Available online at www.sciencedirect.com
ScienceDirect
Mathematics and Computers in Simulation 82 (2012) 1239–1248
MATHEMATICS AND COMPUTERS IN SIMULATION
www.elsevier.com/locate/matcom

Studying Davydov's ODE model of wave motion in α-helix protein using exactly energy–momentum conserving discretizations for Hamiltonian systems

Brenton LeMesurier *

Department of Mathematics, College of Charleston, 175 Calhoun Street, Room 339, Charleston, SC 29424, USA

Received 13 November 2009; received in revised form 3 October 2010; accepted 4 November 2010
Available online 30 December 2010

Abstract

Davydov's modeling of long-range energetic pulse propagation in α-helix protein started with an exciton–phonon ODE system and proceeded to the integrable nonlinear Schrödinger (NLS) equation in the limit of both large pulse width relative to amino acid spacing and high characteristic speed of the "phonon" terms. Soliton solutions of NLS have then been used to propose a mechanism for coherent long-range propagation of energetic pulses in such proteins.

Here ODE models are studied directly, in particular a simplification that considers only coordination bond coupling parallel to the helix axis, discounting interactions along the molecular backbone. The time discretization is constructed by a new method based on discretizing the Hamiltonian using a finite difference calculus for gradients, which ensures exact conservation of both the Hamiltonian and all quadratic and linear conserved quantities, and allows a simple, highly stable iterative method for solving the resulting implicit system.

The simulation results show that as the parameters get further from the continuum limit regime, substantial changes occur in the solution form. For characteristic phonon speed drops below the characteristic speed of the exciton equation, the main exciton pulse slows and narrows, and other faster exciton pulses appear with speeds related to the characteristic phonon speed. This suggests that more careful simulation studies are needed, based on Scott's full model or further refinements.

MSC: 70H05; 65L05; 92C05

PACS: 02.60.Cb; 87.14.E−; 87.15.A−; 45.10.−b; 45.20.Jj

Keywords: Conservative time discretizations; Hamiltonian systems; Protein energetics; Nonlinear wave equations

1. Introduction and main results

1.1. Energy–momentum conserving and symmetry preserving discretizations

Many models of nonlinear wave motion and pulse propagation have a Hamiltonian form, embodying conservation of energy and other "momenta": Noetherian first integrals related to continuous symmetries in the dependent variables.

* Tel.: +1 843 953 5917; fax: +1 843 853 6564.
E-mail address: lemesurierb@cofc.edu

0378-4754/$36.00
doi:10.1016/j.matcom.2010.11.017

These include many important nonlinear dispersive PDEs, and also large systems of ordinary differential equations such as models of wave motions in molecular systems. In fact, these ODE and PDE models are often connected by spatial discretizations in one direction and by continuum limits in the other. Since numerical solution will in the end involve spatial discretization, and the class of wave-equation-like Hamiltonian ODE systems is richer, the focus here is on ODE systems, but ones having features related to quasi-linearity of associated PDEs.

The main system considered here is a model of energetic pulse propagation along protein and other long molecular chains, which originated in the work of Davydov [3,4] and has been developed in particular in the work of Scott [13,14]: see also the more recent survey [15]. Specifically, we consider a modification of Davydov's original ODE system, discounting lateral couplings along the molecular backbone to give a simpler model of the longitudinal coordination bond couplings, where the interesting phenomena lie.

The *discrete gradient method* described here is related to the approach of Gonzales [5]. As there, the first main ingredient is discretizing the Hamiltonian form of an equation by choosing a suitable *discrete gradient*, and using partial counterparts of Noether's Theorem:

1. If a discrete gradient respects an *affine* continuous symmetry, the solutions of the discrete system also do.
2. If a symmetry of the original system is associated with conservation of a *quadratic* (including linear) quantity, this is also conserved by the time-discrete system.

These mimic well-known properties of Hamiltonian systems, but with the added restrictions of *affine* and *quadratic*. Fortunately, both conditions are met by all momenta of many physical systems, including those of interest here. (For example, in a standard mechanical system Hamiltonian $\mathcal{H} = \|\mathbf{p}\|^2/(2m) + V(\mathbf{x})$, invariance under rigid motions is described by affine symmetries related to quadratic first integrals.)

The second main ingredient here is a direct, mostly canonical procedure for constructing a discrete gradient, based on defining a suitable finite difference calculus, which works for a wide variety of cases. For example, this approach works canonically when no term in the Hamiltonian involves products of functions of three or more different variables. Somewhat related approaches were taken by Jimenez [7] and by Li and Vu-Quoc [11], but those works deal with discrtizations of PDEs in a way that respects only a single conservation law, either energy or linear momentum.

The third main ingredient, needed only in cases where the above canonical form fails due to "multiple product nonlinearities", involves factorizing such multiple product terms in terms of quadratic and linear factors that are invariant under all the affine symmetries.

The final ingredient is that the resulting difference equations should preserve the time-reversal symmetry of the differential equations: it has been commented by Hairer et al. [6] that this property seems more important than exact energy conservation itself, though experiments cited below indicate that having both properties can be even better.

Note that there has been complementary work on constructing spatial discretizations for PDEs of Hamiltonian form, such as discretization of the nonlinear Schrödinger equation (NLS) to the Ablowitz–Ladik system [1,2] and the larger class of discretizations studied in [8,9]. However the resulting ODE systems are not quite of the form considered here: for example in the Ablowitz–Ladik system, the discrete conserved quantity corresponding to the L^2 norm in NLS is $\Re(\sum Q_n^* Q_{n+1})$ rather than $\sum |Q_n|^2$, and the Hamiltonian involves transcendental functions, impeding use of the time-discretization methods described here.

1.2. Time-discrete Hamiltonian systems via discrete gradients

Time-discrete Hamiltonian systems are dynamical systems in which the state at one time T is described by a finite or infinite state vector $\mathbf{z}^T = \{z_n^T\}$, and the time advance map is determined by the Hamiltonian function $\mathcal{H}$ of the state in a way that mimics continuous time Hamiltonian dynamics, in particular conserving the Hamiltonian. The Hamiltonian systems of ODEs considered here are of the form

$$\frac{d\mathbf{z}}{dt} = J\nabla\mathcal{H}, \tag{1}$$

with $\mathbf{z}$ an N-component state vector, $\mathcal{H} = \mathcal{H}(\mathbf{z})$, and J an anti-Hermitian $N \times N$ matrix. All systems here are in fact in a mixture of the real and complex canonical forms:

$$\frac{du_n}{dt} = \frac{\partial \mathcal{H}}{\partial p_n}, \quad \frac{dp_n}{dt} = -\frac{\partial \mathcal{H}}{\partial u_n}, \quad \frac{dQ_n}{dt} = -i\frac{\partial \mathcal{H}}{\partial Q_n^*}, \quad \frac{dQ_n^*}{dt} = i\frac{\partial \mathcal{H}}{\partial Q_n}, \tag{2}$$

where formally one considers Q_n and Q_n^* as independent variables, though in practice they will be complex conjugates, making the last equation redundant.

A discrete version of the above will be a time-discrete Hamiltonian system:

$$\Delta \mathbf{z} := \mathbf{z}^{T+1} - \mathbf{z}^T = J\tilde{\nabla}\mathcal{H}\,\Delta t \tag{3}$$

given by a suitable choice of *discrete gradient* $\tilde{\nabla}\mathcal{H}$ having components $\tilde{\partial}_{z_n}\mathcal{H}(\mathbf{z}^T, \mathbf{z}^{T+1})$ that are approximations of the partial derivatives $\partial\mathcal{H}/\partial z_n$. Dependence on $\mathbf{z}^{T+1}$ is necessary, making such schemes implicit.

1.3. A difference calculus for multivariable functions

Conservation of energy $\mathcal{H}$ will be ensured by computing all discrete gradients in a way that satisfies the *difference-gradient rule*

$$\Delta F = \tilde{\nabla} F \cdot \Delta \mathbf{z} = \sum_n \tilde{\partial}_{z_n} F\,\Delta z_n \tag{4}$$

which is a discrete counterpart of the expansion for the differential of a multivariate function in terms of its gradient. This will be done by determining the components $\tilde{\partial}_{z_n} F$ through a difference calculus that combines centered difference quotients for functions of a single variable through rules for linear combinations, compositions, and products.

There are always infinitely many choices for such an expansion, with no generally successful or canonical choice: specifically, problems arise with products involving more than two variables. Thus the critical steps are first finding an essentially canonical choice for products of two functions, and then appropriate handling of higher order products. It is not possible to handle products of more than two functions in a canonical or universally successful way, and this is related to the limitation (also noted by Gonzales [5] from a different perspective) to momenta that are at most quadratic in the state variables. Fortunately the momenta of most physical systems are linear or quadratic, so the discrete gradients of these momenta can be given a canonical form. The handling of higher order products in the Hamiltonian is then done by grouping variables into linear or quadratic terms that are invariant under the symmetries.

2. The single spine Davydov model of pulse propagation in a molecular chain

The motivating example used here is a model of pulse propagation in a one-dimensional quasi-molecular structure, a slight variant of the model introduced by Davydov [3,4] for α-helical protein. The variation is that lateral coupling of amino acid residues along the helical backbone is neglected, giving an equation for a single nearly straight line "spine" of residues coupled by coordination bonds: the interesting physical phenomena appear to be within such spines.

There are natural extensions to include more detailed modeling of protein molecules [13,14], related models of chains and lattices of molecules bound by dipole interactions, and discretizations of various PDE wave equations such as models related to NLS arising in nonlinear optics, plasma physics and elsewhere. In many systems of interest the independent variables describe some mixture of

excitons: complex quantities Q_n evolving under some discrete variant of the Schrödinger equation, and
phonons: position and momentum pairs (u_n, p_n) evolving according to classical mechanics.

In Davydov's words, his ODE system describes a "one-dimensional quasi-molecular structure", with the main features being excitons Q_n at each amino acid residue n describing the probability of a quantum mechanical excitation of the residue's C=O group, in which the main wave of interest propagates through nearest-neighbor dipole interactions; additional phonon oscillations in the stretching u_n of each of the coordination bonds between adjacent residues along the structure; and local coupling between excitons and phonons.

With some rescaling to reduce the number of parameters, the system is Hamiltonian with total energy:

$$\mathcal{H} = \sum_n L|Q_{n+1} - Q_n|^2 + \frac{\omega^2}{2}p_n^2 + (u_{n+1} - u_n)^2 + (u_{n+1} - u_{n-1})|Q_n|^2 \tag{5}$$

where L and ω are positive constants. Various choices of end conditions are possible, of which the simplest is index range $1 \le n \le N$ and the fictitious end-point values

$$Q_0 = 0, \quad Q_{N+1} = 0, \quad u_0 = u_1, \quad u_{N+1} = u_N, \tag{6}$$

akin to zero Dirichlet boundary conditions on Q_n and on the bond stretchings $d_n = u_{n+1} - u_n$.

All methods in this paper extend to the larger class of *exciton–phonon systems* given by Hamiltonians of the form:

$$\mathcal{H} = \sum_{n,m} L_{n,m} Q_n Q_m^* + G(\mathbf{Q}, \mathbf{Q}^*) + \mathrm{V}(\mathbf{u}) + \frac{\mathrm{K}}{2}\sum_{\alpha} \mathrm{p}_\alpha^2 + \sum_{\mathrm{n,m}} \chi_{\mathrm{n,m}}(\mathbf{u})\mathrm{Q_n}\mathrm{Q_m^*} \tag{7}$$

with appropriate reality and symmetry conditions. This form can handle two- and three-dimensional molecular arrays, spatial discretizations of various nonlinear wave equations in any spatial dimension, and multiple chains such as coupled NLS systems of nonlinear optics.

The differential equations are given by the combined real and complex canonical Hamiltonian forms above, giving the single spine Davydov equations:

$$i\frac{dQ_n}{dt} + L(Q_{n+1} - 2Q_n + Q_{n-1}) = (u_{n+1} - u_{n-1})Q_n, \tag{8}$$

$$\frac{1}{\omega^2}\frac{d^2u_n}{dt^2} - (u_{n+1} - 2u_n + u_{n-1}) = \frac{1}{2}(|Q_{n+1}|^2 - |Q_{n-1}|^2), \tag{9}$$

Note that L could also be eliminated by rescaling, but is useful in constructing a continuum limit approximation. In addition to the total energy $\mathcal{H}$, there are two other conserved quantities:

the *exciton number* $\mathcal{E} = \sum_n |Q_n|^2$ and the *phonon momentum* $\mathcal{P} = \sum_n p_n$.

Note that there is no "exciton momentum" corresponding to the momentum $\Im(\int Q^* Q_x dx)$ of the NLS equation; this is already lacking in standard discretizations of the NLS equation.

2.1. Continuum and NLS limits

Following Davydov, we can consider the limit $L \to \infty, \omega \to \infty$ to approximate the above system by a NLS equation. First, a continuum limit is given by letting $L \to \infty$ and $\omega \to \infty$ such that $L/\omega^2 \to \epsilon > 0$, constant. This is the long wavelength limit of slow variation of Q_n values from node to node. Defining $\Delta x = 1/\sqrt{L}$ and letting $Q_n(t) = Q(t, n\Delta x)$, $u_n(t) = u(t, n\Delta x)/\Delta x$, the limit $L \to \infty$ gives what is here called the *continuum Davydov system*:

$$i\frac{\partial Q}{\partial t} + \frac{\partial^2 Q}{\partial x^2} = 2\frac{\partial u}{\partial x}Q_n, \tag{10}$$

$$\epsilon\frac{d^2u_n}{dt^2} - \frac{\partial^2 u}{\partial x^2} = \frac{\partial(|Q|^2)}{\partial x}. \tag{11}$$

Next, the limit $\epsilon \to 0$ eliminates the time derivative from (11), leading to $\partial u/\partial x = -|Q|^2$. This can be used to eliminate u from (10), giving the focusing cubic NLS equation:

$$i\frac{\partial Q}{\partial t} + \frac{\partial^2 Q}{\partial x^2} + 2|Q|^2 Q_n = 0. \tag{12}$$

This is completely integrable, with solutions including the solitons:

$$Q(t, x) = a\,\mathrm{sech}(a(x - vt - x_0))e^{ivx/2 + (a^2 - v^2/4)(t - t_0) + \theta_0}. \tag{13}$$

Davydov proposed that solutions approximating these solitons offer a mechanism for energy transfer in α-helix protein. This paper investigates the extent to which similar pulse-like solutions arise in the underlying more accurate discrete models.

For testing of the numerical method, it will also be convenient to look at the intermediate limit $\omega \to \infty$, L constant, of the single spine Davydov equations, giving:

$$u_n = \frac{1}{2}|Q_n|^2 + \sum_{m>n} |Q_m|^2 \tag{14}$$

and thus a non-standard discrete nonlinear Schrödinger (DNLS) equation:

$$i\frac{dQ_n}{dt} + L(Q_{n+1} - 2Q_n + Q_{n-1}) + \left(|Q_{n-1}|^2/2 + |Q_n|^2 + |Q_{n+1}|^2/2\right) Q_n = 0. \tag{15}$$

The methods developed here are also intended for future use with more detailed models such as the *modified Davydov* system introduced by Scott [13,14]. That model takes account of other weaker interaction terms as well as the coupling of three spines in the molecule's helical structure.

3. Conservative approximations of derivatives

The strategy here is first to characterize discrete approximations of the gradient of the Hamiltonian which generate time-discrete flows conserving that Hamiltonian, and then to choose amongst these ones that also respect certain other symmetries and conserved quantities of the continuous Hamiltonian flow, in particular quadratic invariants such as arise from affine symmetries. In practice, most symmetries and invariants of Hamiltonian models of physical systems have the needed "affine/quadratic" form. One novelty of the approach here is constructing the components of the discrete gradient by a difference calculus mimicking the necessary properties of differentiation: linearity and rules for products and compositions. (A quotient rule is never necessary, as a quotient can be replaced by a product and composition with the reciprocal function.)

Conserved momenta are related to invariance of $\mathcal{H}$ under continuous symmetries, in particular affine symmetries. A key to the associated differential equation conservation laws is equivariance of the gradient under these symmetries, and for analogous reasons, the same equivariance should be imposed on the discrete gradients here.

Notation for differences and difference quotients. For a scalar or vector independent variable $\mathbf{z}$, the values at the beginning and end of the current discrete time step will be denoted as $\mathbf{z}^-$ and $\mathbf{z}^+$ respectively, and the difference and mean of these values as:

$$\Delta\mathbf{z} = \Delta\mathbf{z}(\mathbf{z}^-, \mathbf{z}^+) := \mathbf{z}^+ - \mathbf{z}^-, \quad \bar{\mathbf{z}} := \frac{\mathbf{z}^- + \mathbf{z}^+}{2}. \tag{16}$$

Similarly for a function f of $\mathbf{z}$:

$$f^- := f(\mathbf{z}^-), \quad f^+ = f(\mathbf{z}^+), \quad \Delta f = \Delta f(\mathbf{z}^-, \mathbf{z}^+) := f^+ - f^-, \quad \bar{f} := (f^+ + f^-)/2. \tag{17}$$

As overlines denote temporal averages, complex conjugates are always denoted with stars, as in Q^*.

Conservation of energy and the discrete gradient rule. The first thing to ensure is conservation of energy for a time-discrete Hamiltonian system (3), and this can be verified by mimicking the proof for continuous-time Hamiltonian flows so long as the discrete gradient $\tilde{\nabla}\mathcal{H}$ used satisfies the difference-gradient rule (4):

$$\begin{aligned}
\Delta\mathcal{H} &= \mathcal{H}(\mathbf{z}^+) - \mathcal{H}(\mathbf{z}^-) \\
&= \tilde{\nabla}\mathcal{H} \cdot \Delta\mathbf{z} \quad \text{from} \quad (4), \\
&= \tilde{\nabla}\mathcal{H} \cdot J\tilde{\nabla}\mathcal{H}\,\Delta t \quad \text{from} \quad (3), \\
&= 0 \qquad \text{as} \quad J \quad \text{is anti-Hermitian.}
\end{aligned}$$

Thus, all derivative approximations will be chosen to ensure that the difference-gradient rule holds.

Canonical rules. It is natural to use linearity, which also preserves the difference gradient rule. Linearity combined with imposing time reversal symmetry and the difference gradient rule on each term in a sum then leads to canonical rules for all except multiple products.

First, for a function $f(g)$ of a single variable g, the difference-gradient rule (4) dictates a simple and familiar difference scheme:

$$\tilde{\partial}_x f(g^-, g^+) = \frac{\Delta f}{\Delta g} = \frac{f^+ - f^-}{g^+ - g^-}. \tag{18}$$

That is, the standard centered difference approximation. The apparent problem of possible division by zero can be eliminated by algebraic simplification when f is a power function, sufficient to handle all systems considered here. This approximation is second order accurate, indicating that this is the best that can be expected in this framework of single-step schemes. (However order can be increased if desired with standard symmetric step composition methods.)

Next, for compositions $f(g(\mathbf{z}))$ with f a function of a single variable, one gets the *discrete chain rule*:

$$\tilde{\partial}_{z_n}(f \circ g)(\mathbf{z}^-, \mathbf{z}^+) = \frac{\Delta f}{\Delta g}\, \tilde{\partial}_{z_n} g(\mathbf{z}^-, \mathbf{z}^+). \tag{19}$$

Finally, for a product of two factors, time-reversal symmetry leads to the *discrete product rule*:

$$\Delta(fg) = \bar{g}\Delta f + \bar{f}\Delta g. \tag{20}$$

Handling multiple products with invariant product factors. The one remaining challenge is products of more than two factors. Unfortunately, it is impossible to construct an acceptable general rule for this case. The problem is that if one applies the above product rule to a triple product fgh via the various factorizations $f(gh)$, $g(fh)$, etc., one gets different results, and attempts at symmetrization such as by averaging over all alternatives does not necessarily give a form leading to conservation of all momenta.

Instead, we must choose how to order the factors in products for compatibility with the (affine) symmetries. The key is to group variables into combinations that are invariant under all the affine symmetry transformations, differentiating such factors last in any multiple product. This is illustrated in the next section.

4. Discretizing the single spine Davydov system

We seek a discrete gradient expansion for the single spine Davydov system Hamiltonian (5) that respects the conserved quantities $\mathcal{E}$ and $\mathcal{P}$. Only the term $(u_{n+1} - u_{n-1})Q_n Q_n^*$ involves products of more than two variables, so all the rest is handled canonically. For that term, the product expansion should keep the two invariant factors $u_{n+1} - u_{n-1}$ and $Q_n Q_n^*$ together:

$$\begin{aligned}\Delta((u_{n+1} - u_{n-1})(Q_n Q_n^*)) &= \overline{(u_{n+1} - u_{n-1})}\Delta(Q_n Q_n^*) + \Delta(u_{n+1} - u_{n-1})\overline{Q_n Q_n^*} \\ &= (\bar{u}_{n+1} - \bar{u}_{n-1})\overline{Q_n^*}\Delta Q_n + (\bar{u}_{n+1} - \bar{u}_{n-1})\bar{Q}_n \Delta Q_n^* + \overline{Q_n Q_n^*}(\Delta u_{n+1} - \Delta u_{n-1}).\end{aligned}$$

The resulting *discrete single spine Davydov system* is

$$\Delta Q_n = i\left[L(\bar{Q}_{n+1} - 2\bar{Q}_n + \bar{Q}_{n-1}) + \frac{1}{2}(\bar{u}_{n+1} - \bar{u}_{n-1})(\bar{Q}_n)\right]\Delta t, \tag{21}$$

$$\Delta u_n = \omega^2 \bar{p}_n\, \Delta t, \tag{22}$$

$$\Delta p_n = \left[\bar{u}_{n+1} - 2\bar{u}_n + \bar{u}_{n-1} - \frac{1}{2}\left(\overline{|Q_{n+1}|^2} - \overline{|Q_{n-1}|^2}\right)\right]\Delta t. \tag{23}$$

4.1. Verifying conservation of the two momenta

Exact conservation of the two momenta is again verified by mimicing calculations for the ODE case.

For exciton energy:

$$\frac{\Delta \mathcal{E}}{\Delta t} = \sum_n \frac{\overline{Q_n^*}\Delta Q_n + c.c.}{\Delta t} = i\sum_n \left[L(\bar{Q}_{n+1} - 2\bar{Q}_n + \bar{Q}_{n-1}) + \frac{1}{2}(\bar{u}_{n+1} - \bar{u}_{n-1})(\bar{Q}_n)\right]\overline{Q_n^*} - c.c. = 0.$$

For phonon momentum:

$$\frac{\Delta \mathcal{P}}{\Delta t} = \sum_n \frac{\Delta p_n}{\Delta t} = \sum_n \left[(\bar{u}_{n+1} - \bar{u}_n) - (\bar{u}_n - \bar{u}_{n-1}) - \frac{1}{2} \left(\overline{|Q_{n+1}|^2} - \overline{|Q_{n-1}|^2} \right) \right] = 0.$$

where there are fictitious values at the end-points as in (6), ensuring that the sums telescope to zero.

The key in each case is that the quantities $\mathcal{E}$ and $\mathcal{P}$ do not involve products of more than two variables, and for such forms, the discrete derivatives have canonical form, which duplicates all necessary properties of true derivatives.

4.2. A linearly implicit iterative scheme

The above equations are implicit and nonlinear, so an iterative scheme for their approximate solution is needed. Fortunately, the Q Eq. (21) is linear in the Q variables, and likewise the other equations are linear in u_n and p_n. To describe the iterative method proposed, a modified form of Eqs. (21)–(23) is used:

(a) express each equation with the only unknowns being the "Δ" terms rather than the time average terms, via $\bar{u}_n = u_n + \frac{1}{2}\Delta u_n$ and so on;
(b) eliminate the Δu_n now present in the modified (23) using (22): combined with the above rewriting:

$$\bar{u}_n = u_n + \frac{1}{2}\Delta u_n = u_n + \frac{\omega^2}{2}\,\bar{p}_n \Delta t = u_n + \frac{\omega^2}{2}\left(p_n + \frac{1}{2}\Delta p_n \right) \Delta t.$$

Then cycle through updates of the vectors $\Delta\mathbf{p}$, $\Delta\mathbf{u}$ and $\Delta\mathbf{Q}$:

1. Solve approximately for Δp_n using the latest ΔQ_n approximations in the modified (23).
2. Solve approximately for Δu_n using the latest Δp_n approximation in the modified (22).
3. Solve approximately for ΔQ_n using the latest Δu_n approximations in the modified (21).

This involves only simultaneous tridiagonal linear equations at each stage, so cost is $O(N)$, comparable to an explicit iterative method. However, it has a number of advantages over any explicit method:

- stiffness due to the typically large coefficient L is well controlled, as each iteration is of implicit trapezoid form;
- at each iteration, the exciton energy $\mathcal{E}$ and phonon momentum $\mathcal{P}$ are exactly conserved: the iterative modifications of Equations (21) and (23) work just as well in the above verifications of conservation; this is useful because in practice a low, fixed number k of iterations is often used.
- the approximation of linear terms is second order accurate, with the first iteration limited to first order accuracy only in the typically smaller nonlinear coupling terms: this leads to very accurate conservation of the Hamiltonian after a quite small number of iterations, often to within machine accuracy after a modest number of iterations, as seen in the examples below.

5. Testing the DG method at large ω: handling phonon stiffness

Since as noted above, L can be rescaled, it is fixed at $L = 100$, and thus $\Delta x = 1/10$ is used when relating to continuum limit results and sech pulses. Initial testing is done with high phonon speed $\omega = 1000$ (and with $\omega = 100$, giving very similar results), and initial data a sech pulse close to a discretization of the initial values of the soliton form:

$$Q_n(0) = \operatorname{sech}(x_n) e^{iv x_n/2},\ x_n = n\Delta x,\ \Delta x = 1/10,\ -11{,}000 \le n \le 11{,}000. \tag{24}$$

This combination of L, ω and $Q_n(0)$ is close to the DNLS and NLS limits, and so the initial data used for the phonons is based on the DNLS limit (14):

$$u_n = \frac{1}{2}|Q_n|^2 + \sum_{m>n}|Q_m|^2, \quad p_n = 0. \tag{25}$$

The system is solved initially for very small time step $\Delta t = 1/20,000 \ll 1/\omega$, to be sure of resolving all details; then step size is increased to as high as $\Delta t = 1/100 \gg 1/\omega$, far too large to resolve all details of the phonon solution and well beyond the stability limit of any explicit discretization, but adequate to resolve the slower time scale of the exciton evolution.

Briefly, the solutions for $Q_n(t)$ are very close to the discretization of the NLS soliton solution of (13), and at nodes n anywhere near the soliton pulse, values of $u_n(t)$ stay close to the form of (14). However, the finite signal speed of (9) makes it impossible for u_n to have exactly this form. The discrepancy arises only in low amplitude compression waves going in each direction at speed ω, very quickly clearing the exciton pulse and thus not significantly interacting with that pulse.

Increasing time step size leads to significant inaccuracy in the fast phonon pulses, but negligible changes in either the exciton pulse or of the u_n values in the "exciton pulse zone": stiffness is handled harmlessly, so that exciton pulses can be handled with efficiently large time step sizes. Also, the inaccuracy that does appear is primarily in the velocity of the pulses, while the amplitude and sech form is very well preserved. This good handling of important qualitative features is what is hoped for and often achieved with structure-preserving methods such as this.

Finally, some notes on iteration counts and thus cost. For step sizes small enough to resolve all time scales, the minimal two iterations are sufficient to conserve $\mathcal{H}$ "exactly"; meaning to within machine accuracy. For the largest step size, $\Delta t = 1/100$, fiver iterations suffice for each conservation.

Further details of this algorithmic testing are to appear in [10].

6. Energetic pulses in the single spine Davydov system arising from an initial exciton impulse

Next, we move beyond the rather special initial data close to the soliton form, and study the genesis of sustained compact traveling energetic pulses arising from an initial localized input of energy, akin to what soliton theory predicts for the NLS limit. This is done with initial impulse data, asymmetric in amplitude and phase in order to initiate pulse movement, with the only non-zero initial values being:

$$Q_0(0) = 4,\ Q_0(0) = 16e^{-i/2}. \tag{26}$$

6.1. Initial impulse, large ω

In the absence of interaction with u, the solution for Q with impulsive initial data can be verified to involve dispersive radiation with a maximum speed of about $2L$, $=200$, through the purely linear "discrete Schrödinger" part of the equation. Conversely, with $Q=0$ the solution for u for impulsive initial data consists of a leading phonon compression wave in each direction of speed ω, with a slower trailing rarefaction wave in each direction. Thus for ω large enough relative to 200, one expects the phonon compression wave to be ahead of the Q radiation and have no interaction with Q, while the rarefaction waves can interact, and this interaction with Q can be hoped to approximate the "NLS" limit. All this is much as discussed in the previous section.

This is confirmed for $\omega = 1000$, 500, and even for $\omega = 200$, and is illustrated in Fig. 1 for $\omega = 500$. There is a single Q pulse moving to the right of roughly constant height, width, and speed. Approximate values are:

- $\omega = 1000$: height 8–9, speed 60, width 8 nodes (measured at 1/10 maximum height).
- $\omega = 500$: height 8–9, speed 44, width 9.
- $\omega = 200$: height 10, speed 10, width 7.

The pulse moves in concert with the trailing phonon rarefaction wave, and its speed decreases as ω does. Ahead of this is low amplitude exciton radiation with front speed about 200 and decaying amplitude; its amplitude is low

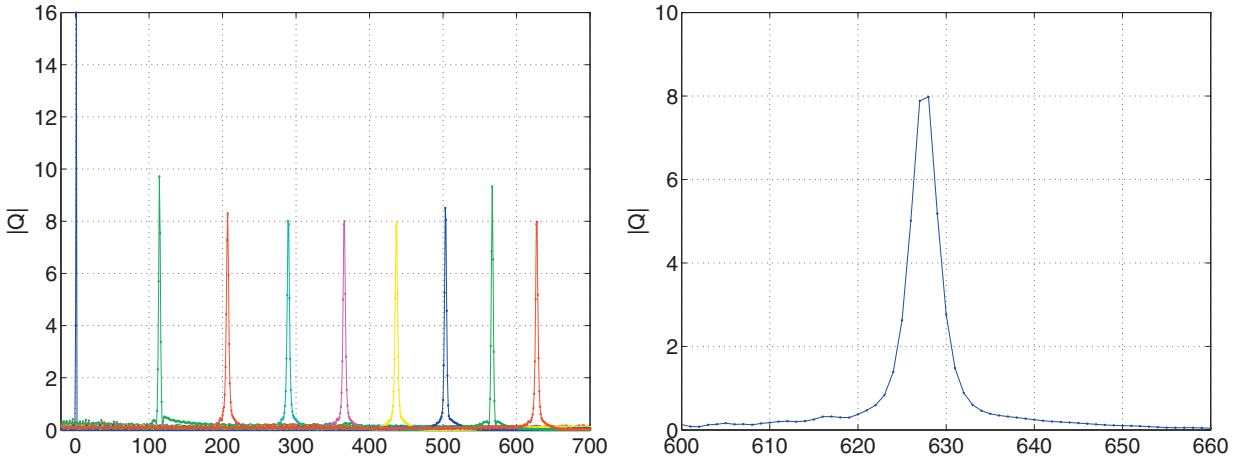

Fig. 1. (a) Rightward moving pulses in $|Q_n(t)|$ arising from initial impulse, $\omega = 500$, $L = 100$, $t = 0, 2, \ldots, 16$. (b) At $t = 16$, near the pulse, showing its width of only a few nodes and almost complete separated from the faster radiation.

enough that it is essentially decoupled from the phonons, and thus propagating "linearly". As time increases, the pulse becomes mostly separated from this dispersing radiation.

6.2. *Initial impulse, small* ω

For ω well below the Q radiation front speed, one still gets a dominant very narrow pulse moving slowly right with the trailing u rarefaction wave, its speed decreasing with ω as before. However, the leading u compression waves are now within the Q radiation, and this has a new effect: a second, smaller, faster exciton pulse in each direction of speed ω, coupled to the phonon compression waves, and again of roughly constant height, width, and speed. Ahead of this is dispersive radiation, as before. Eventually the Q radiation leaves all the pulses behind, leaving nearly isolated narrow pulses. Fig. 2 shows this for $\omega = 50$; results for $\omega = 20$ are very similar.

As one might expect, there is a transition: for $\omega = 100$ one gets the main slow pulse, smaller pulses going in each direction trailing the radiation, slightly faster than ω, but also another pair of pulses at the leading edge of the radiation, speed slightly below the Q radiation speed.

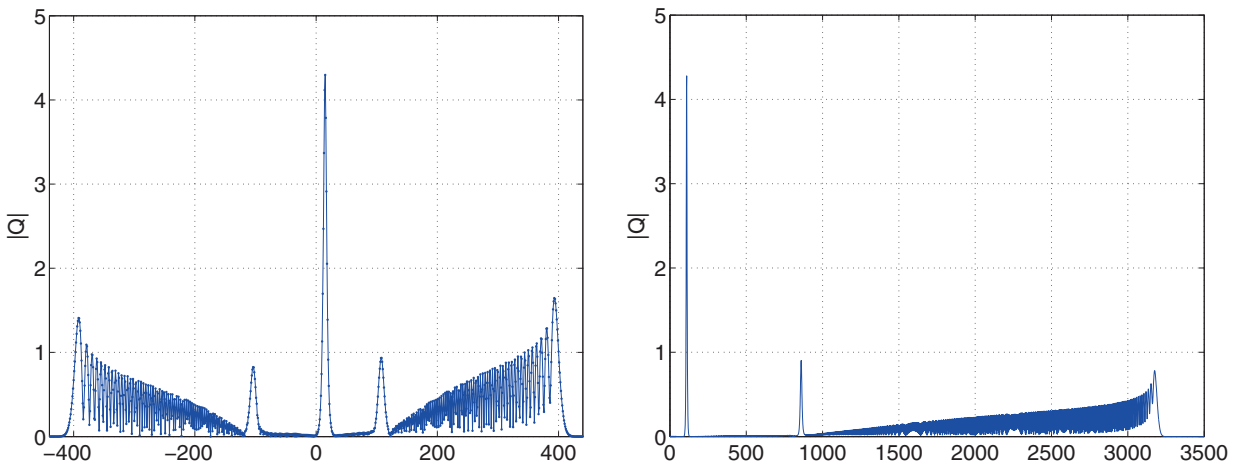

Fig. 2. Pulses in $|Q_n(t)|$ arising from initial impulse, $\omega = 50$, $L = 100$: (a) $t = 2$. (b) $t = 16$. Right half only, due to near symmetry.

7. Discussion and conclusions

The discrete gradient method introduced here gives time discretizations for Hamiltonian ODE systems that conserve energy and all quadratic momenta, and is suited to a range of large, stiff ODE systems including ones arising from molecular systems and as spatial discretizations of various nonlinear wave equations related to NLS. The discretizations retain the benefits of quasi-linearity, leading to simpler nonlinear equation solving than in more comprehensive approaches to conservative discretizations such as that of McLachlan et al. [12]. While discretizations given by the discrete gradient method are of a form described by Gonzales [5], the approach here simplifies construction of a suitable algorithm: in particular, linear terms and those involving at most two unknowns are handled canonically, with no additional constructions or choices required to get a conservative form.

On a modification of Davydov's ODE model of one-dimensional quasi-molecular structures, the algorithm handles well the extreme stiffness and high pulse speeds in the "phonon" term that arise for high characteristic phonon speeds, while confirming the validity of the NLS limit in this case.

For the near-NLS limit of large phonon characteristic speed ω, impulsive initial data leads to pulses resembling sech solitons, trailing low amplitude, dispersing exciton radiation and a low amplitude phonon compression wave in each direction of speed ω: all consistent with expectations based on known behavior of NLS and of the linear, decoupled phonon equation.

For phonon speeds significantly below than the characteristic exciton radiation speed, the slow exciton pulse is still seen, slower for lower ω, but there is also a previously unexpected new phenomenon: a faster, somewhat weaker coherent exciton pulse moving in each direction with the phonon compression waves at speed ω. Both pulses eventually separate out from the low level exciton radiation. Thus there is a second potentially faster coherent exciton pulse mechanism for energy transfer.

References

[1] M.J. Ablowitz, J.F. Ladik, Nonlinear differential-difference equations, Journal of Mathematical Physics (1975) 598–603.
[2] M.J. Ablowitz, J.F. Ladik, Nonlinear differential-difference equations and fourier analysis, Journal of Mathematical Physics 17 (1976) 1011–1018.
[3] A.S. Davydov, Theory of Molecular Excitations, Plenum press, New York, 1971.
[4] A.S. Davydov, N.I. Kislukha, Solitary excitations in one-dimensional molecular chains, Phys Status Solidi B 59 (1973) 465–470.
[5] O. Gonzales, Time integration and discrete Hamiltonian systems, Journal of Nonlinear Science 6 (1996) 449–467.
[6] E. Hairer, C. Lubich, Geometric Numerical Integration: Structure Preserving Algorithms for Ordinary Differential Equations, 2nd ed., Springer, 2006.
[7] S. Jimenez, Derivation of the discrete conservation laws for a family of finite difference schemes, Applied Mathematics and Computation 64 (1994) 13–45.
[8] P.G. Kevrekidis, On a class of discretizations of Hamiltonian nonlinear partial differential equations, Physica D 183 (2003) 68–86.
[9] P.G. Kevrekidis, S.V. Dmitriev, A.A. Sukhorukov, On a class of spatial discretizations of equations of the nonlinear Schrödinger type, Mathematics and Computers in Simulation 74 (2007) 343–351.
[10] B. LeMesurier, Conservative A-stable discretization methods for stiff Hamiltonian equations, and an application to wave motion in lattice equations modeling protein molecules, Physica D, submitted for publication.
[11] S. Li, L. Vu-Quoc, Finite difference calculus invariant structure of a class of algorithms for the nonlinear Klein–Gordon equation, SIAM Journal on Numerical Analysis 32 (6) (1995) 1839–1875.
[12] R.I. McLachlan, G.R.W. Quispel, N. Robidoux, Geometric integration using discrete gradients, Philosophical Transactions: Mathematical, Physical and Engineering Sciences 357 (1754) (1999) 1021–1045.
[13] A.C. Scott, The vibrational structure of Davydov solitons, Physica Scripta 25 (1982) 651–658.
[14] A.C. Scott, Launching a Davydov soliton: I. Soliton analysis, Physica Scripta 29 (1984) 279–283.
[15] A.C. Scott, Davydov's soliton, Physics Reports 217 (1) (1992) 1–67.