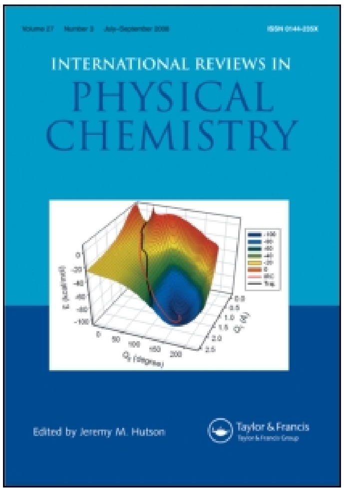

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

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To cite this Article Collins, Michael A.(1986) 'Solitons in resonant energy transfer', International Reviews in Physical Chemistry, 5: 2, 203 — 210
To link to this Article: DOI: 10.1080/01442358609353384
URL: http://dx.doi.org/10.1080/01442358609353384

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1986, VOL. 5, NOS. 2 & 3, 203–210

Solitons in resonant energy transfer

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The way in which localized 'soliton states' arise in systems with resonant energy transport is reviewed. This localization of energy in a mobile 'packet' arises from the coupling of internal states with molecular motions via a feedback mechanism. The connection between classical and quantum treatments of this process is discussed.

1. Introduction

Resonant energy transfer between similar molecules or groups is an efficient mechanism for energy transport in atomic and molecular systems. The relatively slow rates for vibrational to translational, or electronic to translational, energy exchange are in contrast to the rapidity with which large quanta of energy can be exchanged between corresponding modes of similar molecules.

The theoretical study of electronic states in molecular crystals is one area where the role of resonance interactions is central, as explained in the well known texts (Davydov 1971, Craig and Walmsley 1968). In recent years, several authors (Davydov and Kislukha 1973, 1976, Scott 1982 a, b, 1983, Collins and Craig 1983) have drawn attention to the existence of localized, though mobile, states which arise as a consequence of the coupling of resonance interactions and molecular motions. Considerable interest has been generated by the application of those ideas to biology, in particular to energy transport in DNA molecules (Davydov *et al.* 1978, Davydov 1979, 1982, Scott 1982 a, b).

In the α-helix of figure 1, there are one-dimensional chains of amide groups, hydrogen bonded across the spiral. Of the amide group vibrations, one, essentially a $C=0$ stretch with excitation energy near $1650\,\mathrm{cm}^{-1}$, is strongly coupled to neighbouring group motions. A similar effect can be seen in crystalline acetanilide (Careri *et al.* 1983, 1984).

The resonant transport of such vibrational quanta and electronic excitations in molecular crystals have both been modelled in recent times in terms of solitons: localized, highly stable (Eilbeck *et al.* 1984, Carr and Eilbeck 1985), travelling waves. In this short article we re-present, without laborious proofs, the way in which these localized states arise within acceptable approximations to the exact mechanics.

2. The model

We consider a chain of moieties (atoms, molecules, groups of atoms) which is one dimensional in the sense that a single coordinate specifies the group position and each group has only two nearest neighbours. For example, we could consider the radial motion of carbon atoms in benzene using such a model. Denoting this single coordinate by U, we can number a chain of N groups arbitrarily from $n=1$ to $n=N$, and label the coordinates U_n. Each group has an internal degree of freedom (rotational, vibrational

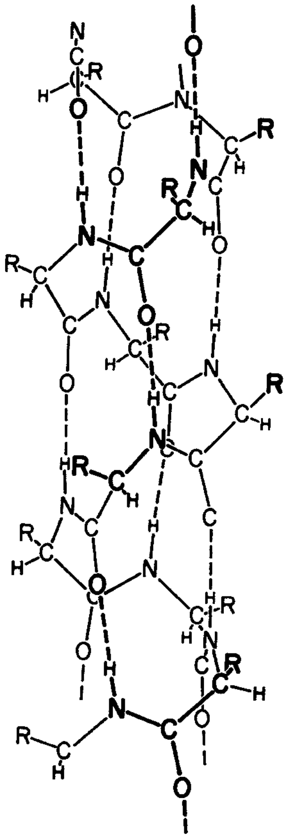

Figure 1. A right-handed α-helix is shown in which three chains of amide groups can be seen. Each chain has its units coupled by hydrogen bonds across the spiral.

or electronic) whose orthogonal ground and first excited states we denote as $|0_n\rangle$ and $|1_n\rangle$ respectively. We define the creation and annihilation operators $B_n^\dagger$ and B_n by

$$B_n^\dagger|0_n\rangle = |1_n\rangle; B_n|1_n\rangle = |0_n\rangle; B_n|0_n\rangle = 0 \tag{1}$$

For simplicity we assume that higher excited states are energetically inaccessible and that only *one* excitation is present in the chain so that whether the excitations are bosons or fermions is irrelevant. Moreover, we assume that only nearest-neighbour interactions occur and depend solely on the relative displacement or 'bond length'.

$$r_n = U_n - U_{n-1} \tag{2}$$

With these definitions, the model hamiltonian is written simply as

$$H = H_0 + \sum_{n=1}^{N} \{\Delta\varepsilon + D(r_n) + D(r_{n+1})\} B_n^\dagger B_n + M(r_n) B_n^\dagger B_{n-1} + M(r_{n+1}) B_n^\dagger B_{n+1} \tag{3}$$

where

$$H_0 = \sum_{n=1}^{N} \frac{1}{2m}(p_n - p_{n+1})^2 + V(r_n)$$

is the ground state hamiltonian for the relative displacements, r_n, and their momenta, p_n. Thus, if the nth group is excited, the energy changes by the $|0\rangle$ to $|1\rangle$ excitation energy $\Delta\varepsilon$, and also by changes, $D(r)$, in the nearest-neighbour interactions. For example, the group may have different electrostatic moments in its ground and first excited states. Moreover, if the excitation is transferred between sites there is an associated resonance energy $M(r)$. Normally, we expect that the resonance interaction *lowers* the total energy and is *attractive*. The same applies to $D(r)$. To eliminate unnecessary parameters we introduce dimensionless variables and take the simplest forms for the potential energy functions, setting

$$\left.\begin{aligned} V(r)&=\tfrac{1}{2}k(r-r_{\text{eq}})^2\\ y_n&=(r_n-r_{\text{eq}})/r_{\text{eq}}\\ P_n&=p_n[4mkr_{\text{eq}}^2]^{-1/2}\\ D(r)&=(-D_0+D_1y)4kr_{\text{eq}}^2,\quad D_0,D_1>0\\ M(r)&=(-M_0+M_1y)4kr_{\text{eq}}^2,\quad M_0,M_1>0\\ h&=H/4kr_{\text{eq}}^2\\ \tau&=(4k/m)^{1/2}t \end{aligned}\right\}\tag{4}$$

So that,

$$h=\sum_{n=1}^{N}\tfrac{1}{2}(P_n-P_{n+1})^2+\tfrac{1}{8}y_n^2+[\Delta\varepsilon-2D_0+D_1(y_n+y_{n+1})]B_n^\dagger B_n$$
$$-(M_0-M_1y_n)B_n^\dagger B_{n-1}-(M_0-M_1y_{n+1})B_n^\dagger B_{n+1}\tag{5}$$

3. Stationary states

Let us now proceed to obtain the stationary states for (5), in the usual way, by assuming a Born–Oppenheimer separation between the internal states and the displacements U_n. Thus, we write a trial form only for the internal state of the whole chain

$$|\psi\rangle=\sum_{n=1}^{N}a_nB_n^\dagger\prod_{m=1}^{N}|0_m\rangle\tag{6}$$

where

$$\sum_{n=1}^{N}|a_n|^2=1\tag{7}$$

by normalization. Here each site may be excited with some probability $|a_n|^2$. The complex coefficients a_n are determined by the variational method

$$\frac{\partial E}{\partial a_n}=\frac{\partial}{\partial a_n}\langle\psi|h|\psi\rangle=0\tag{8}$$

giving the familiar secular equations

$$Ea_n=[\Delta\varepsilon-2D_0+D_1(y_n+y_{n+1})]a_n-(M_0-M_1y_n)a_{n-1}-(M_0-M_1y_{n+1})a_{n+1}\tag{9}$$

We complete the usual approach by 'optimising the geometry', that is finding the minimum on the Born–Oppenheimer potential energy surface:

$$\frac{\partial E}{\partial y_n}=0\tag{10}$$

which implies

$$\frac{y_n}{4} + D_1[|a_n|^2 + |a_{n-1}|^2] + M_1[a_n^* a_{n-1} + a_n a_{n-1}^*] = 0 \tag{11}$$

where a_n^* is the complex conjugate of a_n. In the usual case, when $M(r)$ and $D(r)$ provide *attractive* forces $(M_1, D_1 > 0)$, the solution of (9) and (11) is a localized state for long chains. Clearly, if there is a higher than average probability that the excitation is at n or $n-1$, the bonding is stronger between these sites, and a stronger bond implies a shorter bond, via (11). But a shorter bond makes $M(r)$ (and $D(r)$) larger, more attractive, thus lowering the energy and inducing a_{n-1} and a_n to become even larger still. There is a positive feedback mechanism (Collins 1983) localizing the excitation and contracting the bonds until a balance is reached with the $\{V(r_n)\}$. If the stationary state can be described in a continuum approximation in the sense that

$$a_n - a_{n-1} \approx \frac{\partial a}{\partial n}$$

then (9) and (11) combine, on neglect of higher-order derivatives and powers (Collins and Craig 1983), to give the non-linear Schrödinger equation:

$$Ea(n) = -M_0 \frac{d^2 a(n)}{dn^2} + (\Delta\varepsilon - 2D_0 - 2M_0)a(n) - 16[M_1 + D_1]^2 |a(n)|^2 a(n) \tag{12}$$

For an infinite chain, a localized state is one for which $a(n) \to 0$ as $n \to \pm\infty$. Equation (12) has a localized solution of this type:

$$a(n) = [2(M_1 + D_1)^2 / M_0]^{1/2} \operatorname{sech}[4(M_1 + D_1)^2 (n - n_0)/M_0] \tag{13}$$

where n_0 is arbitrary. Figure 2 depicts the probability distribution $|a_n|^2$ and the corresponding bond lengths for two choices of n_0.

To complete the quantum description we need the states associated with the 'slow' variables in the Born–Opperheimer separation, the relative displacements y_n.

Using (13) in the continuum limit, the zeroth-order energy surface is given by

$$\begin{aligned} E_0(y_1, y_2, \ldots, y_n) &= \langle\psi| h(P_1 = P_2 = \ldots = P_n = 0) |\psi\rangle \\ &= \sum_{n=1}^{N} \{\tfrac{1}{8} y_n^2 + [\Delta\varepsilon - 2D_0 + D_1(y_n + y_{n-1})]|a_n|^2 \qquad (14) \\ &\quad - (M_0 - M_1 y_n) a_n^* a_{n-1} - (M_0 - M_1 y_{n+1}) a_n^* a_{n+1} \\ &= \Delta\varepsilon - 2D_0 - 2M_0 - 16(D_1 + M_1)^4/(3M_0) \\ &\quad + \sum_{n=1}^{N} \frac{1}{8} \left\{ y_n + \frac{16(D_1 + M_1)^3}{M_0} \operatorname{sech}^2 [4(D_1 + M_1)^2 (n - n_0)^2 / M_0] \right\}^2 \qquad (15) \end{aligned}$$

To this order, the coordinates are associated with harmonic phonon modes only displaced in origin as depicted in figure 2. We note that the energy of this localized 'soliton' state is *lower* than that of the plane-wave exciton approximation by $16(D_1 + M_1)^4/(3M_0)$, strongly dependent on the coupling parameters, M_1 and D_1.

The normal Born–Oppenheimer procedure is to evaluate the energy $E(y_1, y_2, \ldots, y_n)$ to second order in the nuclear displacements, including terms due to the first-order perturbations to $|\psi\rangle$ (Born and Huang 1966). Clearly, these higher-order terms will perturb both the zeroth order harmonic frequencies and the displaced origins evident in (15). However, neglecting these small corrections will not affect the

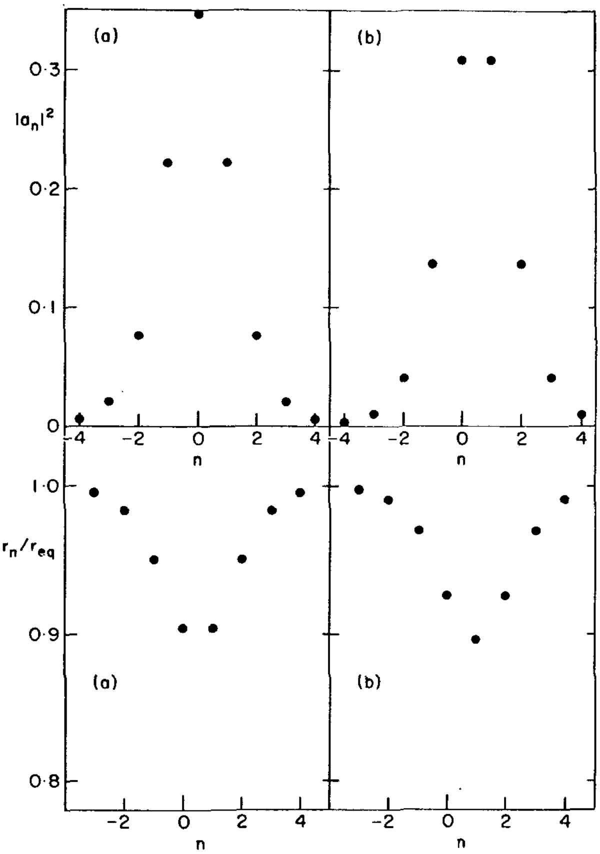

Figure 2. The probability distribution $|a(n)|^2$ of internal excitation for the localized state is shown for two values of n_0 ($n_0 = 0(a)$ and $n_0 = \frac{1}{2}(b)$) using appropriate values of the potential parameters (Collins and Craig 1983). The contraction of the chain accompanying the localization is also depicted, in terms of the relative displacements, r_n.

thrust of the argument, so we assume that the energy surface $E_0(y_1, y_2, \ldots, y_n)$ is an adequate approximation to the Born–Oppenheimer energy surface.

The nuclear energy state $|\chi>$ is then given by the solution of

$$h_{\mathrm{ph}}|\chi\rangle = \varepsilon|\chi\rangle \tag{16}$$

where

$$h_{\mathrm{ph}} = \sum_{n=1}^{N} \tfrac{1}{2}(P_n - P_{n+1})^2 + \frac{1}{8}\left\{ y_n + \frac{16(D_1+M_1)^3}{M_0}\,\mathrm{sech}^2\,[4(D_1+M_1)^2(n-n_0)/M_0] \right\}^2 \tag{17}$$

and ε is the total nuclear eigenenergy. Here ε is clearly the total acoustic phonon energy

$$\varepsilon = \sum_k \hbar\omega_k(\nu_k + \tfrac{1}{2})/4kr_{\mathrm{eq}}^2 \tag{18}$$

where ν_k is the quantum number for the kth phonon mode of frequency ω_k and k is the phonon wavenumber in the first Brillouin zone (Kittel 1963).

The total wavefunction is the usual product

$$|\Phi\rangle = |\chi\rangle|\psi\rangle \tag{19}$$

However, the equilibrium geometry

$$y_n = -\frac{16(D_1+M_1)^3}{M_0}\,\mathrm{sech}^2\,[4(D_1+M_1)^2(n-n_0)/M_0] \tag{20}$$

is determined by the arbritrary origin n_0. For each arbitrary choice of n_0, there corresponds a Born–Oppenheimer product (19). The same situation arises with molecular rotation, where each molecular orientation has an associated Born–Oppenheimer product of nuclear and electronic states referred to that particular origin. In this case we do not have a free rotor but rather a free particle whose position n_0 is arbitrary. Using periodic boundary conditions on the chain of length N, the free particle becomes a particle in a box, whose wavefunctions are plane waves, $\exp\{ikn_0\}$, with wavenumbers k in the first Brillouin zone.

Thus, the arbitrary choice of n_0 is reflected in a Bloch-wave character for the total *wavefunction*:

$$\Phi(k) = \int_0^N dn_0 \exp(ikn_0)\chi(y_1, y_2, \ldots, y_n; n_0)a(n; n_0) \tag{21}$$

where $a(n; n_0)$ is given by (13) for long chains and χ is the corresponding product of harmonic phonon wavefunctions.

The lowest energy eigenfunction corresponds to $k=0$. In so far as the Born–Oppenheimer approximation is valid, all the products $|\chi(n_0)\rangle|\psi(n_0)\rangle$ are energy eigenstates, so that the energy

$$E = \langle\phi(k=0)|h|\phi(k=0)\rangle/\langle\phi(k=0|\phi(k=0)\rangle \tag{22}$$

is just that of a single product 'localized' at n_0.

Venzl and Fischer (1985) have used a trial function similar to (21) to evaluate the ground state in the case where D_1 is very large, the continuum approximation is no longer valid, and trapping may occur. In that case, numerical studies (Collins and Craig 1983) show that only integer values of n_0 correspond to a minimum on the Born–Oppenheimer energy surface, so that the integral of (21) becomes a sum.

It is worth noting that there is no real contradiction between the Bloch-wave character of (21) and the concept of a localized soliton state of the system. The particle in a box has eigenfunctions for which, at given energy, the particle is equally likely to be at any point in the box. Nevertheless, the localization is reflected in the products of (19) with consequences for the observable properties.

Moreover, to continue the analogy with the particle in the box or free rotor, it is sometimes appropriate to consider wavepacket superpositions rather than the stationary wavefunction of (21). The minimum uncertainty (time-dependent) wavepacket which sites the soliton initially at n_s at rest is clearly of the form (Schiff 1968)

$$\Phi(n_0) = C\left[(\Delta n_s) + \frac{i\beta\tau}{2m_s(\Delta n_s)}\right]^{-1/2} \exp\{-(n_0-n_s)^2/[4(\Delta n_s)^2 + 2i\beta\tau/m_s]\}$$
$$\times\,\chi(y_1, y_2, \ldots, y_n; n_0)a(n; n_0) \tag{23}$$

where C is a normalization constant, $\beta = \hbar(4km)^{-1/2}r_{\mathrm{eq}}^{-2}$, and (Δn_s) is the initial ($\tau=0$) uncertainty in the soliton position. The rate at which the 'soliton wavepacket' spreads is determined by the reduced soliton mass, m_s. As we shall see below, this mass can be very large, which justifies the usual approach of employing classical mechanics to describe both the nuclear motion and consequently the soliton motion when transport rather than static properties are considered.

The free-particle character of the localized state arises from the fact that there is no energy change produced by changing the origin, n_0. Thus we expect the localized state can move with uniform velocity. This is easily shown using classical mechanics for the time-dependent displacements:

$$\left.\begin{aligned} \frac{dy_n}{d\tau} &= 2P_n - P_{n+1} - P_{n-1} \\ \frac{dP_n}{d\tau} &= \tfrac{1}{4} y_n + D_1(|a_n|^2 + |a_{n-1}|^2) + M_1(a_n^* a_{n-1} + a_n a_{n-1}^*) \end{aligned}\right\} \tag{24}$$

The internal state obeys the time-dependent Schrödinger equation

$$i\beta \frac{\partial a}{\partial \tau} = [h_0 + \Delta\varepsilon - 2D_0 + D_1(y_n + y_{n+1})]a_n - (M_0 - M_1 y_n)a_{n-1} - (M_0 - M_1 y_{n+1})a_{n+1} \tag{25}$$

where $\beta = \hbar(4km)^{-1/2} r_{\mathrm{eq}}^{-2}$.

Equations (24) and (25) do in fact have a solution which describes a localized state like that of (13), moving with constant velocity. In the continuum limit we have

$$a(n, \tau) = \exp\{-iE\tau\} a(n - v\tau) \tag{26}$$

$$y(n, \tau) = y(n - v\tau) \tag{27}$$

where

$$y(n - v\tau) = (v^2 - \tfrac{1}{4})^{-1} 2(D_1 + M_1)|a(n - v\tau)|^2 \tag{28}$$

$$\begin{aligned} a(n - v\tau) = {} & [2(D_1 + M_1)^2 M_0^{-1}(1 - 4v^2)^{-1}]^{1/2} \exp\{i\beta v(n - v\tau)/2M_0\} \\ & \times \operatorname{sech}[4(D_1 + M_1)^2 M_0^{-1}(1 - 4v^2)^{-1}(n - v\tau)] \end{aligned} \tag{29}$$

These equations describe a pulse like that in figure 2 moving with constant velocity. The velocity of sound in the chain is $\frac{1}{2}$ in these reduced units so that the reduced velocity v is always less than that of sound. The apparent mass of this soliton is given by (see Davydov 1982, for related results)

$$m_s = 2[E(v) - E(v = 0)]/v^2 \tag{30}$$

$$\approx 128(M_1 + D_1)^4/(3M_0) \tag{31}$$

using $v \ll \frac{1}{2}$ and realistic values for the phonon frequencies. Clearly, when the soliton solution (13) is localized and the energy lies well below the exciton band, the soliton mass is large in comparison with the molecular mass. Then, a classical picture in which a stable localized excitation can be transported through the chain is valid, as the corresponding quantum wavepacket spreads only slowly.

4. Conclusion

We have seen how the coupling of resonant transport and molecular motions gives rise to a feedback mechanism that localizes energy in one-dimensional chains. While the actual site of localization is arbitrary, and this is reflected in the ground-state wavefunction, the combination of excitation localization and distortion of molecular positions is clearly physically significant.

Most importantly, the stable localized excitation is mobile, though of large mass. Hence, the soliton may provide the mechanism by which large quanta of localized energy can be transported over large distances without spreading or loss.

Acknowledgment

The author gratefully acknowledges the pleasure and value derived from numerous discussions with David Craig.

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