Condensed Matter Techniques Used for the Study of Magnetic Properties of Conducting Polymers

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Sector 1-3: Condensed Matter,

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THANK YOU VERY MUCH FOR YOUR KIND INVITATION!

From where I am coming:

University of Debrecen

Location of Debrecen

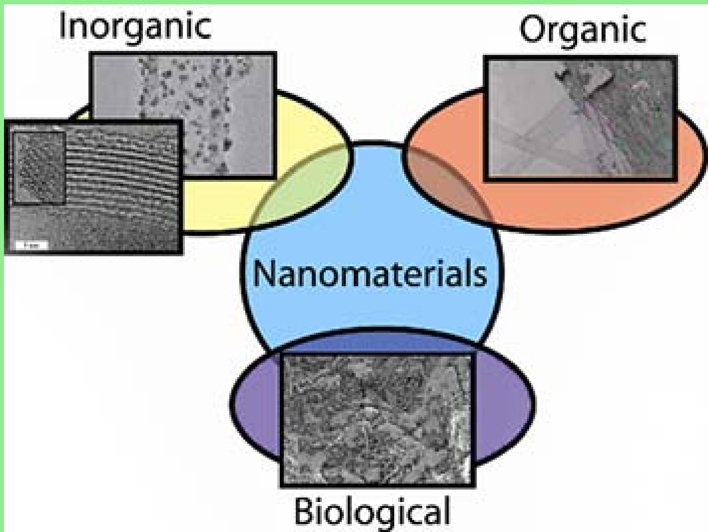
Main Building

Short Outline:

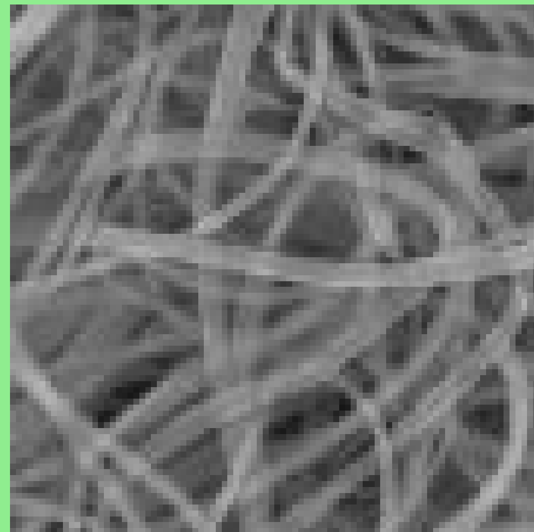
- Introduction (10 %)
- The method used (20 %)
- The steps of the method (30 %)
- The method applied to conducting polymers (35 %)
- Summary and conclusions (5 %)

Collected number of slide pages: 36

Studying polymers in physics



Connecting organic and biological: macromolecules e.g. polymers



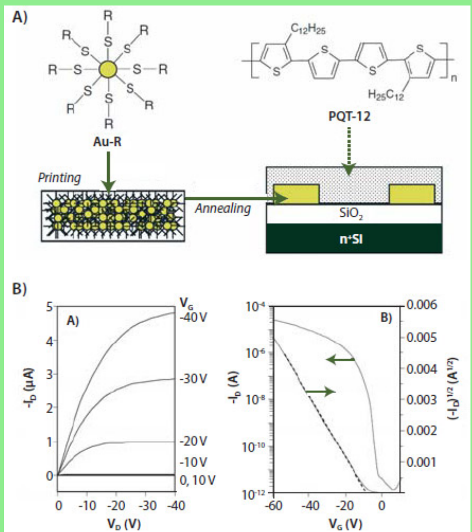
Nanomaterials

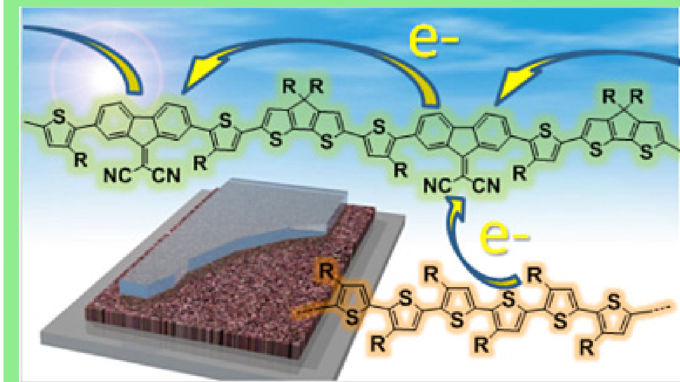
Polymers

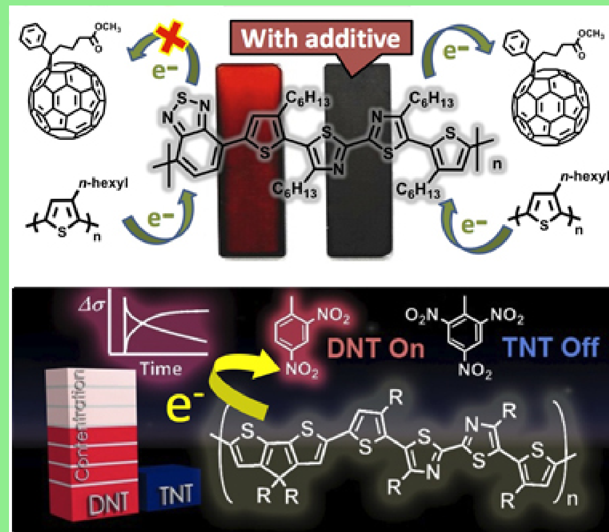
Conducting polymers with pentagon cell

Nobel Prize in Chemistry 2000:
A.J.Heeger, H. Shirakawa, A. MacDiarmid

Several applications today:







Nano transistors

Solar Cells

Detectors

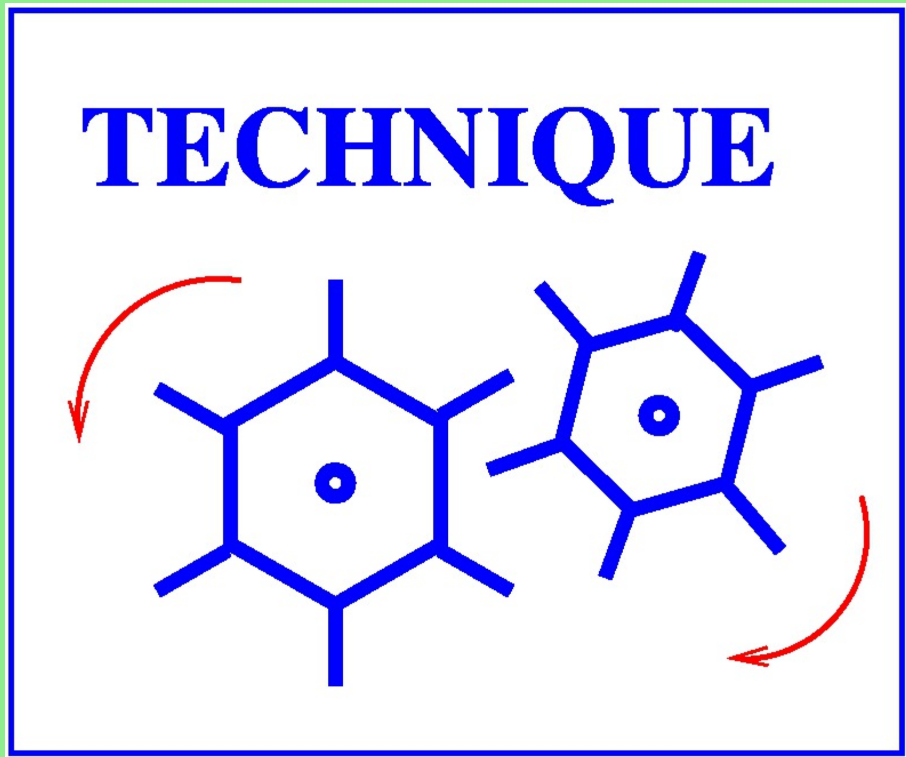
Properties

- On-site Coulomb repulsion is high ($\sim 10eV$). Poor approx. are misleading. We need exact methods.

- No. of degrees of freedom ($N_A \sim 10^{26}$) $>>$ no. of constants of motion ($N_{C.M.} \sim \mathcal{O}(10)$), hence are representing many-body non-integrable systems.

- 99% of the huge literature relating exact solutions is connected to integrable models which describe mostly 1D systems ("Bethe Anzats techniques").

- In order to provide exact results for non-integrable cases special techniques must be used. Cell-periodicity of polymers $\Rightarrow$ condensed matter techniques.

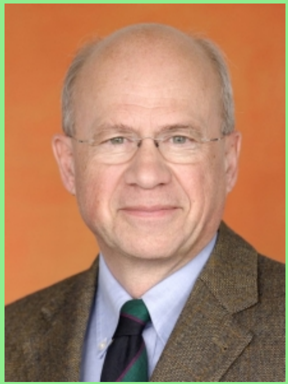


About the Technique Used

Main collaborations on the subject

International collaborations:

A. Kampf



D. Vollhardt

M. Gulacsi

Local people:

Gy. Kovács

E. Kovács

P. Gurin

Method based on Pos.Semidef.Oper.Propert.

Past applications in condensed matter physics:
Non-approx. results in conditions unimaginable befor:

1D Multiband Syst.: Jour. of Phys. A34, L359(2001).

2D Multiband Syst.: Phys. Rev. B64, 045118(2001).

2D Per.Anderson Mod.: Phys. Rev. B66, 165109(2002).

3D Per.Anderson Mod.: Phys.Rev.Lett. 91,186401(2003).

2D Disordered Syst.: Phys. Rev. B69, 054204(2004).

3D Non-Fermi Liq.: Phys. Rev. B72, 075130(2005).

2D Stripes, Droplets: Phys. Rev. B73, 014524(2006).

2D Delocaliz. Effects: Phys. Rev. B77, 245113(2008).

3D Magn. Nanograins: IOP Conf. Ser. 47, 012048(2013).

Interact.-created bands: Europhys.Lett. 107, 57005(2014).

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THE METHOD USED, AND STEPS OF THE METHOD

Positive semidefinite operators ($\hat{O}$)

One considers $\langle\Phi|\Phi\rangle = 1$, *the Hilbert space is* $\mathcal{H}$.

By Definition: $\langle\Phi|\hat{O}|\Phi\rangle \geq 0, \qquad \forall|\Phi\rangle \in \mathcal{H}$

If $|\Phi\rangle$ **is an eigenstate of** $\hat{O}$**, e.g.** $\hat{O}|\Phi\rangle = p|\Phi\rangle$**, it results**

$$\langle\Phi|\hat{O}|\Phi\rangle = p\langle\Phi|\Phi\rangle = p \geq 0$$

Consequently:

The minimum possible eigenvalue of $\hat{O}$ **is zero !**

$\widehat{H}$ as positive semidefinite operator

$\widehat{H}$ for a physical system has always a lover bound E_g of the spectrum

$\widehat{H}|\Psi\rangle = E|\Psi\rangle$**,** $\quad \forall E, \quad E \geq E_g$**,**
where $\widehat{H}|\Psi_g\rangle = E_g|\Psi_g\rangle$ **defines** $|\Psi_g\rangle, E_g$

Consequently:

$\forall \widehat{H}$**,** $\widehat{H}' = \widehat{H} - E_g = \hat{O} =$ **Positive Semidefinite Operator**

e.g. $\quad \forall \widehat{H}$**,** $\quad \widehat{H} = \hat{O} + C$**,** $\quad$ **where** $C = E_g$

Consequences of the $\hat{H} = \hat{O} + C$ relation

- **Each $\hat{H}$ can be decomposed in term of positive semidefinite operators as $\hat{H} = \hat{O} + C$,**
  (independent on dimensionality or integrability)

- **Because C changes, a such decomposition can be done in several different ways, each introducing the problem in different regions of the parameter space.**

- **Since $\hat{H} - C = \hat{O}$, the ground state is obtained from the most general solution of the equation**

$$\hat{O}|\Psi_g\rangle = 0 \qquad \textbf{(1)}$$

- **If (1) allows the solution $|\Psi_g\rangle$, it results** $\qquad E_g = C$

The steps of the method

Step 1: Decomposition in positive semidefinite operators

Meaning: Rewrite the starting $\hat{H}$ as $\hat{H} \equiv \hat{O} + C$, (2)

<u>This job is done by:</u>

- Introduction at each lattice site of block operators $\hat{A}_{\mathbf{i},\sigma}$ as linear or non-linear combination of fermionic operators acting on the sites of a given finite block, than creating positive semidefinite forms as for example $\hat{A}^{\dagger}_{\mathbf{i},\sigma}\hat{A}_{\mathbf{i},\sigma}$.

- Introduction of other possible positive semidefinite operators as $\hat{P}_{\mathbf{i}} = \hat{n}_{\mathbf{i},\sigma}\hat{n}_{\mathbf{i},-\sigma} - (\hat{n}_{\mathbf{i},\sigma} + \hat{n}_{\mathbf{i},-\sigma}) + 1$,

- Matching the value of $\hat{H}$ parameters and positive semidefinite operator coefficients such to obtain Eq.(2). This leads to the *<u>Matching Equations</u>*.

Examples of possible transformed forms:

$$a)\quad \hat{H} \to \sum_{\mathbf{i},\sigma} \hat{A}_{\mathbf{i},\sigma} \hat{A}^{\dagger}_{\mathbf{i},\sigma}, \qquad \hat{A}_{\mathbf{i},\sigma} = \sum_{n \in \mathcal{D}} a_n \hat{c}_{\mathbf{i}+\mathbf{r}_n,\sigma}$$

$$b)\quad \hat{H} \to \sum_{\mathbf{i}} \hat{A}^{\dagger}_{\mathbf{i}} \hat{A}_{\mathbf{i}}, \ \ \textit{or} \ \ \sum_{\mathbf{i}} \hat{A}_{\mathbf{i}} \hat{A}^{\dagger}_{\mathbf{i}}, \qquad \hat{A}_{\mathbf{i}} = \sum_{\sigma} \sum_{n \in \mathcal{D}} a_{n,\sigma} \hat{c}_{\mathbf{i}+\mathbf{r}_n,\sigma}$$

$$c)\quad \hat{H}_U \to \sum_{\mathbf{i}} U_{\mathbf{i}} \hat{P}_{\mathbf{i}}, \ \ \hat{P}_{\mathbf{i}} = \hat{n}_{\mathbf{i},\sigma} \hat{n}_{\mathbf{i},-\sigma} - (\hat{n}_{\mathbf{i},\sigma} + \hat{n}_{\mathbf{i},-\sigma}) + 1,$$

$$d)\quad \hat{H} \to \sum_{\mathbf{i}} \hat{A}^{\dagger}_{\mathbf{i}} \hat{A}_{\mathbf{i}}, \qquad \hat{A}_{\mathbf{i}} = \sum_{\sigma} \sum_{n \in \mathcal{D}} a_{\mathbf{r}_n,\mathbf{r}'_n,\sigma} \hat{c}^{\dagger}_{\mathbf{i}+\mathbf{r}_n,\sigma} \hat{c}^{\dagger}_{\mathbf{i}+\mathbf{r}'_n,-\sigma}$$

$$e)\quad \hat{H} \to \sum_{\mathbf{i},\sigma} \hat{A}^{\dagger}_{\mathbf{i},\sigma} \hat{A}_{\mathbf{i},\sigma}, \qquad \hat{A}_{\mathbf{i},\sigma} = \sum_{n \in \mathcal{D}} (a_n \hat{c}_{\mathbf{i}+\mathbf{r}_n,\sigma} + b_n \hat{c}_{\mathbf{i}+\mathbf{r}_n,\sigma} \hat{n}_{\mathbf{i}+\mathbf{r}_n,-\sigma})$$

$f)$ ....

The steps of the method

Step 2: Construction of the ground states

Meaning: Construct the most general $|\Psi_g\rangle$ such to have $\hat{O}|\Psi_g\rangle = 0$. The corresponding $E_g = C$.

Precondition: The Matching Equations must be solved first

Matching Conditions: Nonlinear complex algebraic system of coupled equations (2D often $\sim 40 - 50$).

- **One obtains explicitly: $\hat{A}_{\mathrm{i}}$ from transformed $\hat{H}$, $\hat{H}(\mathcal{D})$.**
- **Only after this step the $|\Psi_g\rangle$ construction can begin.**

Example for the case: $\hat{O} = \sum_{n,\mathbf{i},\sigma} \hat{A}^{\dagger}_{n,\mathbf{i},\sigma} \hat{A}_{n,\mathbf{i},\sigma} + \hat{O}_2$:

One looks for operators $\hat{B}^{\dagger}_{m,\mathbf{j},\sigma} = \sum_{p \in \mathcal{R}_m} b_{p,m} \hat{c}^{\dagger}_{\mathbf{j}+\mathbf{r}_p,\sigma}$

such to have $\{\hat{A}_{n,\mathbf{i},\alpha}, \hat{B}^{\dagger}_{m,\mathbf{j},\beta}\} = 0, \quad \forall\ n, m, \mathbf{i}, \mathbf{j}, \alpha, \beta,$

since in this case: $|\chi\rangle = [\prod_{m,\mathbf{j},\sigma} \hat{B}^{\dagger}_{m,\mathbf{j},\beta}]|0\rangle$

$$[\sum_{n,\mathbf{i},\sigma} \hat{A}^{\dagger}_{n,\mathbf{i},\sigma} \hat{A}_{n,\mathbf{i},\sigma}]|\chi\rangle = [\sum_{n,\mathbf{i},\sigma} \hat{A}^{\dagger}_{n,\mathbf{i},\sigma} \hat{A}_{n,\mathbf{i},\sigma}][\prod_{m,\mathbf{j},\sigma} \hat{B}^{\dagger}_{m,\mathbf{j},\beta}]|0\rangle = 0.$$

Now $(m, \mathbf{j}, \beta) \in \mathcal{I}$ **such to have** $\hat{O}_2 [\prod_{(m,\mathbf{j},\beta) \in \mathcal{I}} \hat{B}^{\dagger}_{m,\mathbf{j},\beta}]|0\rangle = 0.$

Hence: $|\Psi_g\rangle = [\prod_{(m,\mathbf{j},\beta) \in \mathcal{I}} \hat{B}^{\dagger}_{m,\mathbf{j},\beta}]|0\rangle, \quad E_g = C.$

The steps of the method

Step 3: The proof of the uniqueness

Meaning: To prove that the deduced $|\Psi_g\rangle$ is unique.

The procedure is based on the study of the kernel:

Let $\hat{O} = \hat{H} - E_g$**. Then,** $ker(\hat{O}) := \{|\phi\rangle, \hat{O}|\phi\rangle = 0\}$ **.**

One must prove that $|\Psi_g\rangle$ **spans** $ker(\hat{O})$**.**

The technique has two steps:

a) One proves that $|\Psi_g\rangle \in ker(\hat{O})$

b) One proves that all $|\Phi\rangle \in ker(\hat{O})$ **can be written in terms of** $|\Psi_g\rangle$

c) When degeneracy is present $|\Psi_g\rangle \to |\Psi_g(m)\rangle, \forall m$

The steps of the method

Step 4: The study of physical properties

Meaning: The deduced $|\Psi_g\rangle$, has usually a quite complicated structure, and the physical properties, a priori, are not visible. They must be deduced !

This is done by calculating different expectation values

Remarc: If $(|\Psi_g(N)\rangle, E_g(N))$ is deduced, also the low lying spectrum can be tested. E.g., the charge gap ($\triangle$):

$$\delta\mu = \mu_+ - \mu_- = [(E_g(N+1) - E_g(N)) - (E_g(N) - E_g(N-1))],$$

Where: $\delta\mu = 0, (\delta\mu \neq 0)$, **means** $\triangle = 0$, **(**$\triangle \neq 0$**).**

The steps of the method

References:

Reporting papers:

Z.G, D.Vollhardt, Phys. Rev. Lett. 91,186401(2003),

Z.G,A.Kampf,D.Vollhardt, Phys.Rev.Lett.99,026404(2007),

Z.G, A.K, D.V, Phys. Rev. Lett. 105,266403(2010),

Reviews:

Z.G, D.V., Phys. Rev. B. 72, 075130 (2005),

Z.G, A.K, D.V., Progr.Theor.Phys.Suppl. 176, 1 (2008),

Z.G., Int. Jour. Mod. Phys. B 27, 1330009 (2013).

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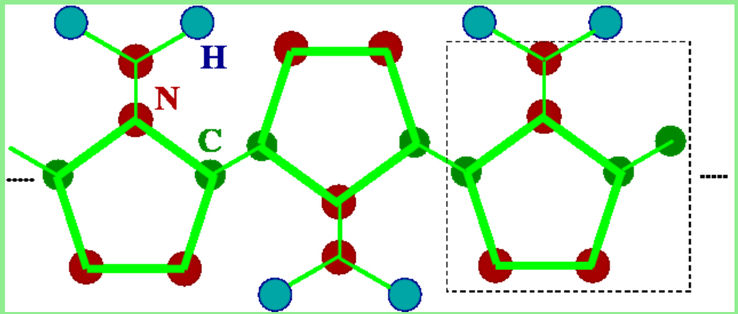
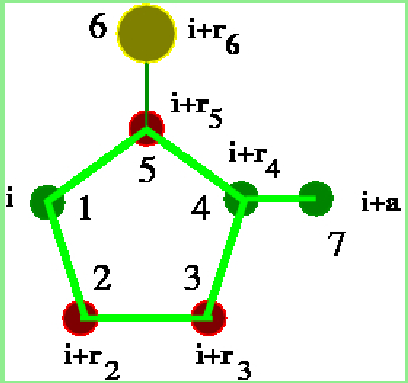
COLLECTED OWN RESULTS RELATING CONDUCTING POLYMERS

APPLICATIONS TO CHAIN STRUCTURES



Pentagon Chains

The Hamiltonian:

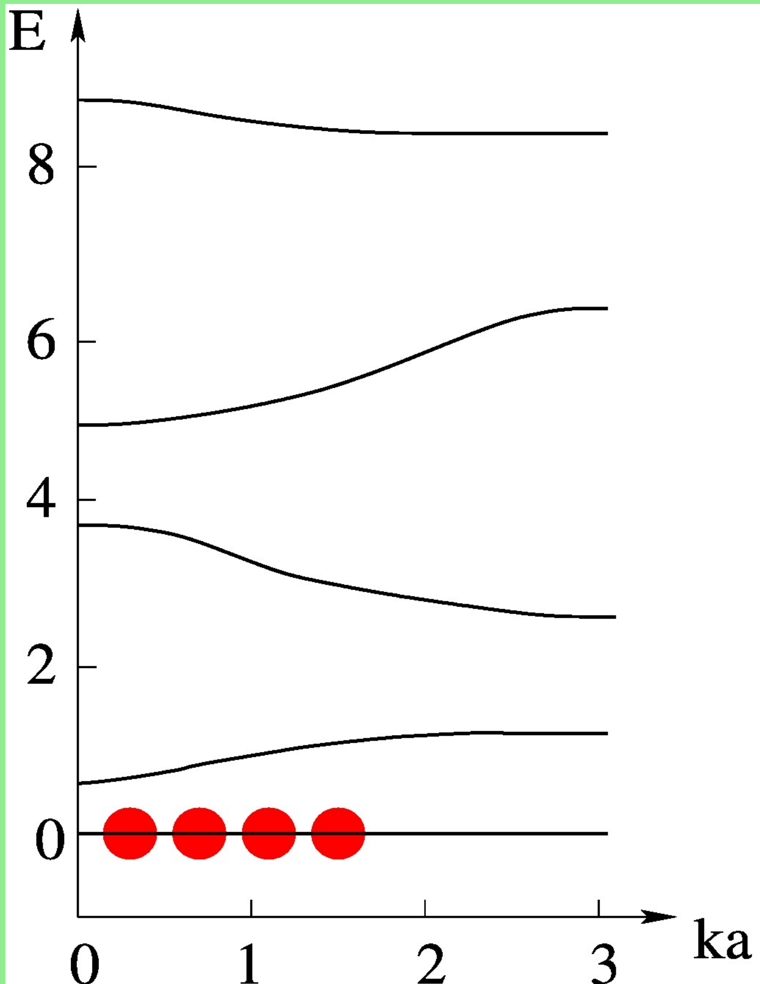


$$\hat{H}_0 = \sum_{\sigma,\mathbf{i}} [\sum_{n,n',(n>n')} (t_{n,n'} \hat{c}^{\dagger}_{\mathbf{i}+\mathbf{r}_n,\sigma} \hat{c}^{\dagger}_{\mathbf{i}+\mathbf{r}_{n'},\sigma} + H.c.) + \sum_{n=1}^{m} \epsilon_n \hat{n}_{\mathbf{i}+\mathbf{r}_n,\sigma}],$$

$$\hat{H}_U = \sum_{\mathbf{i}} \sum_{n=1}^{m} U_n \hat{n}_{\mathbf{i}+\mathbf{r}_n,\sigma} \hat{n}_{\mathbf{i}+\mathbf{r}_n,-\sigma}, \qquad \hat{H} = \hat{H}_0 + \hat{H}_U, \qquad m = 6,$$

$$U_1 = U_4 \neq U_2 = U_3, \qquad \epsilon_1 = \epsilon_4,\ \epsilon_2 = \epsilon_3, \qquad (n, n') : \ nearest\ neighbor$$

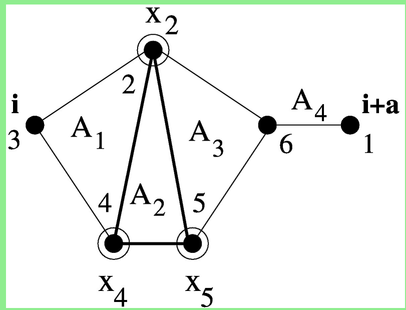
Low concentration limit:



Pentagon Chains: Low concentration limit

The transformed $\hat{H}$:

$U_n = U$, $t_{6,5} = 0$:



$$\hat{H} = \hat{H}_A + \hat{H}_U, \qquad \hat{H}_A = \sum_{\sigma} \sum_{\mathbf{i}=1}^{N_c} \sum_{\alpha=1}^{4} \hat{A}^{\dagger}_{\alpha,\mathbf{i},\sigma} \hat{A}_{\alpha,\mathbf{i},\sigma},$$

$$\begin{aligned}
\hat{A}_{1,\mathbf{i},\sigma} &= a_{1,2}\hat{c}_{\mathbf{i}+\mathbf{r}_2,\sigma} + a_{1,3}\hat{c}_{\mathbf{i}+\mathbf{r}_3,\sigma} + a_{1,4}\hat{c}_{\mathbf{i}+\mathbf{r}_4,\sigma}, \\
\hat{A}_{2,\mathbf{i},\sigma} &= a_{2,2}\hat{c}_{\mathbf{i}+\mathbf{r}_2,\sigma} + a_{2,4}\hat{c}_{\mathbf{i}+\mathbf{r}_4,\sigma} + a_{2,5}\hat{c}_{\mathbf{i}+\mathbf{r}_5,\sigma}, \\
\hat{A}_{3,\mathbf{i},\sigma} &= a_{3,2}\hat{c}_{\mathbf{i}+\mathbf{r}_2,\sigma} + a_{3,5}\hat{c}_{\mathbf{i}+\mathbf{r}_5,\sigma} + a_{3,6}\hat{c}_{\mathbf{i}+\mathbf{r}_6,\sigma}, \\
\hat{A}_{4,\mathbf{i},\sigma} &= a_{4,6}\hat{c}_{\mathbf{i}+\mathbf{r}_6,\sigma} + a_{4,1}\hat{c}_{\mathbf{i}+\mathbf{a},\sigma},
\end{aligned}$$

Pentagon Chains: Low concentration limit

The matching equations:

$$t_n = a^*_{2,4}a_{2,5}, t_c = a^*_{4,6}a_{4,1}, t = a^*_{1,2}a_{1,3} = a^*_{3,6}a_{3,2} = a^*_{1,3}a_{1,4} = a^*_{3,5}a_{3,6},$$

$$t_1 = a^*_{2,2}a_{2,5} + a^*_{3,2}a_{3,5} = a^*_{2,2}a_{2,4} + a^*_{1,2}a_{1,4}, \;\; \epsilon_0 = \sum_{n=1}^{3} |a_{n,2}|^2,$$

$$\epsilon_1 = |a_{1,4}|^2 + |a_{2,4}|^2 = |a_{2,5}|^2 + |a_{3,5}|^2,$$

$$\epsilon_2 = |a_{1,3}|^2 + |a_{4,1}|^2 = |a_{3,6}|^2 + |a_{4,6}|^2.$$

Solutions of matching equations:

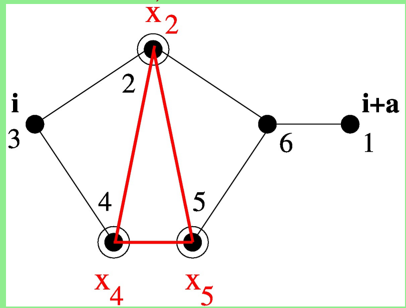
$$a_{1,2} = a_{1,4} = a_{3,2} = a_{3,5} = sign(t)\sqrt{\epsilon_1 - t_n}e^{i\phi_1}, \; a_{1,3} = \frac{|t|}{\sqrt{\epsilon_1 - t_n}}e^{i\phi_1},$$

$$a_{2,4} = a_{2,5} = \sqrt{t_n}e^{i\phi_2}, \qquad a_{2,2} = \frac{t_1 - \epsilon_1 + t_n}{\sqrt{t_n}}e^{i\phi_2}, \; a_{3,6} = a_{1,3},$$

$$a_{4,1} = \sqrt{\frac{\epsilon_2(\epsilon_1 - t_n) - t^2}{\epsilon_1 - t_n}}e^{i\phi_3}, \qquad a_{4,6} = t_c\sqrt{\frac{\epsilon_1 - t_n}{\epsilon_2(\epsilon_1 - t_n) - t^2}}e^{i\phi_3},$$

Pentagon Chains: Low concentration limit

$\widehat{B}^{\dagger}_{\mathbf{i},\sigma}$:

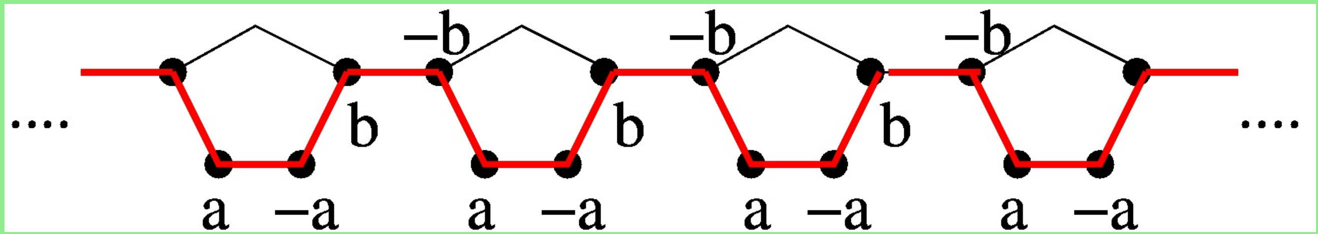


The ground state:

Is a ferromagnetic state

$$|\Psi_g(N_c+1)\rangle = \widehat{B}^{\dagger}_{1,\sigma} \prod_{\mathbf{i}=1}^{N_c} \widehat{B}^{\dagger}_{\mathbf{i},\sigma}|0\rangle,$$

$\widehat{B}^{\dagger}_{1,\sigma}$:



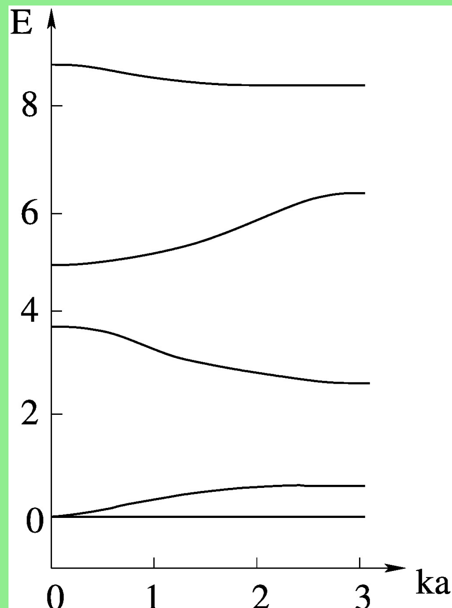
Pentagon Chains: Low concentration limit

The conditions for the solution to appear

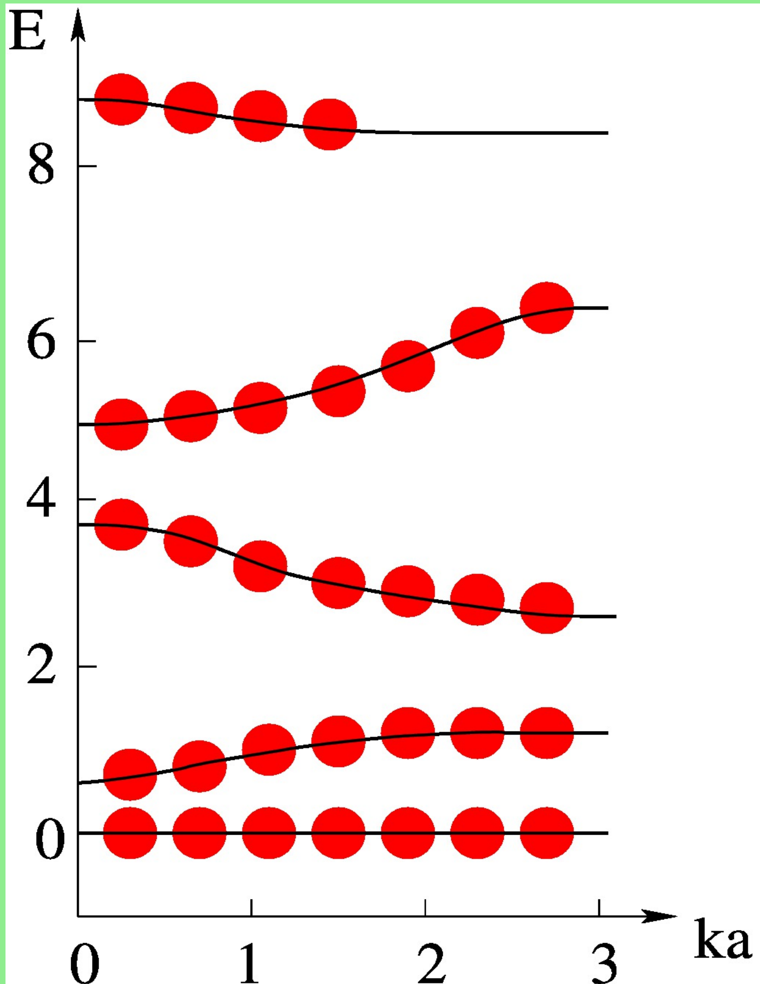
$$t_{1,5} = t,\ \ t_{2,3} = t_n,\ \ t_{4,7} = t_c,\ \ t_{2,5} = t_1,\ \ t_1 = \epsilon_1 + |t_n|,$$

$$\epsilon_0 = 2(\epsilon_1 - t_n) + 4t_n, \qquad \epsilon_2 = \frac{t^2}{\epsilon_1 - t_n} + |t_c|.$$

The dispersive band placed above the flat band gives a touching point with the flat band enforcing the connectivity conditions.



High concentration limit:



Pentagon Chains: high concentration limit

Polymer case: The transformed $\widehat{H}$

The starting $\widehat{H}$

$\widehat{H} = \widehat{H}_0 + \widehat{H}_U, \; \widehat{H}_0 = \widehat{H}_0(t_{n,n'}, \epsilon_n), \; \widehat{H}_U = \sum_{\mathbf{i}} \sum_{n=1}^{m} U_n \widehat{n}_{\mathbf{i}+\mathbf{r}_n,\uparrow} \widehat{n}_{\mathbf{i}+\mathbf{r}_n,\downarrow},$

Flat bands in $\widehat{H}_0$ are excluded.

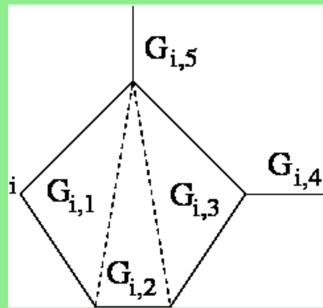
Transformation of $\widehat{H}$ in positive semidefinite form

$\widehat{H} - C_{g,1} = \widehat{H}_G + \widehat{H}_P, \; \widehat{H}_G = \widehat{H}_{kin} + C_{g,2}$

$\epsilon_n^R = \epsilon_n + U_n - q(\{U_n\})$, $\qquad q(\{U_n\})$ **is a nonlinear function.**

Pentagon Chains: high concentration limit

The used operators, and the ground state:



$(m-1)=5$
blocks

One has $m=6$ **(six sites per cell),** $z_\alpha=\{\widehat{G}_{\alpha,\mathbf{i},\sigma},\widehat{G}^\dagger_{\alpha,\mathbf{i},\sigma}\}$**, and**

$$\widehat{H}_G=\sum_{\mathbf{i},\sigma}\sum_{\alpha=1}^{m-1}\widehat{G}_{\alpha,\mathbf{i},\sigma}\widehat{G}^\dagger_{\alpha,\mathbf{i},\sigma},\qquad \widehat{H}_P=\sum_{\mathbf{i}}\sum_{n=1}^{m}U_n\widehat{P}_{\mathbf{i}+\mathbf{r}_n},$$

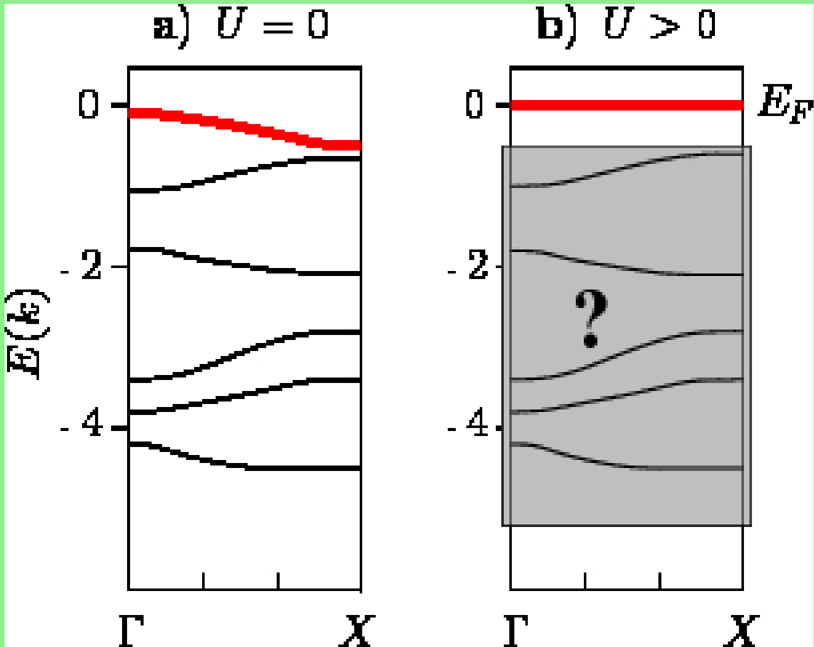
$$\widehat{P}_{\mathbf{j}}=\widehat{n}_{\mathbf{j},\uparrow}\widehat{n}_{\mathbf{j},\downarrow}-(\widehat{n}_{\mathbf{j},\uparrow}+\widehat{n}_{\mathbf{j},\downarrow})+1,\ \ C_{g,1}=Nq(\{U_n\})-N_c\sum_{n=1}^{m}U_n-C_{g,2},$$

$$\widehat{H}_{kin}=-\sum_{\mathbf{i},\sigma}\sum_{\alpha=1}^{m-1}\widehat{G}^\dagger_{\alpha,\mathbf{i},\sigma}\widehat{G}_{\alpha,\mathbf{i},\sigma},\qquad C_{g,2}=2N_c\sum_{\alpha=1}^{m-1}z_\alpha,$$

$$|\Psi_g\rangle=[\prod_{\mathbf{i}}(\prod_{n=1}^{m}\widehat{c}^\dagger_{\mathbf{i}+\mathbf{r}_n,\sigma})(\prod_{\alpha=1}^{m-1}\widehat{G}^\dagger_{\alpha,\mathbf{i},-\sigma})]|0\rangle,\qquad N=11N_c.$$

Pentagon Chains: high concentration limit

Comparison of the $U = 0$ and $U > 0$ cases



The exact behavior inside the shaded region is exactly not known.

$|\Psi_g\rangle$: At $N = 11N_c$ is a nonsaturated ferromagnet localized in the thermodynamic limit. At $11N_c < N < 12N_c$, remaining ferromagnetic, becomes delocalized ($N_c =$ number of cells).

Summary and Conclusions

- Method based on positive semidefinite operators for deducing exact N dependent ground states.

- The steps of the method have been presented in details: i) transcription of $\hat{H}$ in positive semidefinite form, ii) deduction of the ground states, iii) proof of uniqueness, iv) deduction of physical properties.

- The technique not depends on dimensionality or integrability hence has a large potential applicability.

- Example solutions relating physical systems: ferromagnetism in conducting polymers in: a) low, b) high concentration limits.

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