Effect of Torsional Disorder on Exciton Transport

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Outline

Quantum transport in Disordered Systems: The Inspiration

PHYSICAL REVIEW VOLUME 109, NUMBER 5 MARCH 1, 1958

Absence of Diffusion in Certain Random Lattices

P. W. Anderson
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received October 10, 1957)

This paper presents a simple model for such processes as spin diffusion or conduction in the "impurity band." These processes involve transport in a lattice which is in some sense random, and in them diffusion is expected to take place via quantum jumps between localized sites. In this simple model the essential randomness is introduced by requiring the energy to vary randomly from site to site. It is shown that at low enough densities no diffusion at all can take place, and the criteria for transport to occur are given.

Anderson, Philip W. "Absence of diffusion in certain random lattices." Physical review 109.5 (1958): 1492.

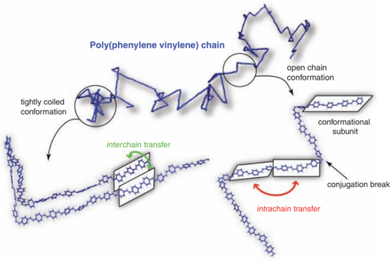
Lagendijk, Aart, Bart Van Tiggelen, and Diederik S. Wiersma. "Fifty years of Anderson localization." Phys. Today 62.8 (2009): 24-29.

" Localization was a different matter: very few believed it at the time, and even fewer saw its importance; among those who failed to fully understand it at first was certainly its author. It has yet to receive adequate mathematical treatment, and one has to resort to the indignity of numerical simulations to settle even the simplest questions about it."

—Philip W. Anderson, Nobel lecture, 8 December 1977

Exciton Transport

- The large variations in mobilities observed in the case of π- conjugated polymers such as MEH-PPV and P3HT.
- The Torsional motion in the backbone of the polymer chain breaks the conjugated pathway
- Femtosecond time-scale Torsional relaxation in Organic Semiconductors.



Grozema, Ferdinand C., et al. "**Intramolecular charge transport along isolated chains of conjugated polymers: Effect of torsional disorder and polymerization defects.**" The Journal of Physical Chemistry B (2002)

Jean-Luc Bredas and Robert Silbey. **Excitons surf along conjugated polymer chains.** Science, 323(5912):348- 349, 2009

Clark, T Nelson, S Tretiak, G Cirmi, and Guglielmo Lanzani. **Femtosecond torsional relaxation.**Nature Physics, 8(3):225, 2012

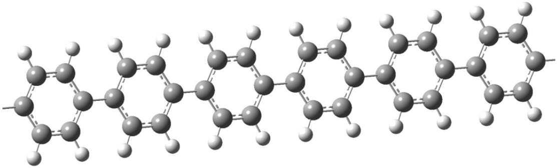
Hamiltonian of the system in the Hilbert space $\mathcal{H}_S = \mathcal{H}_\varepsilon \otimes \mathcal{H}_{\theta_1} \otimes \mathcal{H}_{\theta_2} \otimes ...... \otimes \mathcal{H}_{\theta_N}$

$$\hat{H}_S = -\hbar\omega_\theta \sum_{i=1}^{N} \frac{\partial^2}{\partial\theta_i^2} + \sum_{<i,j>}^{N} U(\theta_{ij}) + \hbar\omega_\varepsilon \sum_{i=1}^{N} \sigma_i^+ \sigma_i^- + \sum_{\substack{i=1 \\ i\neq j}}^{N} \sum_{j=1}^{N} V(\theta_{ij})\sigma^+(i)\sigma^-(j)$$

Lets consider an arbitrary state vector $|\Psi\rangle$ in $\mathcal{H}_S$ and since $[\hat{N}_{ex}, \hat{H}] = 0$ [1]

$$\hat{\mathcal{P}_{ex}}|\Psi(t)\rangle = \sum_{n=1}^{N} \langle n|\Psi\rangle |n\rangle = \sum_{n=1}^{N} \psi_n(\Theta, t)\,|n\rangle$$

$\ni \forall\ \psi_i$'s and $\dot{\psi}_i$'s are periodic with a period 2π with respect each variable θ_i.



[1] Additionally, we also find that $[\hat{P}_{total}, \hat{H}] = 0$ and thus there is conservation of momentum within the system

Considering the Time-dependent Schrödinger equation, $i\hbar\frac{\partial|\Psi\rangle}{\partial t} = \hat{H}_s\,|\Psi\rangle$.

$$i\hbar\frac{\partial|\Psi\rangle}{\partial t} = -\hbar\omega_\theta\sum_{i=1}^{N}\frac{\partial^2|\Psi\rangle}{\partial\theta_i^2} + \sum_{<i,j>}^{N}U(\theta_{ij})|\Psi\rangle + \hbar\omega_\varepsilon\sum_{i=1}^{N}\sigma_i^+\sigma_i^-|\Psi\rangle + \sum_{<i,j>}^{N}V(\theta_{ij})\sigma_i^+\sigma_j^-|\Psi\rangle$$

$$i\hbar\frac{\partial|\Psi\rangle}{\partial t} = -\hbar\omega_\theta\sum_{<i,n>}^{N}\frac{\partial^2\psi_n(\Theta,t)}{\partial\theta_i^2}|n\rangle + \sum_{<i,j>}^{N}\sum_{n=1}^{N}U(\theta_{ij})\psi_n(\Theta,t)|n\rangle + \hbar\omega_\varepsilon\sum_{n=1}^{N}\psi_n(\Theta,t)|n\rangle + \sum_{<n,i>}^{N}V(\theta_{in})\,\psi_n(\Theta,t)|i\rangle$$

We further model the coupling potetials as cosine functions of the $\theta_i's$ as:

$$V(\theta_{ij}) = V_o\cos(\theta_i-\theta_j) \text{ and } U(\theta_{ij}) = U_o\cos(2(\theta_i-\theta_j))$$

The same could be written in the matrix form as follows:

$$i\hbar \frac{\partial}{\partial t}\Psi_{N\times 1} = \left[\hbar\omega_{\varepsilon} + \sum_{<i,j>}^{N} U(\theta_{ij}) - \hbar\omega_{\theta}\sum_{i}^{N}\frac{\partial^2}{\partial\theta_i^2}\right]\mathbb{I}_{N\times N}\Psi_{N\times 1} + \mathbb{V}^{in}_{N\times N}\Psi_{N\times 1}$$

$$\text{where } \mathbb{V}^{in}_{N\times N} = \begin{bmatrix} 0 & V_{12} & \cdots & V_{1N} \\ V_{21} & 0 & \cdots & V_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ V_{N1} & V_{N2} & \cdots & 0 \end{bmatrix} \; and \; \Psi_{N\times 1} = \begin{bmatrix} \psi_1(\Theta, t) \\ \psi_2(\Theta, t) \\ \vdots \\ \psi_N(\Theta, t) \end{bmatrix}$$

Basic Formulation

The way we model the coupling changes the physical picture. As the matrix $\mathbb{V}^{in}_{N\times N}$

Models of Arrangements

Model	Matrix $\mathbb{V}^{in}_{N\times N}$
Linear	$\begin{bmatrix} 0 & V_{12} & 0 & \cdots & \cdots & 0 \\ V_{21} & 0 & V_{23} & \cdots & \cdots & 0 \\ 0 & V_{32} & 0 & \ddots & & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ \vdots & \vdots & & \ddots & \ddots & V_{(N-1)N} \\ 0 & 0 & \cdots & \cdots & V_{N(N-1)} & 0 \end{bmatrix}$
Cyclic	$\begin{bmatrix} 0 & V_{12} & 0 & \cdots & \cdots & V_{1N} \\ V_{21} & 0 & V_{23} & \cdots & \cdots & 0 \\ 0 & V_{32} & 0 & \ddots & & \vdots \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ \vdots & \vdots & & \ddots & \ddots & V_{N(N-1)} \\ V_{N1} & 0 & \cdots & \cdots & V_{N(N-1)} & 0 \end{bmatrix}$
Close Packing	$\begin{bmatrix} 0 & V_{12} & V_{13} & \cdots & V_{1N} \\ V_{21} & 0 & V_{23} & \cdots & V_{2N} \\ V_{31} & V_{32} & 0 & \cdots & V_{3N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ V_{N1} & V_{N2} & V_{N3} & \cdots & 0 \end{bmatrix}$


Figure 3.2: Linear Geometry

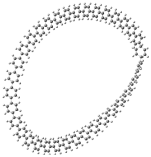


Figure 3.3: Cyclic Geometry (Nano-hoop)

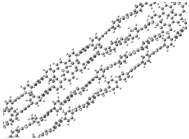


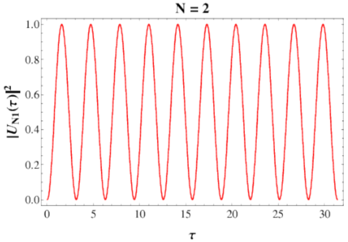
Figure 3.4: Close-packed case

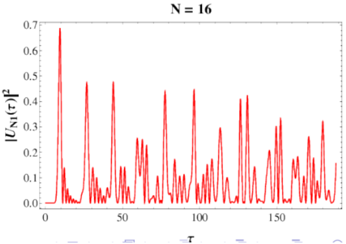
$$\hat{H} = \hbar\omega_\varepsilon \sum_{i}^{N} \sigma_i^+ \sigma_i^- + V_o \sum_{<i,j>} \sigma_i^+ \sigma_j^-$$

The Eigen values and eigen vectors turn out to be:

$$|\phi_m\rangle = \sqrt{\frac{2}{N+1}} \sum_n^N \sin\left(\frac{nm\pi}{N+1}\right)|n\rangle \qquad E_m = \hbar\omega_\varepsilon + 2\cos\left(\frac{m\pi}{N+1}\right)$$

$$|\langle N|e^{-i\hat{H}\tau}|1\rangle|^2 = \left| \frac{2}{N+1} \sum_{m=1}^N e^{-2i\tau\cos\left(\frac{\pi m}{N+1}\right)} \sin\left(\frac{\pi m}{N+1}\right) \sin\left(\frac{\pi N m}{N+1}\right) \right|^2$$



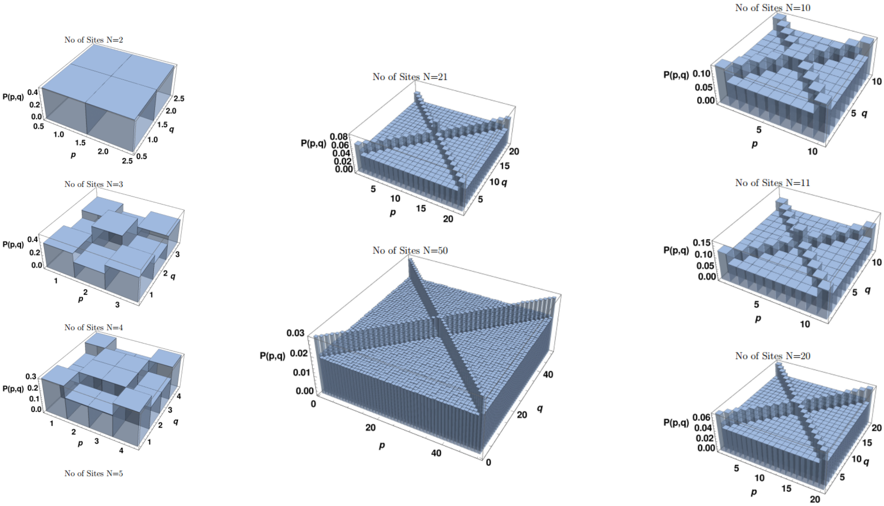


Survival Probabilities

$$P_{tavg}(p,q) = \frac{1}{(N+1)^2}\sum_{m}^{N}\left[1-\cos(\frac{2pm\pi}{N+1})-\cos(\frac{2qm\pi}{N+1})+\frac{1}{2}\cos(\frac{2(p+q)\pi}{N+1})+\frac{1}{2}\cos(\frac{2(p-q)\pi}{N+1})\right]$$

When **N is even** $P_{tavg}(p,q) = \begin{cases} \frac{1.5}{N+1} & p=q \\ \frac{1.5}{N+1} & p\neq q, p+q=N+1 \\ \frac{1}{N+1} & p\neq q, p+q\neq N+1 \end{cases}$

When **N is odd** $P_{tavg}(p,q) = \begin{cases} \frac{1.5}{N+1} & p=q,\ p+q\neq N+1 \\ \frac{2}{N+1} & p=q,\ p+q=N+1 \\ \frac{1.5}{N+1} & p\neq q,\ p+q=N+1 \\ \frac{1}{N+1} & p\neq q,\ p+q\neq N+1 \end{cases}$


No of Sites N=2
No of Sites N=3
No of Sites N=4
No of Sites N=5
No of Sites N=21
No of Sites N=50
No of Sites N=10
No of Sites N=11
No of Sites N=20
P(p,q)
p
q

Defects

Considering the Torsional defects to be a perturbation($\hat{H}_1$) to $\hat{H}$ from Eq(1)

Type I

$$H_1 = \begin{bmatrix} 0 & & & & & \\ & \ddots & & & & \\ & & 0 & 0 & -1+\cos(\alpha-\theta_m) & \\ & & -1+\cos(\alpha-\theta_m) & 0 & -1+\cos(\beta-\theta_m) & \\ & & -1+\cos(\beta-\theta_m) & 0 & 0 & \\ & & & & \ddots & \\ & & & & & 0 \end{bmatrix}$$

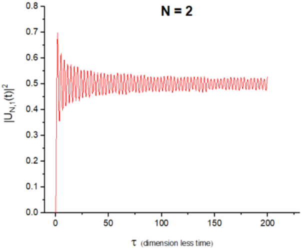
Type II

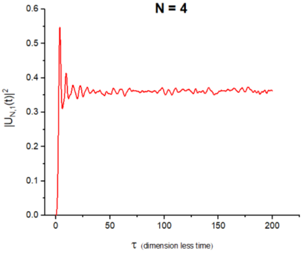
$$H_1 = \begin{bmatrix} 0 & & & & \\ & \ddots & & & \\ & 0 & 0 & -1+\cos(\alpha-\beta) & \\ & -1+\cos(\alpha-\beta) & 0 & 0 & \\ & & & \ddots & \\ & & & & 0 \end{bmatrix}$$

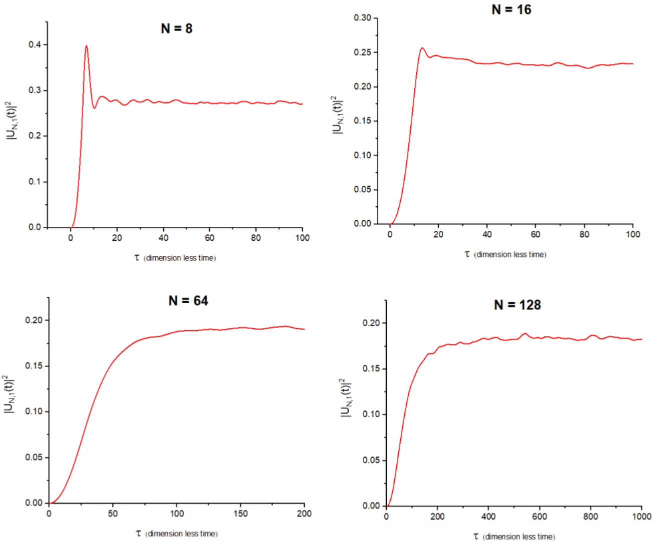
Static Disorder

$$\hat{H} = \sum_{i=1}^{N-1} \cos(\theta_i - \theta_j) \left[|i\rangle\langle i+1| + |i+1\rangle\langle i| \right]$$

$$\langle |\langle N| e^{-i\hat{H}\tau} |1\rangle|^2 \rangle = \int_0^{2\pi} \frac{d\theta_1}{2\pi} \cdots \int_0^{2\pi} \frac{d\theta_N}{2\pi} |\langle N| e^{-i\hat{H}\tau} |1\rangle|^2 P[\{\theta_i\}]$$






N = 8
N = 16
N = 64
N = 128
$|U_{N,1}(t)|^2$
τ (dimension less time)

$$\hat{H}_S = -\hbar\omega_\theta \sum_{i=1}^{N} \frac{\partial^2}{\partial\theta_i^2} + \sum_{<i,j>}^{N} U(\theta_{ij}) + \hbar\omega_\varepsilon \sum_{i=1}^{N} \sigma_i^+ \sigma_i^- + \sum_{\substack{i=1 \\ i\neq j}}^{N} \sum_{j=1}^{N} V(\theta_{ij}) \sigma^+(i) \sigma^-(j)$$

CONTINUUM LIMIT

dN -> 0

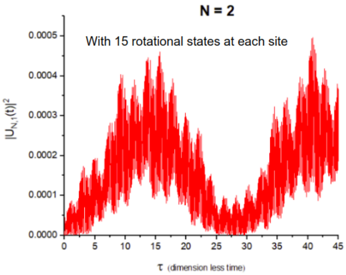
DISCRETE SYSTEMS AND LATTICE MODELS

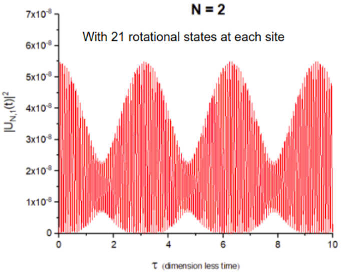
Fourier Transform

We do a Fourier transform of the Hamiltonian and get the TDSE :

$$i\hbar \sum_{n}^{N} \frac{\partial}{\partial t}\tilde{\psi}(K,t)|n\rangle = -\hbar\omega_\theta \sum_{<n,i>}^{N} k_i^2 \psi_n(\tilde{K},t) + \hbar\omega_\varepsilon \sum_{n}^{N} \tilde{\psi}_n(K,t)|n\rangle +$$

$$\sum_{n}^{N}\sum_{<i,j>}^{N} u_{ij}\left[\tilde{\psi}_n(K_{j^-,i^+},t) + \tilde{\psi}_n(K_{j^+,i^-},t)\right] + \sum_{<n,i>}^{N} v_{ij}\left[\tilde{\psi}_i(K_{n^-,i^+},t) + \tilde{\psi}_i(K_{n^+,i^-},t)\right]$$

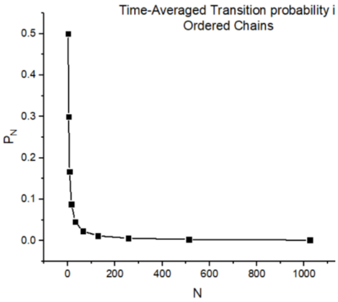


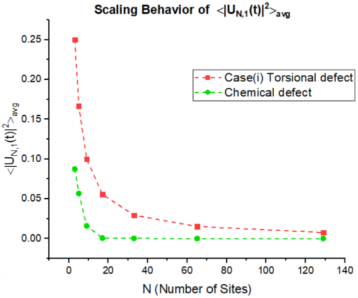


How does the system scale with N?

We find the time averaged Transition Probability(P_n): $P_N = \lim_{\rightarrow\infty} \frac{1}{t}\int_0^t |\mathcal{U}_{N,1}(\tau)|^2 d\tau$

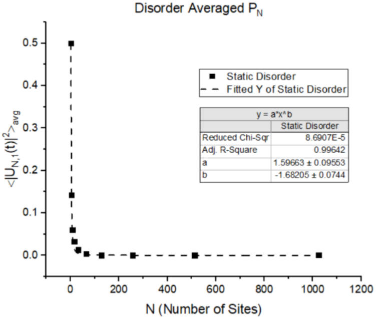
In the case of Ordered Chains, $P_N = \frac{3}{2(N+1)}$

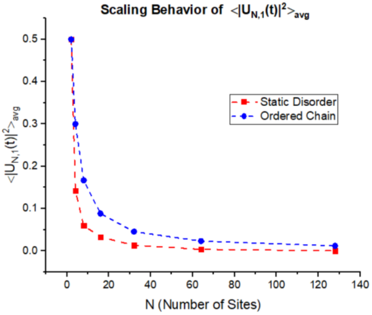




How does the system scale with N?

Disordered chains $P_N = \frac{a}{N^b}$, where $a = 1.5963 \pm 0.09553$ and $b = 1.68205 \pm 0.0744$





Scaling of the Fourier-transformed Hamiltonian

	N * (2M+1)^N						
N	M = 1 (DOF 3)	M = 2 (DOF 5)	M = 3 (DOF 7)	M = 4 (DOF 9)	M = 5 (DOF 11)	M = 6 (DOF 13)	M = 7 (DOF 15)
2	18	50	98	162	242	338	450
3	81	375	1029	2187	3993	6591	10125
4	324	2500	9604	26244	58564	114244	202500
5	1215	15625	84035	295245	805255	1856465	3796875
6	4374	93750	705894	3188646	10629366	28960854	68343750
7	15309	546875	5764801	33480783	136410197	439239619	1196015625
8	52488	3125000	46118408	344373768	1714871048	6525845768	20503125000
9	177147	17578125	363182463	3486784401	21221529219	95440494357	345990234375
16	688747536	2441406250000	531726889113616	2.96483E+16	7.35196E+17	1.06467E+19	1.05095E+20
32	5.92966E+16	7.45058E+23	3.53417E+28	1.09878E+32	6.75641E+34	1.41689E+37	1.38061E+39
64	2.19756E+32	3.46945E+46	7.80647E+55	7.54572E+62	2.85307E+68	1.25474E+73	1.1913E+77
128	1.50914E+63	3.76158E+91	1.9044E+110	1.77931E+124	2.54375E+135	4.91993E+144	4.43497E+152
256	3.55862E+124	2.21086E+181	5.6668E+218	4.94678E+246	1.01104E+269	3.78214E+287	3.07328E+303
512	9.89356E+246						
1024							
2048							

Future Work

Time Evolution by Block Decimation(TEBD)

Implementation of time dependent Density Matrix Renormalisation Group(DMRG) method to capture the Hamiltonian dynamics of the low lying energy states.

Effect of Defects

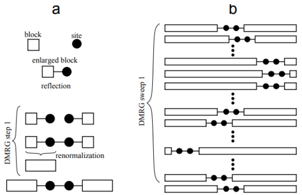
Using Green's functions methods to study the effects of chemical and torsional defects along the chain.

Heat Transport

Study the effects of torsional disorder within the polymer chain on heat transport when the system is coupled to heat baths on the two ends in a linear geometry.

Density Matrix Renormalisation Group Method

1. Start from left block $\mathcal{B}(L, m_L)$, and enlarge it by adding the interaction with a single site.
2. Reflect such enlarged block, in order to form the right enlarged block.
3. Build the super-block from the interaction of the two enlarged blocks.
4. Find the ground state of the super-block and the $m_{L+1} = \min(m_L D, m)$ eigenstates of the reduced density matrix of the left enlarged block with largest eigenvalues.
5. Renormalize all the relevant operators with the matrix $\hat{O}_{L \to L+1}$, thus obtaining $\mathcal{B}(L+1, m_{L+1})$.



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Annals of Physics 326, no. 1: 96-192.

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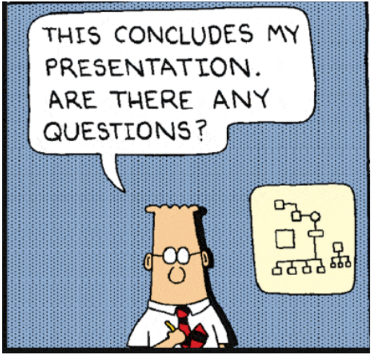

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