

Nonlinear dynamics of electrons in chiral molecules

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Topological Solitons, Durham 2004



Outline

- 1 Introduction
- 2 Some aspects of DNA
- 3 Modelling DNA
 - Molecular Dynamics
 - The interaction between chains
 - A small simplification
 - J dependence
 - Choice of parameters
- 4 Numerical Studies
 - $J = 0.02$
 - $J = 0.03$
 - $J = 0.04$
- 5 Conclusions



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- DNA has been of great interest to chemists and physicists since before Watson and Crick (1953).
- Both structure and dynamics of the molecule have been investigated in great detail.
- DNA is easily assembled
- Potential realisation of a quantum wire.
- One can also use the DNA molecule as a scaffold to grow quantum wires.



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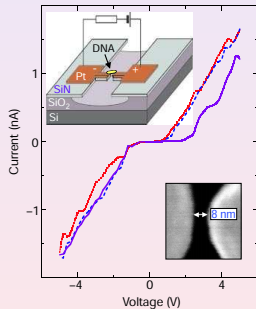
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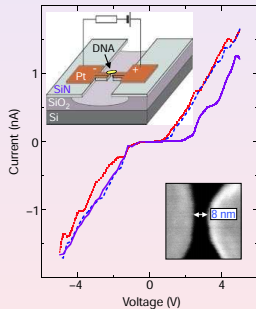


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Dekker and his group [Nature **403** (2000) 635] looked at the conduction of single strands of DNA.

Lots of controversy about the interpretation of such experiments. is DNA a conductor? a semiconductor? A veritable floodgate for theoretical studies has opened. Most of these consider the conduction (or charge transport) along a one-dimensional "pi-stack" (a channel built from overlapping pi orbitals) in the centre of the DNA molecule.

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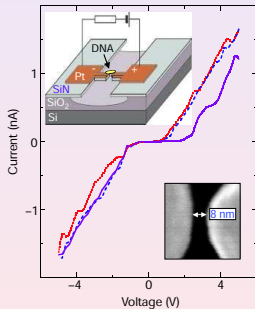


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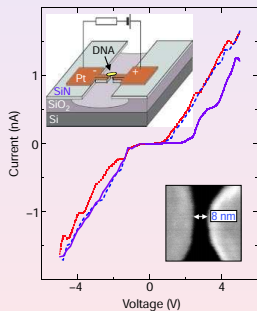
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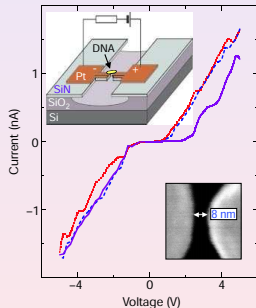


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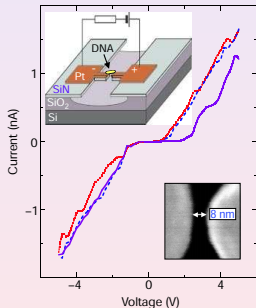
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- **Mathematical modeling of DNA has a long tradition [Yakushevich 1998].**
- In recent years the Peyrard-Bishop model has become quite popular [Peyrard 2004]. (Non-linear model of bond stretching, describes denaturing DNA).
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In this note we a new generalisation. We use this model to investigate various aspects of DNA-like substances. Our model differs in many aspects from the Pyrrard-Bishop one. The two most crucial ones are

- 1 the inclusion of the helicity of the molecule in our models
- 2 and the fact that our electrons are (correctly or incorrectly, that remains to be seen) allowed to propagate along the backbone rather than along the “pi-stack”.

The idea of semi-conduction along pi-stack was first proposed by Eley in 1962.



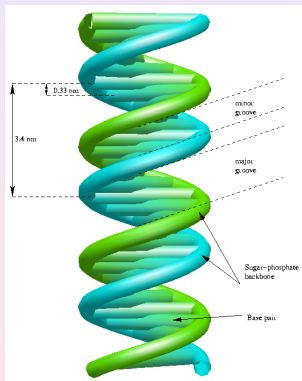
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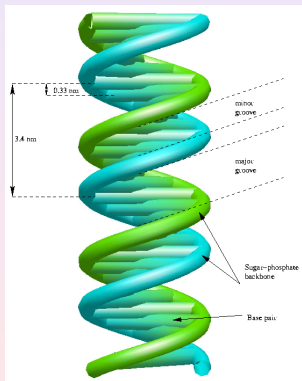
DNA



Characteristics

- **Structure of DNA varies with environment.**
- Standard double helix in aqueous solution.
- Base pair rotation is 36° .
- Not at right angle to backbone. (Major and minor grooves.)
- "Propellor twist"
- Base pairs close in the centre. (overlapping pi-orbitals?)

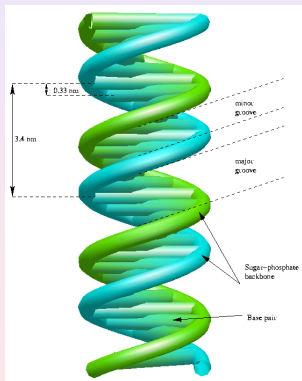
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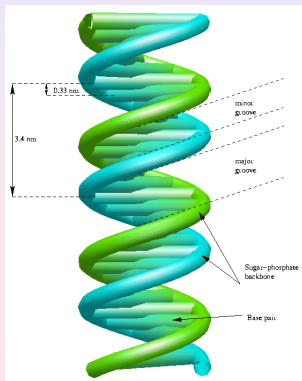
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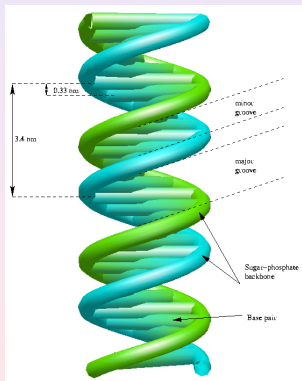
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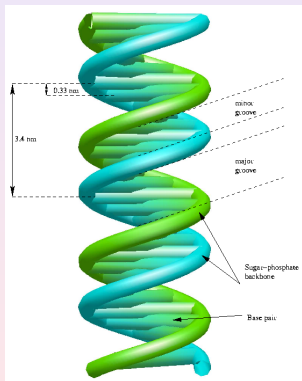
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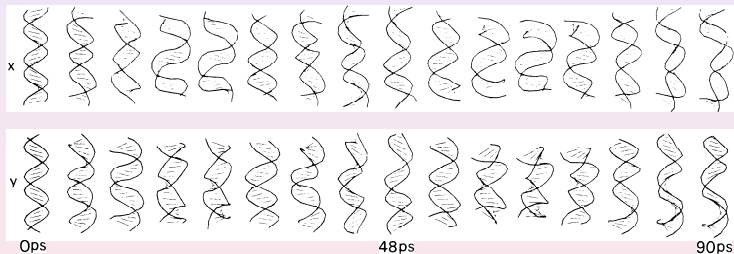
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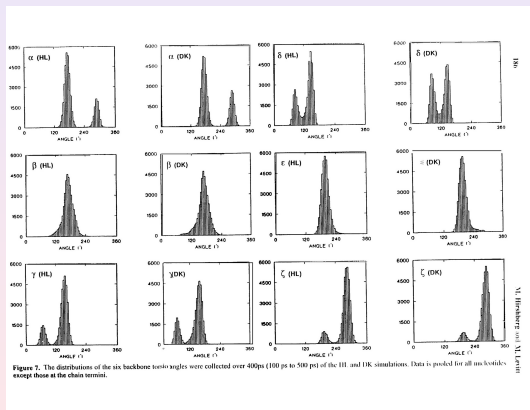
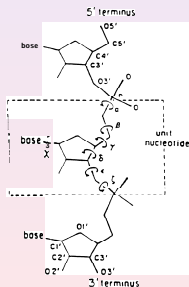
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Mol. dyn. in vacuo (Levitt, 1983)



Mol. dyn. in water (Hirschberg and Levitt, 1991)

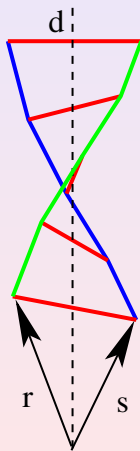


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Our model



figure

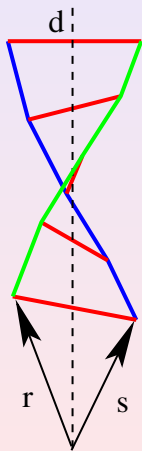
Model straight but twisty molecule . Red lines denote the hydrogen bonds, at straight angles to dashed backbone. Blue and green lines denote DNA chains.

parametrisation

$$\vec{r}_i = z_i \vec{e}_z + \frac{1}{2} d \vec{u}_i, \quad \vec{s}_i = z_i \vec{e}_z - \frac{1}{2} d \vec{u}_i,$$

- \vec{u} 2D unit vector in the xy plane.
- Stretching of the H bonds? Potential for d .
- Necessary to study bending of DNA.

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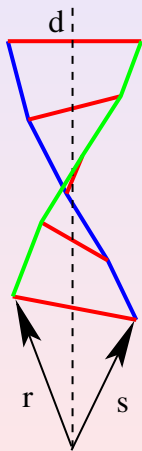
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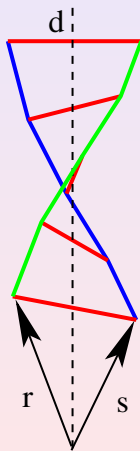
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Energy

Kinetic energy

The kinetic energy is relatively easy to evaluate

$$\begin{aligned} \frac{1}{2}M \sum_i \vec{r}_{i,t}^2 + \vec{s}_{i,t}^2 &= \frac{1}{2}M \sum_i \left(z_i \vec{e}_z + \frac{1}{2} d \vec{u}_i \right)_t^2 + \left(z_i \vec{e}_z - \frac{1}{2} d \vec{u}_i \right)_t^2 \\ &= M \sum_i \left(z_{i,t}^2 + \frac{1}{4} d^2 \vec{u}_{i,t}^2 \right) . \end{aligned}$$

We can easily generalise this to a dynamical d ; in this case the length of each rung becomes $d_i(t)$, and the additional terms in the kinetic energy would be of the form $\frac{1}{4} d_{i,t}^2$. We expect the effects of the variation of d to be small.



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Bending energy

Use bending energy of form

$$U_B \propto \sum_i \left[\left((\vec{r}_i - \vec{r}_{i-1}) \times (\vec{r}_{i+1} - \vec{r}_i) \right)^2 - \alpha_s^2 \right]^2 + \left[\left((\vec{s}_i - \vec{s}_{i-1}) \times (\vec{s}_{i+1} - \vec{s}_i) \right)^2 - \alpha_s^2 \right]^2 .$$

- Too simple, since it allows mixing of the left- and right-handed turns!
- DNA is a chiral molecule, prefers left-handed over right-handed twists.



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Continuum limit

Point on strand is specified by a vector $\vec{\delta}$ from the backbone we write $\vec{\delta} = \delta \vec{e}$ with

$$\vec{e} = (\cos \phi, \sin \phi, 0).$$

Tangent vector

$$\vec{t} = a(-\sin \phi, \cos \phi, 0) + b(0, 0, 1),$$

To introduce chirality add a potential with a bias towards a value of ab .

We can extract $a = \vec{e}_z \cdot (\vec{e} \times \vec{t})$, and $b = \vec{e}_z \cdot \vec{t}$.



Replace $\vec{t} \rightarrow \vec{r}_{i+1} - \vec{r}_i$,

$$\begin{aligned} a_r &\approx \vec{e}_z \cdot \left[\frac{1}{2}(\vec{u}_i + \vec{u}_{i+1}) \times \left((z_{i+1} - z_i)\vec{e}_z - \frac{d}{2}(\vec{u}_{i+1} - \vec{u}_i) \right) \right] \\ &= \frac{d}{2} \vec{e}_z \cdot (\vec{u}_{i+1} \times \vec{u}_i) \quad , \end{aligned}$$

$$\begin{aligned} b_r &\approx \vec{e}_z \cdot \left((z_{i+1} - z_i)\vec{e}_z - \frac{d}{2}(\vec{u}_{i+1} - \vec{u}_i) \right) \\ &= z_{i+1} - z_i \quad . \end{aligned}$$

($a_s = a_r$ and $b_s = b_r$). Use

$$U_B = \sum_i g_\mu \left((z_{i+1} - z_i)\vec{e}_z \cdot (\vec{u}_{i+1} \times \vec{u}_i) \right) \quad ,$$

with g a function that has a minimum at μ , e.g.,

$$g(x) = b(x - \mu)^2.$$



Stretching potential

$$\begin{aligned} U_s &= \sum_i f_{l^2}(|\vec{r}_i - \vec{r}_{i+1}|^2) \\ &= \sum_i f_{l^2} \left((z_{i+1} - z_i)^2 + \frac{d^2}{2} (1 - \vec{u}_{i+1} \cdot \vec{u}_i) \right) , \end{aligned}$$

where f has a minimum at the average distance squared l^2 .
Again, in our simulations we have used

$$f(x) = a(x - l^2)^2.$$



Electrons

Combine this with a standard DNLS action for electrons (within the chains only) where ψ and ϕ are the electron fields on the two chains. This is the semi-classical limit of a tight-binding model (couplings such as $a_i^\dagger a_j$) with a density squared term added.



Action

$$\begin{aligned}
 \mathcal{A} = \int dt & \left\{ -\hbar \sum_i \psi_i^* i \psi_{i,t} - \hbar \sum_i \phi_i^* i \phi_{i,t} \right. \\
 & + M \sum_i \left(z_{i,t}^2 + \frac{1}{4} d^2 \vec{u}_{i,t}^2 \right) + \\
 & - U_B - U_S + \\
 & \left. \sum_i \left[\hbar \omega 2 |\psi_i|^2 - \sum_{j \neq i} J_{|i-j|} \psi_i^* \psi_j - \frac{1}{2} \chi |\psi_i|^4 \right] + \right. \\
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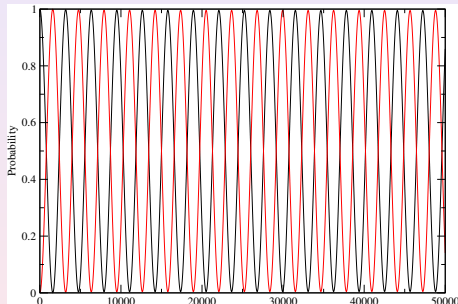
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The most naive choice is

$$V_{\text{int}} = \sum_i K(\phi_i^* \psi_i + \psi_i^* \phi_i) .$$

Rather uninteresting: leads to a simple oscillation of charges from one strand to the other, while their combination behaves as a single wire.



This is due to the fact that we do not take into account the chirality of the molecule.

Make coupling orientation dependent:

$$V_{\text{int}} = \sum_i K(e^{i2g\theta_i} \phi_i^* \psi_i + e^{-i2g\theta_i} \psi_i^* \phi_i) \quad ,$$

(g is yet another parameter).

Not completely satisfactory: for a flat molecule tunneling depends on orientation! Two options:

First of all we can remove the average orientation,

$$V_{\text{int}} = \sum_i K(e^{i2g(\theta_i - \langle \theta \rangle)} \phi_i^* \psi_i + e^{-i2g(\theta_i - \langle \theta \rangle)} \psi_i^* \phi_i) \quad ,$$

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$$V_{\text{int}} = \sum_i K(e^{i2g\theta_i} \phi_i^* \psi_i + e^{-i2g\theta_i} \psi_i^* \phi_i) \quad ,$$

(g is yet another parameter).

Not completely satisfactory: for a flat molecule tunneling depends on orientation! Two options:

First of all we can remove the average orientation,

$$V_{\text{int}} = \sum_i K(e^{i2g(\theta_i - \langle \theta \rangle)} \phi_i^* \psi_i + e^{-i2g(\theta_i - \langle \theta \rangle)} \psi_i^* \phi_i) \quad ,$$

which leads to a rather non-local coupling. **i.e., don't!**



Gauging it

Secondly, we can look upon the expression as a gauge-like transformation, and make the replacements

$$\psi_i \rightarrow e^{ig\theta_i} \psi_i, \quad \phi_i \rightarrow e^{-ig\theta_i} \phi_i$$

everywhere (i.e., also in all the interaction terms within one of the backbones). This means that we must replace the non-local interaction along the backbone by

$$\begin{aligned} & \sum_{i,j \neq i} J_{|i-j|} (\psi_i^* \psi_j + \phi_i^* \phi_j) \\ & \rightarrow \sum_{i,j \neq i} J_{|i-j|} \left(e^{ig(\theta_j - \theta_i)/2} \psi_i^* \psi_j + e^{-ig(\theta_j - \theta_i)/2} \phi_i^* \phi_j \right). \end{aligned}$$

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We can simplify the problem slightly by using a 1D angle representation for \vec{u} ,

$$\vec{u}_i = (\cos \theta_i, \sin \theta_i, 0) \quad .$$

We then find

$$\vec{u}_{i,t}^2 = \dot{\theta}_i^2 \quad ,$$

and

$$U_B = \sum_i g_\mu ((z_{i+1} - z_i) \sin(\theta_{i+1} - \theta_i)) \quad ,$$

as well as

$$U_s = \sum_i f_{j2} ((z_{i+1} - z_i)^2 + \frac{d^2}{2} (1 - \cos(\theta_{i+1} - \theta_i))) \quad .$$



Next we determine the equations of motion for all the fields in our system.

Won't give them here, too complicated.

Please note that we have added a damping term to both the z and θ equations (by adding a velocity dependent term with coefficient α). This helps us to study stable soliton solutions of such problems.

The only remaining question is the choice of f and g . For f , which describes a stretching potential we can either use a harmonic potential, $f(x) = a(x - l^2)^2$, or a Morse potential, $f(x) = a(e^{-(x-l^2)^{1/2}} - 1)^2$. For g the only sensible choice appears to be harmonic, $g_\mu(x) = b(x - \mu)^2$.



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Next we add the J dependent terms which will control electron's mobility. Although, in principle, J can depend on many variables two obvious dependences first spring to mind:

- 1 The tunneling rate is a function of the shortest distance between two spatial points, i.e., $r_{ij} = |\vec{r}_i - \vec{r}_j|$, or
- 2 The tunneling rate depends on the distance along the DNA backbone (the sucrose molecules), $r_{ij} = \sum_{k=i}^{j-1} |\vec{r}_k - \vec{r}_{k+1}|$.

The first case is obviously the easiest one, but leads to rather unphysical results. The second case is more complicated. Nonetheless we write $J_{ij} = h(R_{ij})$ and can work with it.



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Realistic parameters? Molecule: minimise bending and stretching potentials;

$$\begin{aligned}(z_{i+1} - z_i) \vec{e}_z \cdot (\vec{u}_i \times \vec{u}_{i+1}) &= \mu \quad , \\ (z_{i+1} - z_i)^2 - \frac{d^2}{2} \vec{u}_{i+1} \cdot \vec{u}_i &= l^2 - \frac{d^2}{2}\end{aligned}$$

Assuming uniformity we get

$$\begin{aligned}\delta z \sin \delta \theta &= \mu \quad , \\ \delta z^2 + d^2 \sin^2(\delta \theta / 2) &= l^2 \quad .\end{aligned}$$



From

$$\begin{aligned}d &= 2.39 \text{ nm} \quad , \\ \delta z &= 3.38/10 = 0.338 \text{ nm} \quad , \\ \delta \theta &= 2\pi/10 = 0.628 \quad .\end{aligned}$$

we get

$$\mu = 0.20 \text{ nm}, \quad l = 0.81 \text{ nm} \quad .$$

If we look at all the minima for these values of μ , l and d we find that we have a second solution

$$\delta z = 0.62 \text{ nm}, \quad \delta \theta = 0.32 \quad ,$$

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The other degrees of freedom in the electronic part of the model are the stiffness of the energies, and the mass M . Suppose that we express all our units in terms of the electron mass, a number of the order $10^5 m_e$ seems to make sense for M (roughly 50 proton masses). The natural choice for the frequency is

$$\hbar\omega = \frac{\hbar^2}{2m_e^* \delta z^2} = \frac{m_e}{m_e^*} 0.3 \text{ eV.}$$

xs If we require an energy in the meV range, this would correspond to an effective mass roughly 1000 times smaller than the electron mass. The corresponding frequency would still be of the order 10^{11} Hz.



The parameter J_0 should probably be comparable to $\hbar\omega$, whereas χ and K should be substantially smaller (by a factor 10 – 100). That only leaves the parameters a and b to be determined. It seems sensible to require that the lowest energy normal mode lies in the meV range.



Analyse molecular normal mode problem in equilibrium, using the harmonic versions of the potentials. Find linearized equations of motion, using standard values for all the parameters (all lengths are expressed in nm), Express everything in dimensions of mass, scaling $\zeta = z/\delta z$, $\Theta = \theta/\delta\theta$

$$M \begin{pmatrix} \ddot{\zeta}_i \\ \ddot{\Theta}_i \end{pmatrix} = \begin{pmatrix} 0.691a + 0.914b & 0.598a + 4.22b \\ 0.0761a + 0.537b & 0.0658a + 2.48b \end{pmatrix} \begin{pmatrix} \delta^{(2)}\zeta_i \\ \delta^{(2)}\Theta_i \end{pmatrix}$$



Performing a standard diagonalisation, we end up with two uncoupled problems of the form

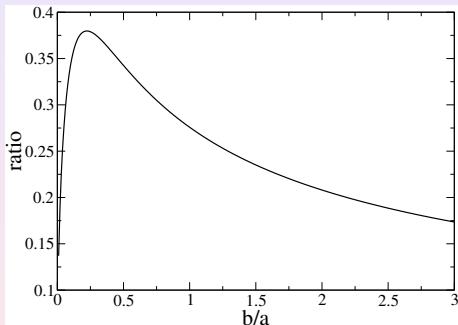
$$M\ddot{x}_i^\pm = f^\pm \delta^{(2)} x_i^\pm,$$
$$f^\pm = 0.378a + 1.670b \pm 0.378\sqrt{a^2 + 1.065ab + 20.1b^2}.$$

It is now standard to evaluate the frequencies of such a model:

$$\omega_{k_j}^2 = \frac{4f^\pm}{M} \sin^2(k_j/2),$$
$$k_j = \pi j/N$$

where we have used the fact that we have unit spacing, and N is the number of atoms in one of the chains. The frequencies are closest for $b/a = 0.223$, where their ratio is about 0.375. The acceptable range is probably a factor of 10 on each side.





The ratio of the frequencies squared as a function of b/a .

Numerical Studies

- Try to study the model numerically.
- Concentrate on properties, not on physical parameters.
- Single electron added to a neutral molecule.
- Expect solitonic solutions, but delocalisation as well.
- Study effect from coupling between strands (non-triviality)!

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Numerical Techniques

Method 1: RK4

This has the advantage of being simple, disadvantage of not being preservative (especially norm). Solved by renormalising after each step

Method 2: Symplectic plus split evolution

Technique borrowed from quantum chemists. Evolve electronic problem with a small timestep using a (norm-preserving) symplectic integrators. Step molecular problem using, e.g., RK4, but with a longer timestep.



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Symplectic

Implicit RK

Implicit RK's are symplectic, and **preserve all quadratic first integrals** (Sanz-Serna, 1988).

midpoint RK2

$$\begin{aligned}K_1 &= f\left(t_n + \frac{h}{2}, y_n + \frac{h}{2}K_1\right) \\y_{n+1} &= y_n + hK_1\end{aligned}$$

Combination

$$U_{el,RK2}(t/(2n))^n U_{mol,RK4}(t) U_{el,RK2}(t/(2n))^n$$



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We have performed several numerical studies of our system. We take sensible parameters, that are not completely inconsistent with the physical constraints discussed above. We take

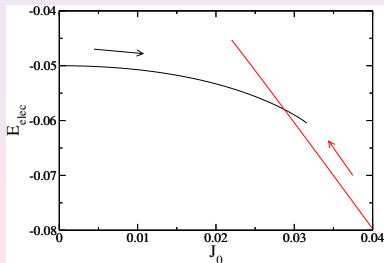
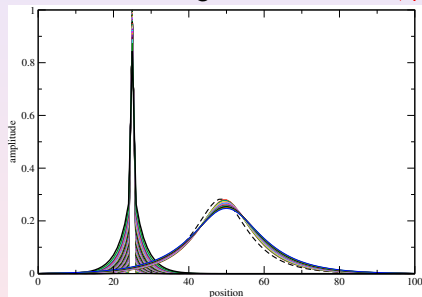
- $\hbar = M = 1$, $\omega = 1$ (time dependence),
- $a = 6$, $\beta^2 = 0.7$ (stretching),
- $b = 6$, $\mu = 0.2$ (bending),
- $K = 0.1$ (Interaction).

The damping for the molecular motion is $\alpha = 0.02$. We have varied the value of J from 0.01 to 10.



Benchmark

Breather in single back-bone, $\psi_i(t) = p_i e^{i\omega t}$



First order phase transition at $J \approx 0.028$.

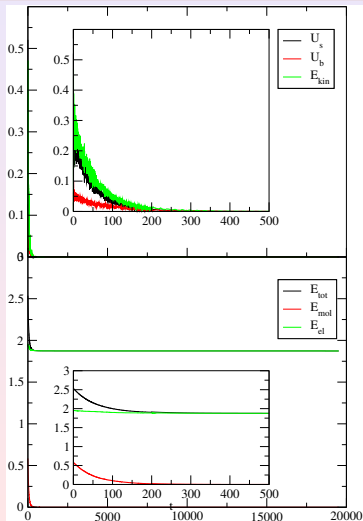
Now look at coupled chains.

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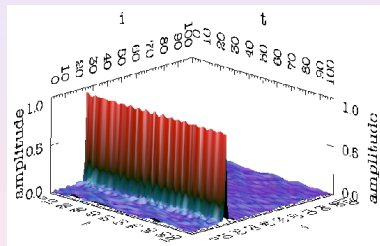
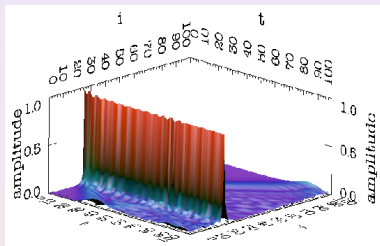
Time evolution



Legend

Energetics of the relaxation of a 101-rung chain for $J = 0.02$. The upper panel with inset shows the decomposition of the mechanical energy, the lower panel total and electronic energy.

dynamics



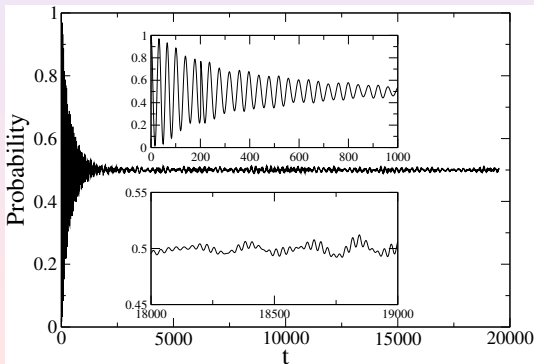
Time evolution of the occupation along the backbone (sum over both) for $J = 0.02$. t gives a time slice number, early and late times.

Explanation

The amplitude of the electron field at one rung shows semi-regular oscillations. We start out with all probability on one site on one backbone; one can see that some probability propagates outward. This is then reflected from the boundaries, and makes the breather's oscillations somewhat non-periodic, and results in a small sea of background oscillations.

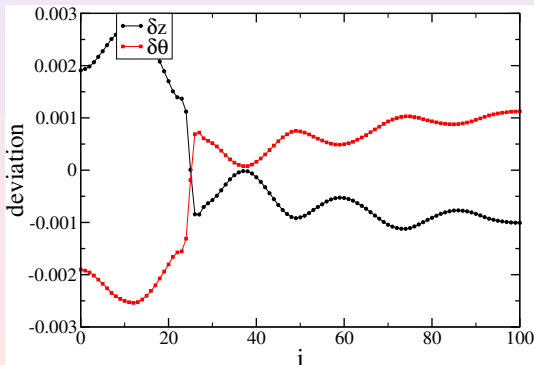
Oscillations

Time evolution of the total occupation of one of the backbones as a function of time for $J = 0.02$. The insets show both early and late oscillations of this quantity.



Backbone

Deviation of θ (red squares) and z (black circles) from their equilibrium values for the final simulation point, $t = 19318$, as a function of lattice point label i .



Conclusions

We can see that the presence of the soliton leads to a pronounced deviation of θ and z from their equilibrium values, with a sharp jump at the position of the soliton. There seems to be more correlation between these two quantities than one would have naively expected, but the overall picture shows that there is deformation and relaxation of the double helix.

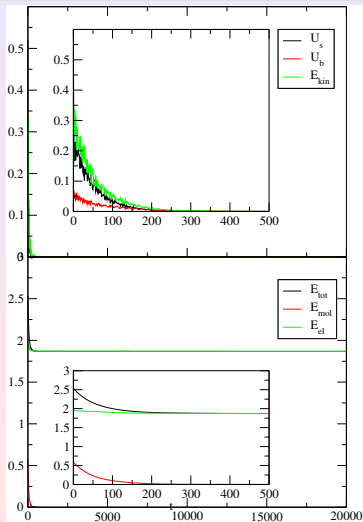


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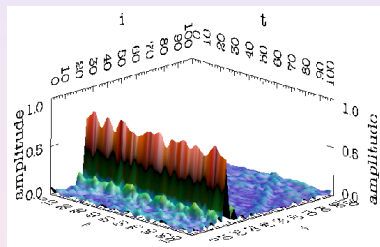
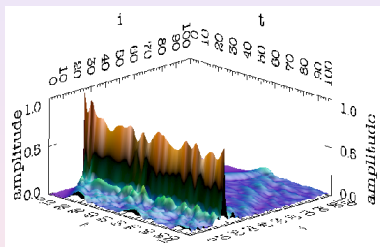
Time evolution



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Energetics of the relaxation of a 101-rung chain for $J = 0.03$. The upper panel with inset shows the decomposition of the mechanical energy, the lower panel total and electronic energy.

dynamics



Time evolution of the occupation along the backbone (sum over both) for $J = 0.04$. t gives a time slice number, early and late times.

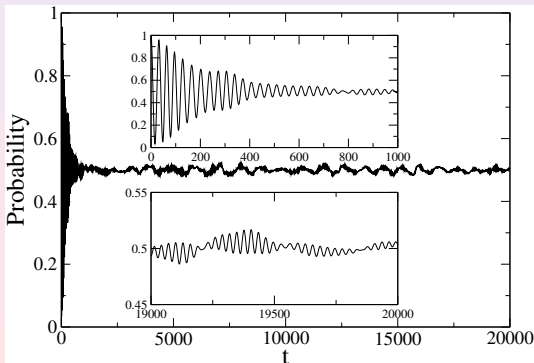
Explanation

Once again relaxation to equilibrium is quick and uneventful, at least as far as the energies are concerned. The time evolution of the amplitude shows that we do have a stationary solution, but the effect of the small part of the probability density that propagates is much more pronounced, and makes things look much more chaotic. In the early time picture we can also see how these waves get reflected back towards the soliton (and get reflected by the soliton). The interesting dynamics deserves further study.



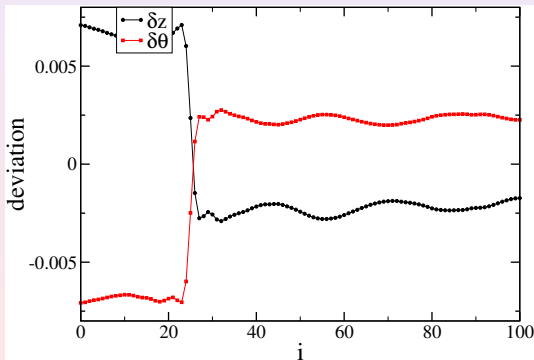
Oscillations

Time evolution of the total occupation of one of the backbones as a function of time for $J = 0.03$. The insets show both early and late oscillations of this quantity.



Backbone

Deviation of θ (red squares) and z (black circles) from their equilibrium values for the final simulation point, as a function of lattice point label i .

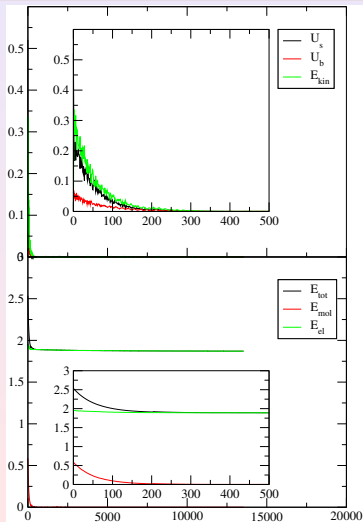


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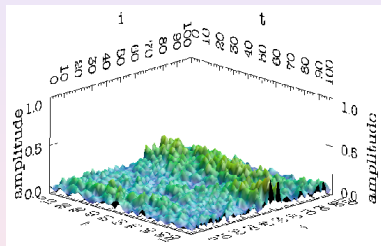
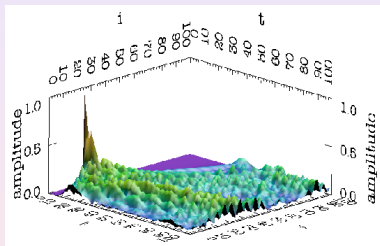
Time evolution



Legend

Energetics of the relaxation of a 101-rung chain for $J = 0.04$. The upper panel with inset shows the decomposition of the mechanical energy, the lower panel total and electronic energy.

dynamics



Time evolution of the occupation along the backbone (sum over both) for $J = 0.04$. t gives a time slice number, early and late times.

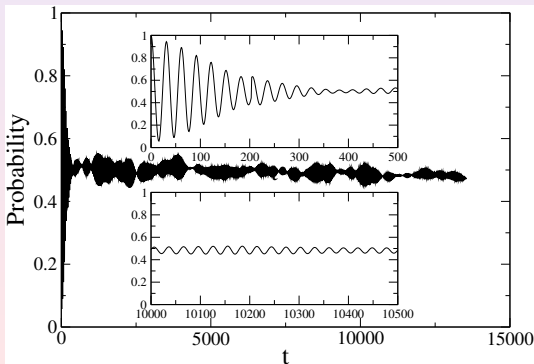
Explanation

In the figure we see a fast decay of the soliton, even before the reflected waves return. This suggests the absence of a stable breather. At late times, in the lower panel, we see that a soliton-like structure reforms at a different position. This may well indicate that at this point the solitons are only marginally unstable.



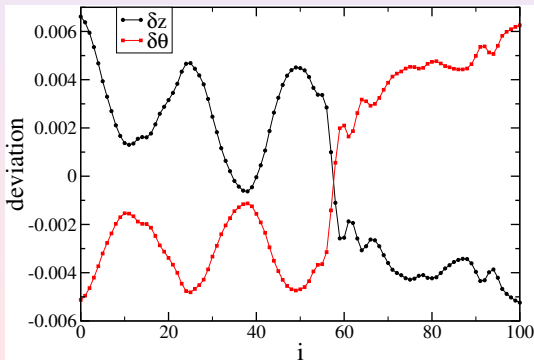
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Time evolution of the total occupation of one of the backbones as a function of time for $J = 0.04$. The insets show both early and late oscillations of this quantity.



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Conclusions

- Dynamics in a chiral molecule can be complicated and interesting
- interesting interplay of stretching and twisting of the underlying double helix with the movement of the electrons
- There seems to be a sharp transition from localised solitons (charge density) to a completely delocalised with complicated temporal structure.

Outlook

- Calculate charge transport, where electrons come in on one backbone at one end, and leave through the same or the other backbone at the other side.
- Fix parameters to realistic molecules!



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