Conservative, unconditionally stable discretization methods for Hamiltonian equations, applied to wave motion in lattice equations modeling protein molecules

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ABSTRACT

A new approach is described for generating exactly energy–momentum conserving time discretizations for a wide class of Hamiltonian systems of DEs with quadratic momenta, including mechanical systems with central forces; it is well-suited in particular to the large systems that arise in both spatial discretizations of nonlinear wave equations and lattice equations such as the Davydov System modeling energetic pulse propagation in protein molecules. The method is unconditionally stable, making it well-suited to equations of broadly "Discrete NLS form", including many arising in nonlinear optics.

Key features of the resulting discretizations are exact conservation of both the Hamiltonian and quadratic conserved quantities related to continuous linear symmetries, preservation of time reversal symmetry, unconditional stability, and respecting the linearity of certain terms. The last feature allows a simple, efficient iterative solution of the resulting nonlinear algebraic systems that retain unconditional stability, avoiding the need for full Newton-type solvers. One distinction from earlier work on conservative discretizations is a new and more straightforward nearly canonical procedure for constructing the discretizations, based on a "discrete gradient calculus with product rule" that mimics the essential properties of partial derivatives.

This numerical method is then used to study the Davydov system, revealing that previously conjectured continuum limit approximations by NLS do not hold, but that sech-like pulses related to NLS solitons can nevertheless sometimes arise.

1. Introduction

Diverse physical problems lead to mathematical models in the form of large, stiff Hamiltonian systems in the form of discrete Nonlinear Schrödinger [DNLS] equations, N-body particle systems, or combinations of the two. The most familiar are perhaps particle systems with Hamiltonian splitting into kinetic and potential energy terms

$$\mathcal{H} = \sum_k \frac{\|p_k\|^2}{2m_k} + V(q), \tag{1}$$

discretizations of the nonlinear Schrödinger [NLS] equation and of the Zakharov system modeling Langmuir turbulence in plasmas [1] (essentially a nonlinear coupling of the Schrödinger equation and the wave equation), and various coupled systems of NLS equations [CNLS] arising in nonlinear optics. A richer class of equations arises in inherently discrete situations such as the so-called *lattice wave equations*, which arise, for example, as models of interactions within large bio-molecules and in large collections of molecules.

The primary illustrative examples used here are based on the Davydov system: a model originated by Davydov [2–4] and Davydov and Kislukha [5], for energy transfer along α-helix protein molecules. This is chosen in part because of the algorithmic challenges that arise from its combination of both classical particle interactions and discrete Schrödinger-like equations, and the presence of non-local nonlinearities.

The Schrödinger-like equations prevent the above-seen separation into kinetic and potential energy terms, which hampers some popular methods for mechanical systems, such as the symplectic method of Störmer and Verlet and introduces stiffness through linear terms, while the non-local nonlinearity rules out some methods that work well for discretizations of PDE's, such as the conservative method of Chang and Xu [6]. These challenges motivate the development of time discretizations that conserve energy and other first integrals while offering good handling of stiffness through linear stability for any time step size. This is done here by combining discrete gradient methods with a new difference calculus that includes a method for handling products; the failure to handle products appropriately in previous difference calculus methods prevented the handling of multiple conservation laws.

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1.1. Quantum-classical Hamiltonian systems

The systems of immediate interest are either discrete nonlinear Schrödinger equations or couplings of these with classical interacting particle systems as in (1). These fit into a framework that also includes purely classical particle systems, and which will be referred to as *quantum-classical Hamiltonian systems*:

$$\frac{dz_n}{dt} = i\frac{\partial \mathcal{H}}{\partial z_n^*}, \qquad \frac{dz_n^*}{dt} = -i\frac{\partial \mathcal{H}}{\partial z_n},$$
$$\frac{dq_k}{dt} = \frac{\partial \mathcal{H}}{\partial p_k}, \qquad \frac{dp_k}{dt} = -\frac{\partial \mathcal{H}}{\partial q_k}, \tag{2}$$

with Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{quantum}} + \mathcal{H}_{\text{classical}} + \mathcal{H}_{\text{coupling}},$$

$$\mathcal{H}_{\text{quantum}} = \sum_{n,m} L_{n,m} z_n^* z_m + G(\mathbf{z}, \mathbf{z}^*),$$

$$\mathcal{H}_{\text{classical}} = \sum_k \frac{p_k^2}{2m_k} + V(\mathbf{q}), \quad m_k > 0 \text{ constants}, \tag{3}$$

$$\mathcal{H}_{\text{coupling}} = \sum_{n,m} \chi_{n,m}(\mathbf{q}) z_n^* z_m.$$

Here

- $\mathbf{z}$ and $\mathbf{z}^*$ are N-component complex vectors of "quantum" or "Schrödinger Equation" components z_n, z_n^* (these vectors are formally considered as independent, but, in practice, are complex conjugates);
- $\mathbf{q}$ and $\mathbf{p}$ are M-component real vectors of "classical" or "wave equation" components q_k, p_k;
- $L_{n,m}$ and $\chi_{n,m}(\mathbf{q})$ are components of real, symmetric matrices;
- $G(\mathbf{z}, \mathbf{z}^*)$ is real valued when $\mathbf{z}$ and $\mathbf{z}^*$ are complex conjugates, and is invariant under the interchange $\mathbf{z} \leftrightarrow \mathbf{z}^*$;
- G, V and $\chi_{n,m}$ are typically elementary algebraic functions, and often polynomial.

Note: the term $G(\mathbf{z}, \mathbf{z}^*)$, arises mainly in systems of "DNLS-type": ones with only the quantum variables present.

The resulting DEs are

$$i\frac{dz_n}{dt} + \sum_m [L_{n,m} + \chi_{n,m}(\mathbf{q}) + g_{n,m}(\mathbf{z}, \mathbf{z}^*)]z_m = 0, \tag{4}$$

$$m_k\frac{d^2q_k}{dt^2} + \frac{\partial V}{\partial q_k} + \sum_{n,m} \frac{\partial \chi_{n,m}}{\partial q_k} z_n^* z_m = 0. \tag{5}$$

The conditions on $L_{n,m}$, $\chi_{n,m}$ and G ensure invariance of such Hamiltonians under the phase shift symmetry $z_n \to e^{i\theta} z_n$, $z_n^* \to e^{-i\theta} z_n^*$ and conservation of

$$\mathcal{E} = \sum_n z_n^* z_n, \quad \text{the exciton number.} \tag{6}$$

Other likely symmetries are the usual rigid motion symmetries in $\mathbf{q}$ and $\mathbf{p}$, leading to conservation of classical linear and angular momenta.

1.2. Real and complex canonical Hamiltonian form

The above system can be put in the canonical form

$$\frac{d\mathbf{y}}{dt} = \mathcal{J}\nabla\mathcal{H} \tag{7}$$

with $\mathbf{y}$ the concatenation of $\mathbf{z}$, $\mathbf{z}^*$, $\mathbf{q}$, and $\mathbf{p}$, $\mathcal{H} = \mathcal{H}(\mathbf{y})$, and symplectic matrix

$$\mathcal{J} = \begin{bmatrix} iJ_N & 0 \\ 0 & J_M \end{bmatrix}, \qquad J_s := \begin{bmatrix} 0 & I_s \\ -I_s & 0 \end{bmatrix}.$$

In many places below, all that matters is that the equations have form (7) with $\mathcal{J}$ a constant anti-symmetric matrix.

Aside: applying the change of variables $z_n = (Q_n + iP_n)/\sqrt{2}$, $z_n^* = (Q_n - iP_n)/\sqrt{2}$ to the above system and some renaming and reindexing of variables gives the familiar real canonical Hamiltonian form with $\mathcal{J} = J_{N+M}$; then the above condition on G is simply that it is real-valued for real Q_n and P_n. However, the partially complex form is more convenient here.

The time discretization procedure introduced here works best for Hamiltonians that are algebraic elementary functions: ones constructed from rational power functions through basic arithmetic operations and compositions. However, it is, in principle, possible to extend it to all elementary functions, as will be explained in the description of iterative schemes given below, for solving the discrete system.

1.3. Main examples: the Davydov system, and a non-standard DNLS approximation

The form above includes spatial discretizations of nonlinear Schrödinger equations and coupled systems of such ($\mathcal{H} = \mathcal{H}_{\text{quantum}}$), the Zakharov system, and the form of G also allows for nonlocal interactions, such as NLS equations with nonlinearities given by convolution integrals. However, the archetypical example used herein is one of inherently discrete origins, in the modeling of energetic pulse propagation in the α-helix protein originated by Davydov [2–4], Davydov and Kislukha [5] and advanced, in particular, by Scott [7,8], which includes all the interesting complications and challenges of such systems: the *Davydov System* [DS]

$$i\frac{dz_n}{dt} + K(z_{n-3} + z_{n+3}) - L(z_{n-1} + z_{n+1}) = (q_{n+3} - q_{n-3})z_n, \tag{8}$$

$$m_0\frac{d^2q_n}{dt^2} - (q_{n-3} - 2q_n + q_{n+3}) = |z_{n+3}|^2 - |z_{n-3}|^2, \tag{9}$$

where $0 \le n \le n_{\max}$, and the boundary conditions are given by zero values for z_n and the *bond stretchings* $d_n := q_{n+3} - q_n$ for out-of-bounds values of any index. This has Hamiltonian

$$\mathcal{H} = \sum_n -K(z_n^* z_{n+3} + z_n z_{n+3}^*) + L(z_n^* z_{n+1} + z_n z_{n+1}^*)$$
$$+ \sum_n \frac{p_n^2}{2m_0} + \frac{1}{2}(q_{n+3} - q_n)^2 + \sum_n (q_{n+3} - q_{n-3})z_n^* z_n. \tag{10}$$

The physical meaning of the quantities and values of parameters are given in Section 2.

1.4. Properties desired in time discretizations

For the various equations considered above, several criteria are desirable in time discretizations to give simulations that are accurate and preserve important qualitative features of the exact solutions:

1. Respecting all conserved quantities of the DEs, meaning, in particular, the Hamiltonian and the exciton number, and also any classical momenta.
2. Respecting symmetries: both the continuous phase space symmetries related to conserved quantities (such as exciton phase shift invariance) and time reversal symmetry. Empirical evidence suggests that time reversal symmetry is beneficial to good qualitative long-time behavior (see [9] Section V.5).
3. Unconditional stability when the equations have stiff linear terms. For example, it is likely that the main pulses in solutions of the Davydov system have a far slower time scale than any of the three time scales embodied in parameters K, L and ω above, so it is desirable to be able to use time step sizes considerably larger than would be required with any explicit method.

4. As unconditional stability generally requires implicit methods, and the number of unknowns can be very large, it is highly desirable that the coupling in the time-discrete system is predominantly linear, so that the iterative solution can handle nonlinear terms with a simple fixed point approach, rather than requiring a full Newton-like method that would require evaluation of and solving with a large Jacobian matrix. (This rules out the conservative numerical methods of McLachlan et al. [10] for general Hamiltonian systems, which are better suited to highly nonlinear dynamical systems with relatively few degrees of freedom.)

5. The option of high order accuracy in time, if needed.

All but one of these criteria are met by the second order accurate symplectic Implicit Midpoint Method [MP] combined with symmetric step-composition methods to increase order, or equivalently, by suitable symplectic diagonally implicit Runge–Kutta methods; see [9], in particular V.3 and VI.4, Theorem 4.4.

However, the crucial feature unavoidably missing from any symplectic method is *exact conservation of the Hamiltonian* [11,12]. Related to this, as noted in the discussion in Section 4.2 below, discrete gradient methods can have better stability than A-stable symplectic methods when using large time steps for stiff, nonlinear systems. Thus a method is described and used here which adds conservation of the Hamiltonian and the above-mentioned nonlinear stability properties while preserving almost all virtues of the MP method, including, for example, the option of increasing order to arbitrarily high degree by using symmetric step-composition methods (see [9]).

1.5. Conservative time discretization via discrete gradients and a discrete difference calculus with product law

The two main ingredients are a Discrete Gradient approach such as that described by Gonzales [13], and a nearly canonical difference calculus for elementary function expressions, which can handle products in a way that respects conserved quantities of linear or quadratic form and related affine symmetries.

In a Discrete Gradient time discretization of the Hamiltonian system Eq. (7), the state vector $\mathbf{y}(t) = \{y_n(t)\}$ is approximated by the discrete values $\mathbf{y}^l = \{y_n^l\} \approx \{y_n(t_l)\}$, $t_l = l\Delta t$, which solve a *Time Discrete Hamiltonian System*

$$\Delta \mathbf{y} := \mathbf{y}^{l+1} - \mathbf{y}^l = \mathcal{J}\tilde{\nabla}\mathcal{H}\,\Delta t. \tag{11}$$

Here, the *Discrete Gradient* $\tilde{\nabla}\mathcal{H} = \tilde{\nabla}\mathcal{H}(\mathbf{y}^l, \mathbf{y}^{l+1})$ has components

$$\frac{\delta\mathcal{H}}{\delta y_n} = \frac{\delta\mathcal{H}}{\delta y_n}(\mathbf{y}^l, \mathbf{y}^{l+1})$$

that are suitable approximations of the partial derivatives $\partial\mathcal{H}/\partial y_n$.

It will be seen below that there are many choices of discrete gradient, and it is easy to find ones that ensure exact conservation of the Hamiltonian, by an argument that mimics the derivation for continuous-time Hamiltonian systems. The challenge is to then find a discrete gradient that also gives conservation of other first integrals, or "momenta"; for this, a new approach is introduced based on a finite difference calculus, with this calculus preserving enough properties of actual derivatives that the verification of a conservation law for the DE system translates directly to one for the time-discrete system.

The main technical challenge is that it is apparently impossible to create such a difference calculus with a product rule that respects the associativity of multiplication along with other needed symmetry properties. Thus the difference calculus works at the level of explicit formulas for functions, with the orders of products needing to be specified, and chosen in a way that relates to the conservation laws. This limits the approach to conserving momenta that are quadratic (or linear) in the state variables; fortunately all common momenta are of this form.

In the rest of this paper, Section 2 describes the Davydov system, various reductions of it, and some previously proposed continuum limits; Section 3 develops the discrete gradient calculus and gives the main result on conservation of energy and quadratic momenta; Section 4 describes the exactly momentum-conserving iterative schemes that will be used in practice and makes some comparisons to alternative approaches; Section 5 tests the discrete gradient method in comparison to previous approaches, in particular, the implicit midpoint method; Section 6 presents a numerical study of the Davydov system. This study reveals that previously conjectured continuum limit behavior is not typically seen, and instead one gets either sech form pulses of slow amplitude variation through a different mechanism, or (more commonly) persistent traveling pulses that are far too narrow for a continuum limit explanation.

2. The Davydov system and some approximations and reductions

In the Davydov system of Eqs. (8) and (9) above:

- Index n labels amino acid residues (herein-under *residues*). Each consecutive triple of residues forms one turn of the helix with the K terms giving coupling of residues in successive twists into roughly straight lines called *spines*. It is sometimes convenient to use a spine index $\sigma = 0, 1, 2$ and twist index m, with $n = 3m + \sigma$.
- Quantum state variables z_n describe the quantized excited states of the C=O amide-I group in residue n.
- q_n is the longitudinal displacement of that C=O bond from equilibrium position.
- K is the strength of the [attractive] dipole interaction between quantum states in residues that are longitudinally adjacent within a spine.
- L is the strength of the [repulsive] dipole interaction between quantum states in residues that are laterally adjacent along the protein's backbone.
- m_0 is an effective oscillator mass, so that $\omega := 1/\sqrt{m_0}$ the natural frequency of the oscillations in the length of bond between adjacent residues in a spine.
- The constants are all time scales, relevant to further simplifying approximations:

$$K = 1.4\,\text{THz}, \qquad L = 2.3\,\text{THz}, \qquad \omega = 12\,\text{THz}. \tag{12}$$

2.1. CDNLS: a non-locally nonlinear NLS limit of the above

As the oscillator frequency ω gives by far the fastest time scale in the system, a plausible approximation is to take the limit of high frequency, or very small m_0. For this it helps to first express the equations in terms of the bond-stretchings $d_n = q_{n+3} - q_n$, so that in this limit

$$d_n - d_{n-3} = q_{n-3} - 2q_n + q_{n+3} \approx |z_{n-3}|^2 - |z_{n+3}|^2,$$

giving

$$d_n \approx -(|z_{n+3}|^2 + |z_n|^2). \tag{13}$$

Then Eq. (8) is approximated in terms of the z_n's alone by a system of Coupled Discrete NLS equations [CDNLS], with a non-local nonlinearity different from that arising in standard discretizations of Coupled NLS equations:

$$i\frac{dz_n}{dt} + K(z_{n-3} + z_{n+3}) - L(z_{n-1} + z_{n+1})$$
$$+ \left[|z_{n-3}|^2 + 2|z_n|^2 + |z_{n+3}|^2\right]z_n = 0, \tag{14}$$

with Hamiltonian

$$\mathcal{H} = -K(z_n^* z_{n+3} + z_n z_{n+3}^*) + L(z_n^* z_{n+1} + z_n z_{n+1}^*)$$
$$+ (z_n^* z_n)(z_n^* z_n + z_{n+3}^* z_{n+3}). \tag{15}$$

2.2. NLDNLS: an uncoupled system as the simplest test case

A further simplification for the sake of assessing numerical methods is to eliminate the spine structure: setting $L = 0$ above gives separate equations on each spine. Doing so in CDNLS (14) and reducing the index shift from 3 to 1 gives a Non-local Discrete NLS equation

$$i\frac{dz_n}{dt} + K(z_{n+1} + z_{n-1}) + (|z_{n-1}|^2 + 2|z_n|^2 + |z_{n+1}|^2)z_n = 0 \quad (16)$$

with Hamiltonian

$$\mathcal{H} = \sum_n -K(z_n^* z_{n+1} + z_n z_{n+1}^*) + (z_n^* z_n)(z_n^* z_n + z_{n+1}^* z_{n+1}). \quad (17)$$

2.3. Continuum limits: coupled NLS and connections to the integrable NLS equation

Previous studies of the above systems have sought solutions with slow variation along spines, which can be approximated by continuum limits, as described for example by Scott [7]. The first step is to remove an overall fast phase factor of $-2iKt$ arising from the expected slow variation along spines; this changes the K term in the ODEs to the second difference form $-K(z_{n-3} - 2z_n + z_{n+3})$, and so on, and in the Hamiltonians to $-K(z_{n+3}^* - z_n^*)(z_{n+3} - z_n) = -K|z_{n+3} - z_n|^2$ and so on. Then the residue index m is a natural position index, and approximation $z_n = z_{3m+\sigma}(t) \approx z_\sigma(m\Delta x, t)$ gives the Coupled NLS [CNLS] system

$$i\frac{\partial z_\sigma}{\partial t} + K(\Delta x)^2 \frac{\partial^2 z_\sigma}{\partial x^2} + 2|z_\sigma|^2 z_\sigma = L(z_{\sigma-1} + z_{\sigma+1}). \quad (18)$$

The further assumption of simple phase relationship $z_\sigma = e^{i\phi}z$, $\phi = 0$ or $\pm 2\pi/3$ and rescaling $z(t, x) = \kappa\psi(\kappa^2 t, x)\exp(i\gamma t)$, $\kappa = \Delta x\sqrt{K/2}$ and $\gamma = 2L$ for $\phi = 0$, $\gamma = -L$ for $\phi = \pm 2\pi/3$ gives the completely integrable NLS equation

$$i\frac{\partial\psi}{\partial t} + \frac{\partial^2\psi}{\partial x^2} + 2|\psi|^2\psi = 0 \quad (19)$$

with solutions including the hyperbolic secant solitons

$$\psi(t, x) = A\,\text{sech}(A(x - vt))\exp\left[-\frac{i}{2}(vx - (v^2/4 - A^2)t)\right]. \quad (20)$$

Another special case indicated in [7] is solutions with one spine mode vanishing and the other two negatives of each other: $z_0 = 0$, $z_1 = -z_2 = z(t, x)$, and again a rescaling of $z(t, x)$ then satisfies NLS.

One objective of this paper is to demonstrate that, although solutions of the Davydov system do approach forms with exciton density $|z_n|^2$ fitting such a sech^2 form, the phase and other details are not as predicted, and it is more common for solutions to have pulses with no slow variation and so no clear continuum limit model applicable.

3. Discrete gradient discretizations via a discrete gradient calculus with product rule

First, some notation is introduced. For a scalar or vector independent variable $\mathbf{y}$, the values at the beginning and end of the current discrete time step will be denoted as $\mathbf{y}^- = \mathbf{y}^l$ and $\mathbf{y}^+ = \mathbf{y}^{l+1}$ respectively, and the difference and mean of these values as

$$\Delta\mathbf{y} = \Delta\mathbf{y}(\mathbf{y}^-, \mathbf{y}^+) := \mathbf{y}^+ - \mathbf{y}^-, \qquad \bar{\mathbf{y}} := \frac{\mathbf{y}^- + \mathbf{y}^+}{2}. \quad (21)$$

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

$$f^- := f(\mathbf{y}^-), \qquad f^+ = f(\mathbf{y}^+),$$

$$\Delta f = \Delta f(\mathbf{y}^-, \mathbf{y}^+) := f^+ - f^-, \qquad \bar{f} := \frac{f^+ + f^-}{2}. \quad (22)$$

Next, a key strategy is to choose a discrete gradient that shares enough of the properties of the true gradient, and conservation of the Hamiltonian itself is ensured by mimicking the differential identity

$$dF = \nabla F \cdot d\mathbf{y} = \sum_n \frac{\partial F}{\partial y_n} dy_n, \quad (23)$$

with the requirement that

$$\Delta F = \tilde{\nabla}F \cdot \Delta\mathbf{y} = \tilde{\nabla}_\mathbf{y}F \cdot \Delta\mathbf{y} = \sum_n \frac{\delta F}{\delta y_n}\Delta y_n. \quad (24)$$

The proof is then that

$$\begin{aligned}
\Delta\mathcal{H} &= \mathcal{H}(\mathbf{y}^+) - \mathcal{H}(\mathbf{y}^-) \\
&= \tilde{\nabla}\mathcal{H} \cdot \Delta\mathbf{y} \quad \text{from (24),} \\
&= \tilde{\nabla}\mathcal{H} \cdot \mathcal{J}\tilde{\nabla}\mathcal{H}\,\Delta t \quad \text{from (11),} \\
&= 0 \quad \text{from the anti-symmetry of } \mathcal{J}.
\end{aligned} \quad (25)$$

Discrete counterparts of differentiation rules. Other conserved quantities 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 the same is true for the difference equations here.

The novel approach here is to construct the components of the discrete gradient by rules mimicking those used for calculation of derivatives: linearity, a discrete product rule, and a discrete chain rule for compositions $f(g(\mathbf{y}))$ with f a function of a single variable; all respecting appropriate symmetries in the Hamiltonian. (A quotient rule is not necessary, as quotients can be replaced by products and composition with the reciprocal function.)

Functions of one variable. For functions $f(x)$ of a single variable, the Discrete Gradient Rule (24) dictates a simple and familiar difference scheme:

$$\begin{aligned}
\frac{\delta f}{\delta x}(x^-, x^+) &= \tilde{D}f(x^-, x^+) \\
&:= \begin{cases} \dfrac{\Delta f}{\Delta x} = \dfrac{f^+ - f^-}{x^+ - x^-}, & x^+ \neq x^- \\[2mm] \dfrac{df}{dx}(\bar{x}), & x^+ = x^- = \bar{x}, \end{cases}
\end{aligned} \quad (26)$$

that is, the standard centered difference approximation, with the exact derivative used when needed. This approximation is second order accurate, indicating that this is the best that can be expected in the basic DG framework. However, standard symmetric step composition methods, combining forward and backward DG steps, can then be used to achieve composite methods of arbitrarily high order, as in [9], Section V.3.

A potential problem here is that the choice between the two forms in Eq. (26) depends on x^+ which in evaluation of $\tilde{\nabla}\mathcal{H}$ will depend on the unknown quantity $\mathbf{y}^+$. Thus it is desirable (but not quite essential, as explained in Section 4.1) to simplify the first form so as to eliminate division by Δx giving a universally valid formula. This is possible for natural number powers with

$$\frac{\Delta(x^n)}{\Delta x} = (x^-)^{n-1} + (x^-)^{n-2}(x^+) + \cdots + (x^+)^{n-1}$$

and, using the rules described next, can be extended to all algebraic elementary functions.

Linearity, the chain rule, and inverses. Sums and constant factors are naturally handled by linearity, and there is a canonical choice for a Discrete Chain Rule

$$\frac{\delta(f \circ g)}{\delta y_n}(y^-, y^+) = \tilde{D}f(g^-, g^+)\frac{\delta g}{\delta y_n}(y^-, y^+). \quad (27)$$

Also, for the inverse of a function of one variable, $y = f^{(-1)}(x)$:

$$\frac{\delta f^{(-1)}}{\delta x}(x^-, x^+) = \frac{1}{\tilde{D}f(y^-, y^+)} = \frac{\Delta x}{\Delta y}$$

with special handling of $\Delta y = 0$ as above.

Products. For a product of two factors, the infinite possibilities include

$$\Delta(fg) = g^- \Delta f + f^+ \Delta g$$
$$= g^+ \Delta f + f^- \Delta g$$
$$= \bar{g} \Delta f + \bar{f} \Delta g,$$

but the last is most reasonable, both for its time reversal symmetry and for being the only option giving second order accuracy. Thus we adopt the *Discrete Product Rule*

$$\Delta(fg) = \bar{g} \Delta f + \bar{f} \Delta g. \tag{28}$$

However, for products of more than two factors, it is impossible to construct a generally applicable rule. If one applies the rule above to product fgh via the various factorizations $f(gh)$, $g(fh)$ etc., one gets different results, with different consequences for conservation of momenta in system (11). Also, symmetrizations such as averaging over all alternatives do not necessarily give a form that respects the symmetries and conservation laws of the Hamiltonian. Instead, we must choose how to handle products for compatibility with symmetries, and accept that the calculus cannot respect associativity of products: this is why it is a calculus on explicit formulas, not for the functions represented by such formulas.

The resolution is the following proposition.

Proposition 1. *If a Hamiltonian system (7) has a collection of conserved quadratic momenta that depend on state variables only, these being the Noetherian first integrals related to invariance of the Hamiltonian under a group of affine transformations of the variables, and the Hamiltonian is "manifestly invariant" in that it can be expressed entirely in terms of quadratic combinations $\hat{y}_a(\mathbf{y})$ of the original variables that are invariant under this symmetry group*

$$\mathcal{H}(\mathbf{y}) = \hat{\mathcal{H}}(\hat{\mathbf{y}}(\mathbf{y})), \tag{29}$$

then the time discrete Hamiltonian system (11) conserves these momenta so long as the discrete gradient is constructed by applying the above discrete chain rule to formula (29): formally,

$$\tilde{\nabla}_{\mathbf{y}} \mathcal{H} = \tilde{\nabla}_{\hat{\mathbf{y}}} \hat{\mathcal{H}} \cdot \tilde{\nabla}_{\mathbf{y}} \hat{\mathbf{y}}, \tag{30}$$

and the discrete gradient scheme is

$$\mathbf{y}^+ - \mathbf{y}^- = \mathcal{J} \tilde{\nabla}_{\hat{\mathbf{y}}} \hat{\mathcal{H}}(\hat{\mathbf{y}}^-, \hat{\mathbf{y}}^+) \cdot \tilde{\nabla}_{\mathbf{y}} \hat{\mathbf{y}}(\mathbf{y}^-, \mathbf{y}^+) \Delta t. \tag{31}$$

Note that the choice of the discrete gradient $\tilde{\nabla}_{\hat{\mathbf{y}}} \hat{\mathcal{H}}$ in the first factor does not matter, while the second factor $\tilde{\nabla}_{\mathbf{y}} \hat{\mathbf{y}}$ is determined by the discrete product rule and linearity from terms like

$$\frac{\delta(y_a y_b)}{\delta y_a} = \bar{y}_b \quad (a \neq b), \qquad \frac{\delta((y_a)^2)}{\delta y_a} = 2\bar{y}_a$$

so that $\tilde{\nabla}_{\mathbf{y}} \hat{\mathbf{y}}$ comes from the exact gradient through the substitution $y_n \to \bar{y}_n$.

The idea of the proof is simple, and will only be sketched here, and illustrated below for the case of conservation of exciton number in the Discrete Davydov System. It is to observe that, for any quadratic conserved quantity Q, the calculation that

$$\frac{dQ}{dt} = \nabla Q(\mathbf{y}) \cdot \mathcal{J} \tilde{\nabla}_{\hat{\mathbf{y}}} \cdot \nabla_{\mathbf{y}} \hat{\mathbf{y}} = 0$$

does not depend at all on the details of the function $\hat{\mathcal{H}}$, which after all can be chosen arbitrarily and still give these conservation laws. Instead, the result depends only on the linear terms $\nabla Q(\mathbf{y})$ and $\nabla_{\mathbf{y}} \hat{\mathbf{y}}$ which are linear in the y_n. When one computes $\frac{\Delta Q}{\Delta t}$ for the discrete gradient scheme, the only change in these linear gradient terms is the substitution $y_n \to \bar{y}_n$, which is merely a "renaming", and does not affect the validity of the identity:

$$\frac{\Delta Q}{\Delta t} = 0,$$

so quadratic momentum Q is conserved.

The required "manifest invariance" is present in the Davydov system, in both reductions mentioned in Section 3, in standard DNLS equations, and in central force mechanical systems of the form of (1) with potential of form

$$V(\mathbf{q}) = \sum_{k<k'} V_{k,k'}(\|q_k - q_{k'}\|), \tag{32}$$

so that the familiar conserved quantities exciton number, linear momentum, and angular momentum where applicable are respected in the examples here and in a wide variety of physical systems.

More generally, for the quantum-classical systems of (2), (3), r system with only quantum or only classical parts present: conservation of exciton number requires that the term $G(\mathbf{z}, \mathbf{z}^*)$ achieves its phase-shift invariance manifestly through being built from terms $z_a^* z_b$, conservation of linear momentum requires that $V(\mathbf{q})$ achieves its translation invariance manifestly through being expressed in terms of differences $q_k - q_{k'}$, and conservation of linear and angular momenta in such systems requires that the variables q_k appear only through the distances $\|q_k - q_{k'}\|$, as in (32).

3.1. Discretizing the Davydov system

For the main example of the Davydov system, the only part of the Hamiltonian (10) where the order of products matters is the final, coupling term, for which the required discrete gradient is

$$\Delta \left[\sum_n (q_{n+3} - q_{n-3})|z_n|^2 \right]$$
$$= \sum_n \overline{|z_n|^2}(\Delta q_{n+3} - \Delta q_{n-3}) + \overline{(q_{n+3} - q_{n-3})}\Delta(z_n^* z_n)$$
$$= \sum_n \left[\overline{|z_{n-3}|^2} - \overline{|z_{n+3}|^2} \right] \Delta q_n$$
$$\quad + (\bar{q}_{n+3} - \bar{q}_{n-3})\bar{z}_n \Delta z_n^* + c.c. \tag{33}$$

This leads to the *Discrete Davydov System*

$$\frac{\Delta z_n}{\Delta t} = i[K(\bar{z}_{n-3} + \bar{z}_{n+3}) - L(\bar{z}_{n-1} + \bar{z}_{n+1}) \\ - (\bar{q}_{n+3} - \bar{q}_{n-3})\bar{z}_n], \tag{34}$$

$$\frac{\Delta q_n}{\Delta t} = \frac{1}{m_0} \bar{p}_n, \tag{35}$$

$$\frac{\Delta p_n}{\Delta t} = \left[\bar{q}_{n-3} - 2\bar{q}_n + \bar{q}_{n+3} + \left(\overline{|z_{n+3}|^2} - \overline{|z_{n-3}|^2} \right) \right]. \tag{36}$$

To illustrate how this approach ensures conservation of momenta, the conservation of exciton number can be shown more generally for the corresponding discretization of a general quantum-classical lattice nonlinear wave equation with z Eq. (4), for which (34) becomes

$$\Delta z_n = i\Delta t \sum_m \left(L_{n,m} + \overline{\chi_{n,m}(\mathbf{u})} \right) \bar{z}_m. \tag{37}$$

As noted in the discussion of Proposition 1, one simply mimics the calculations used in the DE case, using the Hermitian form of $L_{n,m} + \overline{\chi_{n,m}(\mathbf{u})}$:

$$\frac{\Delta\mathscr{E}}{\Delta t} = \sum_n \frac{\overline{z_n}\Delta z_n + c.c.}{\Delta t}$$
$$= i \sum_n \sum_m \left[L_{n,m} + \overline{\chi_{n,m}(\mathbf{u})} \right] \overline{z_n}\, \overline{z_m^*} - c.c. = 0.$$

4. Linearly implicit iterative schemes for solving discrete gradient systems

The nonlinear systems of equations such as the Discrete Davy-dov System (34)–(36) derived using discrete gradients of the form (30) need an iterative solution method, and to preserve the linear stability properties and exact momentum conservation, the following method is proposed: construct successive approximations $\mathbf{y}^{(k)}$ of $\mathbf{y}^+$ with $\mathbf{y}^0 = \mathbf{y}^-$ and then update from $\mathbf{y}^{(k)}$ to $\mathbf{y}^{(k+1)}$ by solving a variant of (31) by approximating the $\hat{\mathscr{H}}$ term there with the most recent known approximation $\mathbf{y}^{(k)}$ in place of $\mathbf{y}^+$, but using the (unknown) $\mathbf{y}^{(k+1)}$ in place of $\mathbf{y}^+$ in the linear term $\tilde{\nabla}_{\mathbf{y}}\hat{\mathbf{y}}$ and at left. That is,

$$\mathbf{y}^{(k+1)} - \mathbf{y}^- = \mathscr{J}\tilde{\nabla}_{\hat{\mathbf{y}}}\hat{\mathscr{H}}(\mathbf{y}^-, \mathbf{y}^{(k)}) \cdot \tilde{\nabla}_{\mathbf{y}}\hat{\mathbf{y}}(\mathbf{y}^-, \mathbf{y}^{(k+1)}) \, \Delta t. \quad (38)$$

This is linear in the unknowns $\mathbf{y}^{(k+1)}$, and so mimicking the proof of Proposition 1 gives the following proposition.

Proposition 2. *Each iterate $\mathbf{y}^{(k)}$ given by the above scheme conserves all quadratic momenta as in Proposition 1.*

The key is again the irrelevance of the form of the approximation of $\tilde{\nabla}_{\hat{\mathbf{y}}}\hat{\mathscr{H}}$, which is the only term that changes between the iterative scheme and the origin scheme.

Energy, however, is only conserved in the limit, but assuming convergence, sufficient iterations will give energy accuracy far greater than for a scheme that does not conserve energy, such as a symplectic scheme.

Another advantage of this approach to iterative solution is that it has unconditional linear stability, since for a linear system, $\tilde{\nabla}_{\hat{\mathbf{y}}}\hat{\mathscr{H}}$ is constant, and the scheme converges in a single iteration and is identical to the A-stable MP method. This second order accuracy after one iteration for linear systems is seen in practice to carry over in part to mildly nonlinear systems; for example, with the test cases in the following sections, the accuracy at each iteration is about what one would expect with one more iteration of a standard explicit predictor–corrector approach.

Aside on general elementary function Hamiltonians. When this iterative method is applied for a non-algebraic Hamiltonian, the difficulties noted above with the definition of $\tilde{D}f(x^-, x^+)$ in (26) can be avoided, as the problem arises only in the approximation of $\tilde{\nabla}_{\hat{\mathbf{y}}}\hat{\mathscr{H}}$ at each iteration, and this depends only on known quantities $\mathbf{y}^-$ and $\mathbf{y}^{(k)}$, so one knows whether to use the difference quotient form or the exact derivative. More carefully, the exact derivative should be used if Δx is smaller than some threshold related to rounding error.

4.1. A linearly implicit iterative scheme for the Discrete Davydov System

The iterative scheme described above takes this form. First, eliminate the "bar" quantities via $\Delta z_n = z_n + \Delta z_n/2$ etc., so that the only unknowns are the "deltas", and use (35) to eliminate the Δq_n from (36); then alternately

1. Solve (34) approximately for the Δz_n by inserting the latest approximations of the Δp_n at right.

2. Solve (36) approximately for the Δp_n by inserting the latest approximation of the Δz_n at right.

Two cycles are enough for second order accuracy; three or more improve the accuracy of conservation of H beyond second order. This involves only simultaneous linear equations of small bandwidth, giving cost only linear in the number of variables.

In practice, a fixed number k of iterations is often used rather than iterating to full convergence, and the resulting method will be called DGk.

4.2. A priori comparisons to previous approaches

The previous work closest to the method introduced here is that for a more limited class of nonlinear Schrödinger equations by Chang and Xu [6], and the work on energy and momentum conserving integrators for Hamiltonian systems by Gonzales [13], and earlier related work of Simo et al. [14]. The approach of Gonzales can produce the same difference equations, but by a different and sometimes more difficult path: it starts with discrete gradient formulas that do not inherently respect symmetries, and goes through the construction of a reduced Hamiltonian to impose necessary symmetries.

Finite difference calculus approaches have been taken for example by Jimenez [15], and Li and Vu-Quoc [16] but those approaches do not address the product law issues discussed above, and respect only a single conserved quantity.

The state of the art for general fully conservative approaches is probably the work of McLachlan et al. [10] based on discretizing the Nambu generalization of Hamiltonian form, with a tensor product of the gradients of each conserved quantity explicitly appearing. The disadvantage of that approach for the current large and "quasi-linear" systems is that the resulting discrete equations are always fully nonlinear, involving products of the discrete partial derivatives of each conserved quantity, divided by determinants involving the unknown values at the end of the time step. Thus iterative solution is potentially far more difficult in the current context of a very large number of unknowns. Also the exact conservation of $\mathscr{E}$ after a finite number of iterations is unlikely to be reproducible.

For performance comparisons, the most natural comparison is to symplectic methods (see the pioneering works [17–20] and the surveys in [21] and Chapter 6 of [9]). Specifically the Implicit Midpoint [MP] method is the closest, sharing many properties with DG including unconditional linear stability, and differing mainly in not conserving the Hamiltonian but instead conserving the symplectic form. The nonlinear stability results and numerical examples in [22,13,23] for several mechanical systems show that despite the good linear stability (A-stability) of the MP method, it can suffer nonlinear instability at large enough time-step sizes while energy–momentum conserving methods such as those given by the approach of this paper are stable and more accurate. For this reason, the current method is worth consideration in comparison to symplectic methods when choosing a scheme for a particular problem. Thus computational comparisons to MP are presented below.

As far as higher order symplectic schemes, all symplectic diagonally implicit Runge–Kutta methods can be put in the form of symmetric step compositions applied to MP, and applying the same step composition schemes to the DG method give corresponding higher order energy–momentum schemes. However, the relative efficiency and performance of these methods have not yet been tested. With respect to the well-considered symplectic higher order Gauss methods, it should be noted that for systems with many unknowns, the non diagonally implicit form of those methods leads to a larger systems of simultaneous equations to be solved, which suggests a possible cost advantage of higher order extensions of DG schemes. So a comparative study of, say, 4th order schemes seems worthwhile, but this has not yet been done.

5. Testing the method: computational comparisons to previous approaches for NLDNLS

The first experimental tests of the Discrete Gradient [DG] method are primarily to assess convergence and accuracy and to compare to alternative methods, and these are done using the simplest "interesting" test case, the NLDNLS Eq. (16). This equation is distinguished from the standard Discrete NLS by the complication of coupling between nearby loci in nonlinearities rather than single point nonlinearities, so that methods like that of Chang and Xu [6] do not apply.

On the other hand, NLDNLS has the simplification of a single "type" of variable, z_n, facilitating graphical assessments and comparisons, and having solutions for suitable choices of initial data to be close to known solutions of NLS like the hyperbolic secant pulses of (20).

As noted earlier, it is worth comparing the DG method to the symplectic implicit midpoint method which conserves $\mathcal{E}$ but not $\mathcal{H}$. Some comparisons have also been made to the implicit trapezoid [TR] method, another popular A-stable, time-symmetric method for equations like the NLS, but its performance is consistently the worst of the three, so little more will be said of it. The same iterative solution approach described above was used for all methods. Note that $\mathcal{E}$ is exactly conserved at each iterative step with MP, as it is with DG.

To compare speed and cost, time step sizes are sometimes described by a speed-up relative to the stability-based time step limits of explicit methods. The classical Runge–Kutta method is amongst the best of these in the current situation of conservative equations with stability limits dictated by imaginary eigenvalues, so its restriction of $\Delta t = 1/(K\sqrt{2})$ is used as the reference. This is also a reasonable cost comparison if about four iterations are used with DG, which is a typical value in the cases here.

Test cases all use initial data of a hyperbolic secant pulse form

$$z_n(0) = A\Delta x\sqrt{2K}\,\text{sech}(n\Delta x)e^{i\xi n\Delta x}. \tag{39}$$

This varies on a scale of $O(1/\Delta x)$ nodes, so $\Delta x \ll 1$ makes the continuum limit good for initial data at least.

The first choice of parameters is

$$A = 1, \qquad \Delta x = 0.025, \qquad \xi = 0.5, \qquad -1000 \le n \le 4000, \tag{40}$$

which corresponds to a spatial discretization of the initial data for a soliton solution (20) of the NLS Eq. (19) with x domain truncated to $[-25, 100]$; indeed the solutions stay extremely close to that soliton. The range of node indices is chosen large enough that the amplitude of the z_n remains negligible near the endpoints, because the primary interest is if and how pulses can travel a substantial distance within a molecule or other exciton chain.

This test case allows gauging whether the conservative, symmetry respecting features of the DG method give an advantage in preservation of distinctive qualitative features, beyond what is expected from the order of the local truncation error: in this case, by observing how well the traveling wave form is preserved. Other tests in this section differ only in using higher initial pulses, $A = 2$.

5.1. Accuracy

Comparisons are generally done with sufficient iterations to give convergence in the practical sense that further iterations produce no visible changes in any of the graphs presented below or used as the basis for any observations made below.

All solutions are dominated by a pulse propagating with approximately the speed of the corresponding soliton solution. For the $A = 1$ near-soliton case, the solution is very close to the NLS soliton solution in pulse shape and position. Thus, variation between methods is illustrated in Fig. 1 by plotting the change in
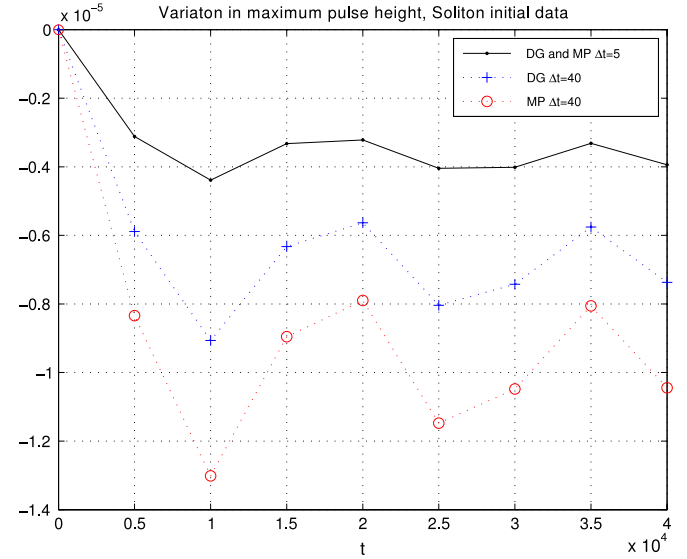

Fig. 1. NLDNLS: near-soliton case $A = 1$, $dx = .025$, variation in maximum pulse height for the Discrete Gradient [DG] and Implicit Midpoint [MP] methods, with time steps $\Delta t = 5$ (giving visually perfect results) and $\Delta t = 80$.

$\max_n(|z_n(t)|)$ as a function of t. Here and below, accuracy is judged against solutions having Δt so small that no change is seen in any graphs by either reducing Δt or by changing method; thus the reference curve is in fact two superimposed curves for both the DG and MP methods with $\Delta t = 5$. Note that this reference case already represents a speed-up of $5K\sqrt{2} \approx 10$ relative to explicit methods such as RK.

Overall errors have the expected $O(\Delta t^2)$ under time step size refinement, but at equal step size, DG is seen to be clearly more accurate than MP (or TR), and to far better respect the near constancy of magnitude in the near traveling wave solutions of the ODE system. (Thus it probably also better for space–time discretization of the NLS equation.) By the way, both "conservative" methods, DG and MP, reproduce the pulse speed far better than does TR.

For larger initial amplitude $A = 2$, the solution structure is more complicated and smaller time step size $\Delta t = 2$ is needed for visual accuracy of all graphs, but the accuracy comparisons are similar, with DG again the most accurate. Fig. 2 shows this with comparison to $\Delta t = 8$: note in particular that the key features of pulse height and velocity are far better resolved by DG.

On the other hand, halving step size is consistently more beneficial than choice amongst these second order accurate methods, so cost considerations relate to step costs, which is closely proportional to the number of iterations needed, as discussed in the next subsection.

5.2. Cost: iterations needed for convergence or adequate accuracy

To estimate the overall computational cost, one must consider both time step size and the number of iterations needed. Formally, the error in the iterative approximation relative to the solution of the underlying fully implicit scheme is $O(\Delta t^{k+1})$. Thus for three or more iterations this error should be of higher order than the $O(\Delta t^3)$ local truncation error in a single time step of the underlying implicit method, and thus should give better overall accuracy than $k \le 2$. This is solidly confirmed in all experimental comparisons; thus all results cited for all methods are for $k \ge 3$. In fact with large time steps, the convergence of iterations is slow enough that the MP method can benefit from at least a third iteration.

For DG, errors in $\mathcal{H}$ are entirely due to the iterative approximation and thus are formally $O(\Delta t^{k+1})$, and so as expected,
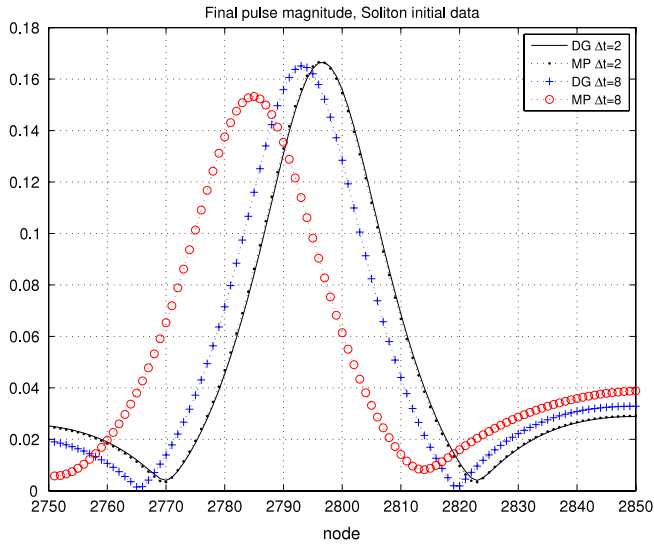
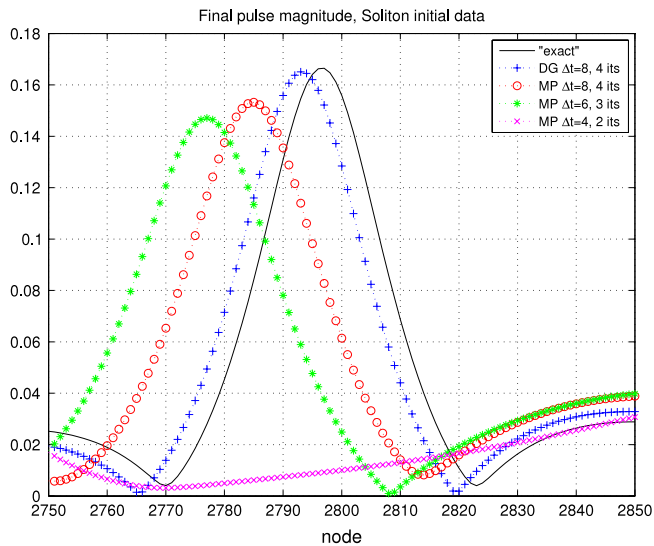**Fig. 2.** NLDNLS, $A = 2$: $|z_n|$ at time $t = 40,000$.

Fig. 3. NLDNLS, $A = 2$: $|z_n|$ at time $t = 40,000$, methods of roughly equal time cost.

this error improves with k until rounding error dominates, so that in contrast to the other methods, significantly more than three iterations are potentially valuable.

For most of the results above, a time step small enough to give good accuracy also gives convergence good enough that there is no need for more than four iterations: any increase in accuracy in using more than four iterations is outdone at equal computational cost by reducing the step size instead. On the other hand, even MP benefits in equal cost comparisons by going to three or four iterations.

Thus a cost comparison is done by repeating the previous case of $A = 2$ with four methods of near equal computational cost: in decreasing order of the accuracy seen in Fig. 3, these are DG with $\Delta t = 8$, 4 iterations; MP with $\Delta t = 8$, 4 iterations; MP with $\Delta t = 6$, 3 iterations; MP with $\Delta t = 4$, 2 iterations. The execution times of the four latter runs were 221 s, 230 s, 229 s, and 218 s respectively.

The dramatic improvement in accuracy seen in going from two to three iterations (while increasing step size) with MP is quite common with both MP and DG: clearly, despite their equal order Δt^3, the error in the iterative scheme is substantially larger than the truncation error in the underlying time discretizations.

6. Numerical results on the Davydov system: pulse narrowing with arrest of motion, and other deviations from continuum limit predictions

To summarize, the following behavior is seen.

(a) For suitable initial data, such as an exciton impulse at one end of the chain, solutions develop that fit part of the above slow variation approximations: sustained pulses with exciton density $|z_n|^2$ slowly varying both in time and along the chain, thus validating both the "DNLS" approximation $d_n \approx -(|z_{n-3}|^2 + 2|z_n|^2 + |z_{n+3}|^2)$ and the CNLS continuum limit (18), and showing approximately the expected sech^2 form for exciton density.

(b) However, there is no slow variation of z_n, because the phase shifts by roughly a factor $-i$ between consecutive residues along the backbone and thus a factor i between consecutive residues along spines. This pattern emerges in the low-amplitude leading edge of the pulse, where linear terms dominate, and is as given by the constant amplitude solutions $z_n = A \exp(i4A^3t)$ of CDNLS. Thus the pulses do not fit any of the phase relations between chains suggested by the continuum limit approximations described in Section 2.3.

(c) Initial data with an impulse very near but not at an end of the chain is seen to produce a dominant pulse traveling at a steady speed, but with no slow variation in amplitude or phase even within spines, and thus a phenomenon that again cannot be explained by any of the continuum limits described above.

(d) Initial impulses not close to an end of the chain have not been seen to produce any coherent pulse; the only coherence seen is a stationary narrow pulse around the initial locus.

Two main choices of initial data are considered:

1. end of chain impulse $z_0 = 1$ (all other initial data zero),
2. near end of chain impulse $z_1 = 1$.

6.1. Initial impulse at one end of the chain: main pulse with slow amplitude variation, factor $-i$ phase shifts between adjacent residues

Perhaps the most interesting solutions, and the only ones with a strong relationship to a slowly varying continuum limit approximation, originate from a localized initial excitation if that excitation is at one or several residues starting at one end of the chain. It is sufficient to consider the simplest such excitation, with the only non-zero initial data being $z_0(0) = 1$. Then as shown in Fig. 4 the exciton density $|z_n|^2$ propagates mostly in a single narrow pulse at a nearly constant speed, of 4 twists per unit time. By $t = 10$ a solitary pulse of roughly shape dominates ahead of the rest of the signal. At time increases, the pulse becomes more separated ahead of the remaining weak signal and ever closer to sech form and persisting until at least $t = 2000$. Fig. 5 shows details at $t = 1000$.

In the low-amplitude leading edge of the pulse, the phase shift between residues is very close to $-\pi/4$ (so $z_{n+1} \approx -iz_n$) from as early as $t = 10$, and then in the main pulse itself, the phase shift reduces only slightly, that is, a slow increase in phase is superimposed on the $-\pi/2$ background. This is illustrated, again at $t = 1000$, in Fig. 6 parts (a) and (b) respectively.

6.2. Initial impulse near one end of the chain: traveling main pulse, but with no slow variation

For all other initial data tried, there is at best a very small leading pulse with the behavior seen above. For an initial impulse near but not at the end, a slower dominant pulse follows that one, but with no slowly varying structure, and that with no sign of being explicable by a PDE continuum limit. Fig. 7 shows the case of an
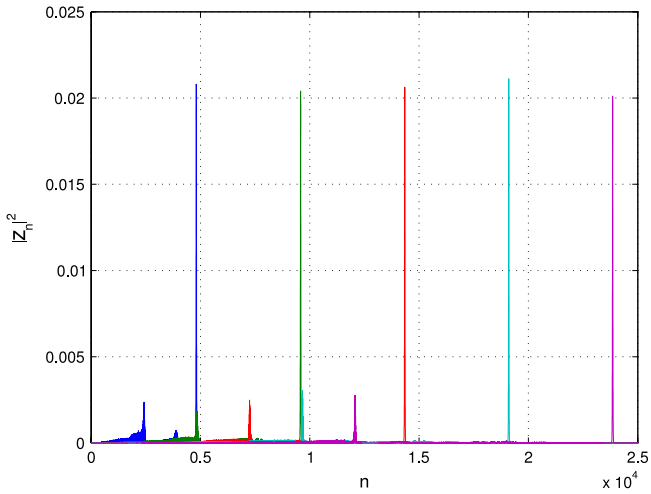
Fig. 4. Exciton density $|z_n|^2$ as a function of residue index n, for initial impulse $z_0(0) = 1$, $t = 400 : 400 : 2000$.
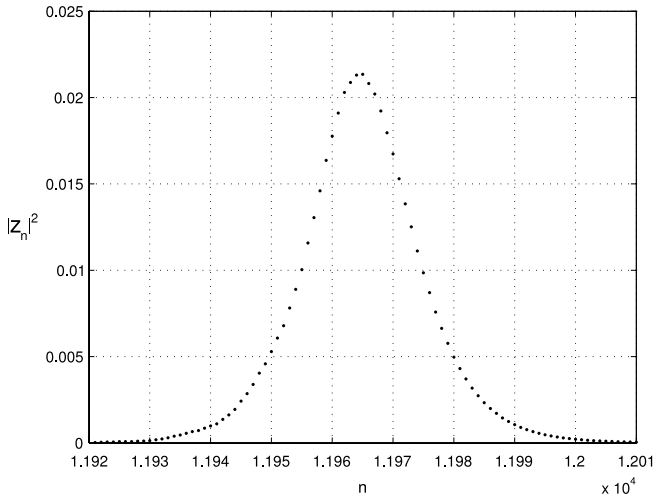

Fig. 5. Exciton density $|z_n|^2$: pulse detail, $t = 1000$.

initial single-point impulse $z_1 = 0$. Two pulses are seen at each time. Closer examination of the small leading one shows it to have the same amplitude and phase behavior observed above, but as seen in Fig. 8 for spine 1, most exciton density travels in a cluster of several narrow pulses with rapid variation of amplitude. The same is seen for all spines and a fortiori the variation is even less smooth viewed over all residues. For other initial data less close to an end, even less exciton density enters a smooth leading pulse, and there is an even less sign of slow variation along the chain or any spine.

7. Conclusions

The Discrete Gradient method introduced here has been shown to give energy–momentum conserving time discretizations for stiff DE systems arising in various molecular models, such as the model of Davydov for α-helix protein, and also as spatial discretizations of a variety of nonlinear wave equations related to NLS. These 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. [10].

While the discretizations given by the Discrete Gradient method can also be attained by the approach of Gonzales [13], the approach here simplifies construction of such discretizations, especially for systems with many degrees of freedom: in particular,
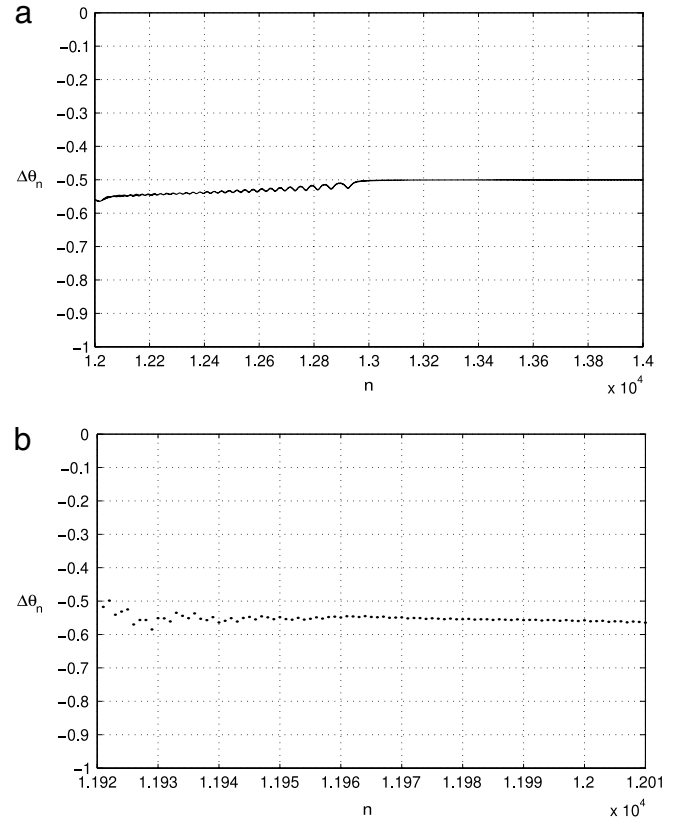
Fig. 6. Phase shift between residues at $t = 1000$ (a) ahead of the main pulse (b) in and around the main pulse.
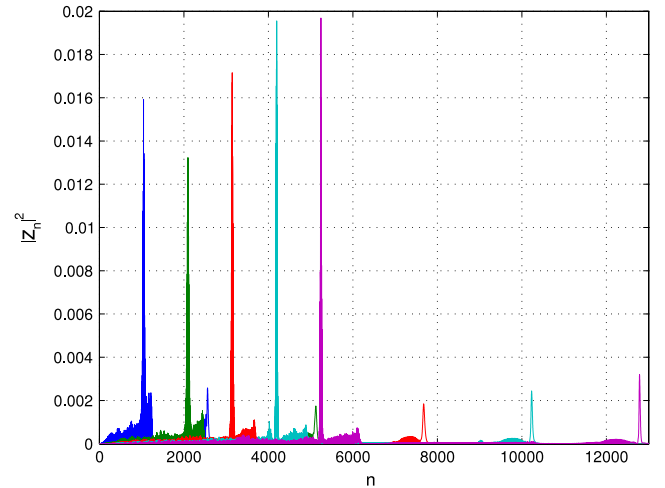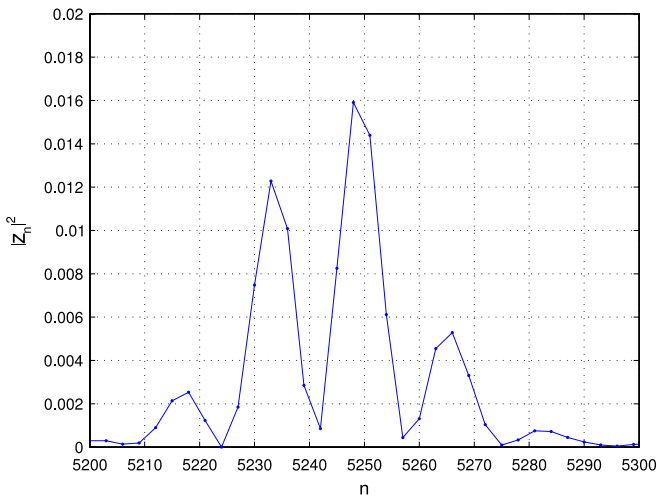

Fig. 7. Exciton density $|z_n|^2$ for initial impulse $z_1(0) = 1$, $t = 200 : 200 : 1000$.

linear terms are handled canonically, with no additional constructions or choices required to get a conservative form.

On the test case of a non-standard discrete NLS equation arising from Davydov's work on protein modeling, accuracy is seen to be superior to that of the Implicit Midpoint Method, a popular choice in such situations due to its symplectic, A-stable, and time-reversal symmetric form.

For the Davydov system, part but not all of previous continuum limit modeling is confirmed: one class of impulsive initial data leads to solutions with pulses with both slow temporal variation of exciton density $|z_n|^2$ – justifying both elimination of the fast classical oscillator components – and also slow variation along the chain and fitting the sech^2 pulse form of NLS solitons. However

Fig. 8. Exciton density $|z_n|^2$ for initial impulse $z_1(0) = 1$: main pulse detail at $t = 1000$.

the phase is never seen to have any slow variation, as assumed in previous continuum limits. Instead a pattern of quarter turns in phase between adjacent nodes (residues) is seen; this pattern can be motivated by the behavior in the near-linear regime at the leading edge of the pulse.

This combination of observations indicates that a different continuum limit form should be sought for such pulses. However for most initial data, such slowly varying pulses have little or no part in solutions. Instead, another type of coherent propagating pulse is seen more often, with no sign of slow variation along the chain, and thus probably needing an explanation in discrete terms rather than through continuum limit approximations and PDE theory.

In future work, other modeling refinements could include allowing for asymmetry in the strength of the coupling along spines, non-uniformity in coefficients along the chain due to variations in the amino acid residues, stochastic terms describing thermal effects, and additional interaction terms such as those given in [7]. The time discretization methods introduced here readily accommodate such models.

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