while, for $\epsilon>1, \Delta\omega \propto \sqrt{\epsilon^2-1}$. At the transition point $\Delta\omega=0$, as expected on the basis of the theory presented above.

Besides the effect of lowering the transition energy, the substrate gives rise to rich dynamical behavior above the transition point. As the energy is raised above the transition point [for the set of parameters given in Figs. (1)] one observes three dynamical phases, while from the point of view of the energy transfer alone, there are only two phases. Following the transition at $2E_c$, the amplitude of the motion of the heavy atom is relatively small and the dependence of the corresponding frequency ω_2 on E_0 is very weak. At $v_0 \simeq 1.1-1.5$ (here v_0 is the initial velocity of the leftmost atom, i.e., $v_0=\sqrt{2E_0}$) the ratio ω_1/ω_2 equals 2 and beyond this resonant range these two frequencies strongly depend on E_0 yet they seem to be commensurate. The amplitude of motion of the heavy atom is enhanced by a resonant mechanism. Figure (2) displays the transition to resonance in the plot of the kinetic energies of the leftmost and heavy atoms, respectively, versus v_0. A further transition at $v_0 \simeq 1.7$ gives rise to chaotic dynamics (III) and complete energy transfer is restored. When the energy is raised even further the chain dissociates or performs diffusive motion on the substrate (IV).

The dependence of the degree of energy transfer (on several parameters), as measured by $\eta=E_R/E_L$, is demonstrated for the case $N=5$ in Fig. (3). Figure (3a) exhibits two transitions. The first transition leads the chain from its delocalized state ($\eta=1$) to a localized one ($\eta \ll 1$). The second transition brings about chaotic behavior and restores the complete energy transfer ($\eta=1$). The transition from the delocalized phase to the localized one is also evident in Figs. (3b), (3c). Notice that in the latter plots there is no second transition, since for the corresponding values of the additional parameters [v_0 and γ for Fig. (3b) and v_0 and κ for Fig. (3c)] there is no chaotic state. Figure (4) demonstrates that the case $N=9$(η versus v_0) exhibits the same qualitative properties as those corresponding to $N=3$ and 5.

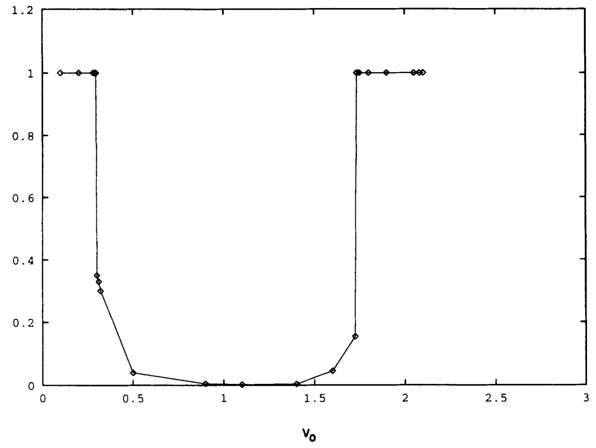

FIG. 4. The energy transfer coefficient $\eta=E_R/E_L$ for $N=9$ as a function of v_0 with $\gamma=5$, $\beta=1$, and $\kappa=5$.

The fact that the symmetric and antisymmetric solutions correspond to close eigenfrequencies gives rise to a low frequency mode $\Delta\omega$ which plays a major role in the energy transfer process. Indeed we have checked that a $N=4$ atomic chain containing a heavy atom, which cannot have a symmetric mode, does not allow for energy transfer unless the energy is high enough to allow for chaotic dynamics. Numerical studies of larger symmetric chains ($N=5-15$) reveal, for low excitation energies, a (quasi)linear spectrum containing N major modes, which can be divided into pairs, corresponding to close frequencies, consisting of a symmetric and an antisymmetric mode each, and an additional slow mode which corresponds to the vibration of the heavy atom.

In summary, we have demonstrated that the coupling to the substrate is responsible for the arising of distinct features in the dynamics of the chain. The presence of the substrate helps to keep the energy localized. It decreases the minimal mass of the "heavy" atom required for localization and it decreases the transition energy. These conclusions suggest the importance of introducing a substrate in studying IVR processes in molecules. The theoretical framework presented in this work is clearly classical, though, we believe, the results should be relevant to real molecules.

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