

Targeted Energy Transfer through Discrete Breathers in Nonlinear Systems

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(Received 10 November 2000; published 26 September 2001)

We propose a simple, novel mechanism for inducing highly selective and efficient energy transfer and focusing in certain discrete nonlinear systems. Under a precise condition of nonlinear resonance, when a specific amount of energy is injected as a discrete breather at a donor system, it can be transferred as a discrete breather to another weakly coupled acceptor system. This general mechanism could be relevant for energy transfer in bioenergetics and electron transfer in chemical reactions and could be used for engineering functional materials and devices.

DOI: 10.1103/PhysRevLett.87.165501

PACS numbers: 63.20.Ry, 34.70.+e, 82.20.Rp, 87.15.-v

One of the current most puzzling problems in physics is understanding if a general mechanism is operative in energy self-focusing and transport in biopolymers. In a photosynthetic unit, for example, consisting of an aggregate of many different chlorophyll molecules, light harvesting occurs through photon capture by the antennalike function of the unit. Subsequently, energy self-focusing takes place and light is transferred in the form of an exciton coherently through a complex cascade of transfer within and between pigment proteins, and upon reaching a photosynthetic unit the energy is released. This process lasts less than a picosecond and it is very efficient (about 95%) (see, e.g., [1]). Bioenergetics also requires that localized energy deposition through, e.g., adenosine triphosphate hydrolysis be transferred almost losslessly over a relatively large distance enabling conformational biomolecular changes and conversion into mechanical energy (biological motors) (see, e.g., [2]). These and other molecular transfer features led Davydov several years ago to propose that solitons might be the coherent agents of energy transfer in biological molecules [3,4]. While this transfer mechanism is quite appealing, subsequent work by several groups has shown several theoretical as well as practical weaknesses to the soliton idea [4,5].

The aim of this Letter is to propose an alternative, more general principle that could be applicable to a wide range of physical, chemical, and biological phenomena and which is naturally linked to the concept of discrete breather (DB). DBs are spatially localized and temporally periodic solutions of coupled nonlinear oscillator systems. The existence of DBs or intrinsic localized modes was already empirically suggested long ago in chemical physics for the study of vibrational states of molecules (local modes, see relevant discussion and references in [4]). Its ubiquity in physics emerged later, and progressively, when considering the discrete aspects of nonlinear lattice problems (see [6,7] for reviews). The DBs' universal character was first recognized in [8]. It was later proved [9] that they can be generic exact solutions in the weak coupling (anticontinuous) limit

when their frequency and its harmonics are outside the linear spectrum, thus making energy radiation by phonons impossible. Unlike solutions of integrable systems, DBs are robust and can survive to model complexity. Among the wealth of interesting properties discovered recently, existence proof and stability [6,9], modification of lattice thermodynamics [10], direct observation in coupled nonlinear optical waveguides [11], arrays of Josephson junctions [12], nonlinear [13] and magnetic [14] materials, and possibly myoglobin [15], point to the very important role that DBs could play in a variety of contexts. Under very special circumstances, DBs can move almost freely through periodic systems, thus enabling coherent discrete energy transfer [16]. However, translational invariance is not generally fulfilled in biomolecules. A detailed investigation of random nonlinear lattices with discrete linear spectrum showed that Anderson modes are replaced by DBs localized at a given site with frequencies between forbidden gaps generated by resonances with the linear modes [17].

In this Letter we demonstrate that it is possible to tune the nonlinear lattice in such a way that a very selective, efficient, targeted energy transfer (TET) between specific sites results. Such an effect in a randomly chosen system is *a priori* improbable but its possible occurrence and its optimization in bioenergetics could be explained by long adaptive processes during life evolution.

When two harmonic oscillators are resonant, any amount of energy injected on one oscillator oscillates between them with a frequency proportional to their coupling. This picture is drastically changed when the oscillators are anharmonic because the frequencies depend on the amplitude of oscillation. When a finite amount of energy is injected into one of them, if by chance the initial frequency is resonant with the other oscillator, a small fraction of energy is transferred, but then the frequencies of both oscillators change so that the resonance condition is generally no longer fulfilled and the transfer stops. However, there are exceptional situations where the resonance *persists* during the transfer, and complete transfer becomes possible. This

happens for weak coupling where the selective TET occurs. Here, we briefly outline the theory that produces the conditions for TET. A detailed derivation as well as the solution for two coupled oscillators are presented elsewhere [18]. We then treat the general case of TET between DBs of two weakly coupled random nonlinear systems. These systems could represent two independent molecules, two linked parts of the same folded macromolecule, two weakly coupled layers or clusters of atoms, etc. We present results in a pedagogical model, but our methods are applicable to complex models. We show that a specific amount of energy injected as a DB in the “donor” system (D) may be totally transferred to the “acceptor” system (A) and oscillate back and forth between D and A . The necessary condition is that a well-defined “detuning function” is bounded by a coupling function. Moreover, we show how extra resonances make this transfer irreversible and suggest how TET cascades can be realized.

The DB solutions on D and A are continuous families parametrized through their frequency or action, I_X with $X = D$ or $X = A$, obtained by the integration on the loop representing the DB in phase space. The DB’s energy $E_X = H_X(I_X)$ is a function of the action with frequency $\omega_X = dH_X/dI_X$. In the ideal situation for TET the DB family is gapless ($E_X = 0$ for $I_X = 0$), i.e., no resonances with linear modes are involved (in [19] there is a detailed analysis of all bifurcations in general, with the energy parametrized in frequency). We introduce a weak coupling between D and A , which could physically represent contact interactions (hydrogen bonds, van der Waals forces), Coulomb interactions, could be mediated by a solvent, could come directly from the intermediate link of the macromolecule, etc. We have searched for the conditions for the complete transfer of the energy E_T of a DB on D with initial action I_T to a DB on A . Since the coupling between D and A is weak, this transfer is adiabatic. The dynamics during this process is well described by DBs on D and A , over a time scale long compared to the DB period, $t_b = 2\pi/\omega_b$. The action of a loop evolving in the phase space is time constant, i.e., $I_T = I_D + I_A$. The total energy $E_T = H_D + H_A + H_V$ is conserved and, since the coupling energy H_V is small, the condition of resonance during the transfer is almost fulfilled,

$$H_D(I_D) + H_A(I_T - I_D) \approx E_T$$

$$\Leftrightarrow \omega_D = \frac{dH_D}{dI_D} \approx \frac{dH_A}{dI_A} = \omega_A. \quad (1)$$

The small coupling energy H_V depends on the action on D and A and on the corresponding conjugate angle variables, θ_D, θ_A . With the assumptions of weak coupling and almost resonance, the total angle $\theta_0 = \theta_D + \theta_A$ varies fast while the difference $\theta = \theta_D - \theta_A$ varies slowly, so that the θ_0 dependence can be averaged out, i.e., $H_V(I_D, I_A, \theta)$. Then, θ essentially represents the difference between the DB phases on D and A . We can split H_V in two terms, $H_V(I_D, I_A, \theta) = H_{V0}(I_D, I_A) + V(I_D, I_A, \theta)$, where H_{V0}

is the average of H_V over θ while the average of V over θ is zero. The Hamiltonian of the system is now written as $H_0(I_D, I_A) + V(I_D, I_A, \theta)$, where $H_0(I_D, I_A) = H_D(I_D) + H_A(I_A) + H_{V0}(I_D, I_A)$. A necessary and sufficient condition for TET is

$$\min_{\theta} V(I_D, I_A, \theta) < \epsilon(I_D, I_A) < \max_{\theta} V(I_D, I_A, \theta), \quad (2)$$

where the detuning function ϵ is defined as

$$\begin{aligned} \epsilon(I_D, I_A) &= H_0(I_D, I_A) - H_0(I_T, 0) \\ &= H_0(I_D, I_T - I_D) - H_0(I_T, 0). \end{aligned} \quad (3)$$

Function (3) characterizes the detuning between the DBs on D and A during the transfer and is zero in the beginning and at the end [$\epsilon(I_T, 0) = \epsilon(0, I_T) = 0$]. In some sense it extends the concept of an energy barrier of static excitations to DBs and may be positive or negative. Condition (2) is valid for physically reasonable sinelike dependence of V on θ (since V is small, expansion to the lowest order yields such a dependence with one min and one max and two zeros per period). It shows that TET occurs even when Eq. (1) is not strictly satisfied, as long as ϵ is bounded by V .

As an example, we consider here discrete nonlinear Schrödinger (DNLS) models which also describe Klein-Gordon chains in some limits and, thus, are relevant to both vibrations and quantum excitations. Moreover, the self-consistent DB calculations are greatly simplified in DNLS since the time dependence is removed (see [19] for Newton-method-based DB calculations in random models). The Hamiltonian for D and A is

$$H_X = \sum_i \left\{ -E_{X,i} |\psi_{X,i}|^2 - \frac{1}{2} \sigma_X |\psi_{X,i}|^4 - C(\psi_{X,i} \psi_{X,i+1}^* + \psi_{X,i+1}^* \psi_{X,i}) \right\}, \quad (4)$$

where $E_{X,i}$ are the randomly chosen on-site energies, $\psi_{X,i}$ are the amplitudes on sites i , $X = D$ or A , C is the

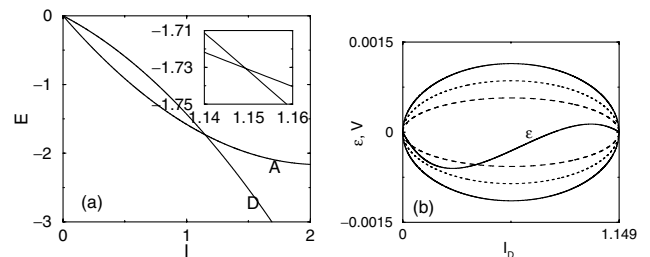


FIG. 1. (a) Energy E_X versus action I_X of the DBs on the uncoupled D and A systems. In this example, each system consists of ten sites with $E_{D,i} = 0.265, 0.346, 0.928, 0.542, 0.165, 0.692, 0.863, 0.097, 0.412, 0.700$ and $E_{A,i} = 2.655, 2.931, 2.083, 2.748, 2.109, 2.578, 2.308, 2.489, 2.851, 2.222$. The DBs are localized on site $i = 3$ of D and A . The intramolecular coupling is $C = 0.05$. The intersection (zoom) is at $I_T = 1.149297647$, $E_T = -1.730521602$. (b) The detuning ϵ and coupling V functions versus I_D are plotted for intermolecular coupling $\lambda = 0.001, 0.00075$, and 0.0005 (solid, dashed, and long-dashed lines, respectively).

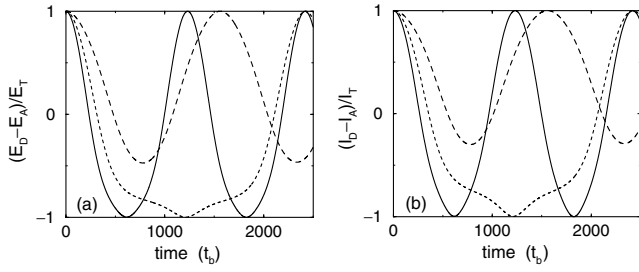


FIG. 2. (a) $(E_D - E_A)/E_T$ and (b) $(I_D - I_A)/I_T$ versus time for the system of Fig. 1. The initial condition is the DB on D at the intersection of the curves in Fig. 1(a) with frequency $\omega_b = 2.0781937765$. The intermolecular coupling is $\lambda = 0.001, 0.00075$, and 0.0005 (solid, dashed, and long-dashed lines, respectively). The time unit is the period t_b of the initial DB on D .

“intramolecular” coupling constant (between the “atoms” of the same D or A “molecule”), and, in our examples here, $\sigma_D = 1$ while $\sigma_A = -1$. The opposite sign of the nonlinear terms in Eq. (4) makes D a system of hard anharmonic oscillators (the amplitude of oscillation increases with frequency) and A a system of soft oscillators. A simple “intermolecular” coupling, as explained above, is

$$H_V = -\lambda \sum_i (\psi_{A,i} \psi_{D,i}^* + \psi_{A,i}^* \psi_{D,i}) \quad (5)$$

so that the equations of motion are

$$i\dot{\psi}_{X,i} + \sigma_X |\psi_{X,i}|^2 \psi_{X,i} + C(\psi_{X,i+1} + \psi_{X,i-1}) + E_{X,i} \psi_{X,i} + \lambda \psi_{Y,i} = 0, \quad (6)$$

where $(X, Y) = (D, A)$ or (A, D) . In DNLS models, the action is the norm, i.e., $I_X = \sum_i \psi_{X,i}^* \psi_{X,i}$.

Figure 1(a) plots the energy E_D, E_A given by Eq. (4) of DBs on D, A as a function of the action, I_D, I_A , respectively. The DB solutions localized on sites $d = 3$ and $a = 3$ are calculated by continuation [19]. The on-site energies were randomly chosen in a certain interval. The possibility of ideal TET was detected between the DB on sites d and a , for which $E_{D,d} > E_{D,i} (i \neq d)$, $E_{A,a} < E_{A,i} (i \neq a)$ and $0 < E_{D,i} < 1$, $2 < E_{A,i} < 3$,

so that there is a large domain of existence in the gap with no bifurcations for these DBs in continuation of the linear modes $E_{D,3}$ and $E_{A,3}$. The point of intersection (which is better presented in the inset) is where $I_D = I_A = I_T$, i.e., where the TET is produced, if condition (2) is satisfied. In the example of Fig. 1, $I_T = 1.149297647$, $E_T = -1.730521602$.

Figure 1(b) plots the detuning function [Eq. (3)] and the coupling function, which in this DNLS model is given by Eq. (5), i.e., $V = H_V$, for three different values of the intermolecular coupling $\lambda = 0.001, 0.00075, 0.0005$. Note that λ is 2 orders of magnitude less than the intramolecular coupling $C = 0.05$. According to (2), complete TET should occur for $\lambda = 0.001$ and 0.00075 .

This is depicted in Fig. 2, where the time evolution of the ratio of the energy difference between D and A over the total energy, $r_E = (E_D - E_A)/E_T$, is plotted in (a), and similarly for the action, $r_I = (I_D - I_A)/I_T$, in (b), for the system in Fig. 1. The initial condition is the DB on D at the intersection of the curves of Fig. 1(a). The TET is practically complete for $\lambda = 0.001$ (solid line) and $\lambda = 0.00075$ (dashed line), with the ratios oscillating between 1 (when $E_D = E_T, I_D = I_T, E_A = 0, I_A = 0$) and -1 (when $E_D = 0, I_D = 0, E_A = E_T, I_A = I_T$). For $\lambda = 0.0005$ (long-dashed line) there is a partial transfer at $r_E = -0.472$, $r_I = -0.300$, and the ratio of the maximum E_A, I_A over E_T, I_T is $E_{Amax}/E_T = 0.736$, $I_{Amax}/I_T = 0.650$, respectively. These results are expected from the curves in Fig. 1(b). Although complete TET occurs only when condition (2) is satisfied, we observe that there is a substantial TET even when the detuning function is not completely bounded by the coupling. This is expected since TET proceeds for the values of I_D for which $|V| > |\epsilon|$ and stops when $|V| < |\epsilon|$.

This TET is very selective, as Fig. 3 demonstrates, where the ratio of energy and action transferred from D to A is plotted, $E_{Amax}/E_T, I_{Amax}/I_T$, as a function of E_T in (a) and I_T in (b). It is clear that TET rapidly vanishes as the energy of the initial DB on D moves away from the intersection of E_D and E_A in Fig. 1(a). It becomes possible only in a narrow window in E_T or I_T . The

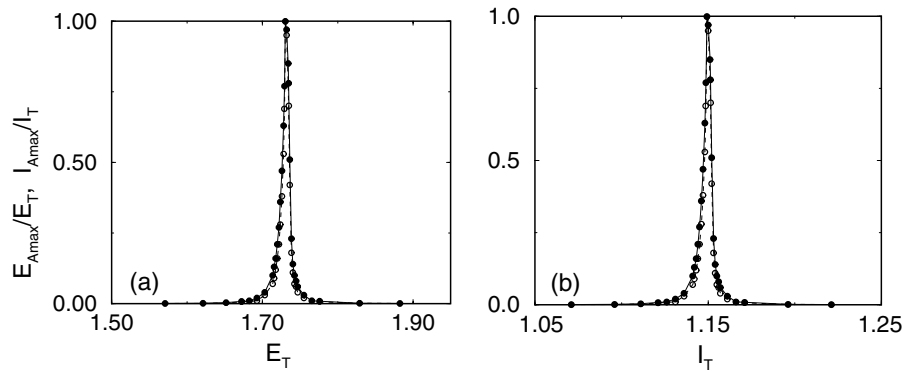


FIG. 3. The ratio of the energy and action transferred from D to A , E_{Amax}/E_T and I_{Amax}/I_T (solid circles connected by a solid line, empty circles connected by a dashed line, respectively), as a function of E_T in (a) and I_T in (b). The DB is initially localized on site d of D .

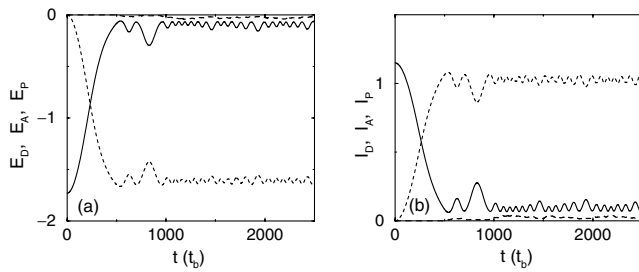


FIG. 4. (a) Energies E_D , E_A , and E_P and (b) actions I_D , I_A , and I_P versus time (solid, dashed, and long-dashed lines, respectively) for the system of Figs. 1 and 2 with $\lambda = 0.001$, but coupled to a linear system P with on-site energies $E_{P,i} = 0.933$.

example presented here is quite general since, besides the choice of DB sites d, a and the fact that D is hard and A is soft, it does not contain other built-in elements. Still, TET occurs for very weak intermolecular coupling. One can fine-tune the model parameters (linear and nonlinear terms) in order to obtain TET for even weaker coupling and an even narrower window.

In a real physical or biological system the D - A pair may be interacting with additional degrees of freedom. A direct consequence of this interaction is that, under appropriate conditions, TET becomes irreversible. While the exact resonance condition is kept, most D energy is transferred to A ; however, as a result of energy loss and of the high selectivity of TET, the resonance condition can be broken, making a significant energy return to D impossible. As a result, irreversible targeting occurs with almost complete energy transfer. The situation depicted in Fig. 4 represents such a case whereby the pair is coupled to a third linear system P through the same coupling constant $\lambda = 0.001$. The initial condition is again the DB on D at the intersection of Fig. 1(a). Indeed, such transfer occurs very efficiently ($E_{A\max} \approx 0.96$) and subsequently, as a result of the interaction with P , most energy E_A remains localized on A , a small fraction is absorbed by the phonons of P , and a small part returns to D .

Whenever resonance condition (1) is broken at the end of the transfer, TET becomes irreversible. This may happen because of resonances in the gap, when both D and A are coupled to a phonon band, to dissipative systems with noise, etc. This is crucial in real situations, where the system is surrounded by a thermalized medium. One can design efficient transfer and funneling by cascades through networks of D - A systems, such as in chlorophyll, which could also be important both from a materials science and a biotechnology point of view for distant coherent energy transfer.

We illustrated TET in a simple model example but the general methodology for detecting through condition (2) the possibility for TET applies to more complex models and, possibly, to *ab initio* calculations combined with self-consistent DB calculation methods. The phenomenon of TET that we introduced is very general and relies on non-

linearity and discreteness on one side, which localize energy in the form of hard and soft DBs, and judicious disorder on the other, which exploits specific nonlinear resonances. It can be applied to vibrational, electronic, polaronic, excitonic, etc., transfers, and as a result it could help resolve questions that range from bioenergetics to dynamics of chemical reactions, synthetic and biological catalysts, etc. Future work should connect the present approach to standard exciton transport theories. TET can also be used as a guiding principle for the design of nano-devices with specific energy transfer features.

G.K. acknowledges support by Greek GSRT. This work has been supported by EC under RTN Contract No. HPRN-CT-1999-00163.

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