A New Mechanism Producing Ferromagnetism in Conducting Polymers

Zsolt Gulacsi,
University of Debrecen, Department of Theoretical Physics, Debrecen, Hungary.

BIT's 3rd Annual World Congress of Nano Science and Technology

- 27 September 2013, Xi'an, China -

University of Debrecen

Location of Debrecen

Main Building

Short Outline:

- Introduction (5 %)
- The method used (5 %)
- The steps of the method (35 %)
- The method applied to chain structures (25 %)
- The mechanism leading to ferromagnetism (25 %)
- Summary and conclusions (5 %)

Collected number of slide pages: 28

Main collaborations on the subject

International collaborations:

A. Kampf

D. Vollhardt

M. Gulacsi

Local people:

R. Trencsényi

E. Kovács

P. Gurin

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

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 !**

$\hat{H}$ as positive semidefinite operator

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

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

Consequently:

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

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

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)

This job is done by:

- 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 *Matching Equations*.

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

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 $|\Psi_g\rangle \rightarrow |\Psi_g(m)\rangle, \forall m$

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 (Δ):

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

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

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),

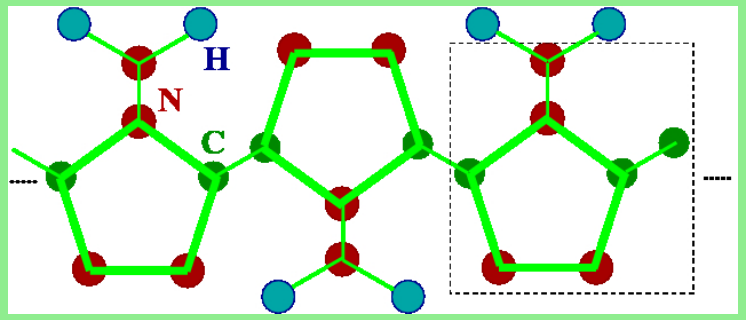
Reviews:

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

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

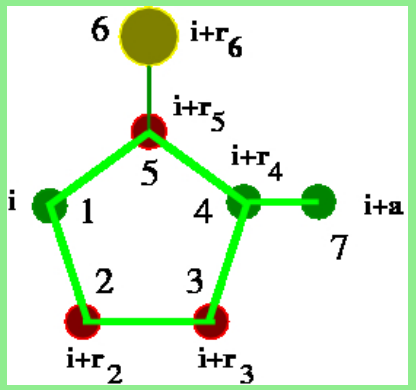
Z.G., Int. Jour. Mod. Phys. B 27, 1330009 (2013).

II. APPLICATION TO CHAIN STRUCTURES



Pentagon Chains

Polymer case: The Hamiltonian



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

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

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

Pentagon Chains

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

The starting $\hat{H}$

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

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

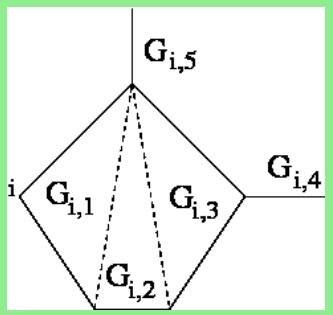
Transformation of $\hat{H}$ in positive semidefinite form

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

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

Pentagon Chains

The used operators, and the ground state:



$(m-1)=5$ **blocks**

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

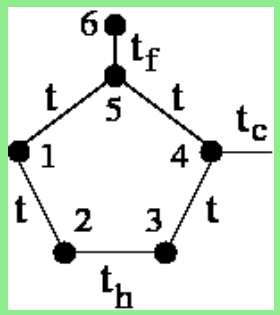
$$\hat{H}_G=\sum_{\mathbf{i},\sigma}\sum_{\alpha=1}^{m-1}\hat{G}_{\alpha,\mathbf{i},\sigma}\hat{G}^\dagger_{\alpha,\mathbf{i},\sigma},\qquad \hat{H}_P=\sum_{\mathbf{i}}\sum_{n=1}^{m}U_n\hat{P}_{\mathbf{i}+\mathbf{r}_n},$$

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

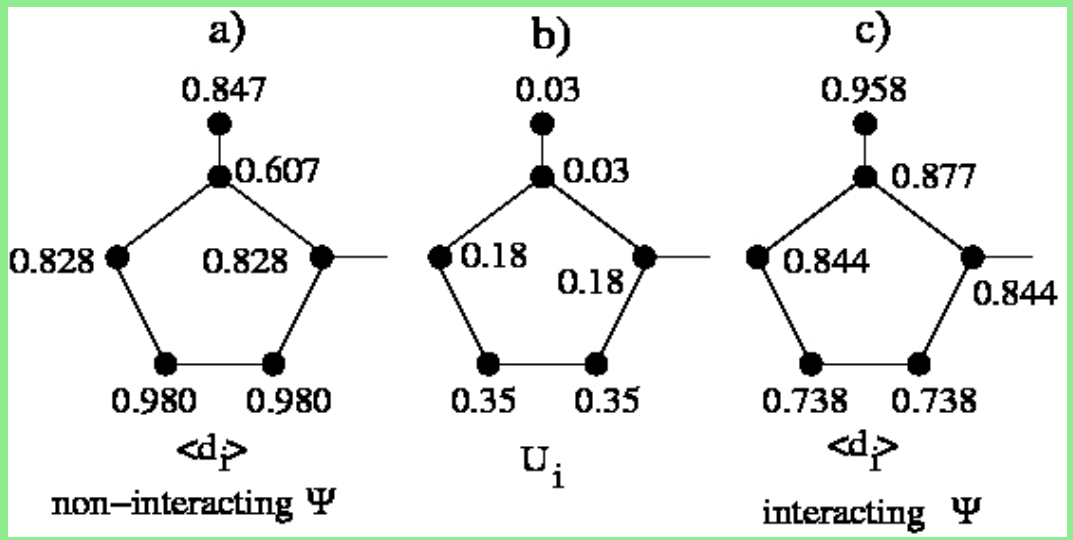
$$\hat{H}_{kin}=-\sum_{\mathbf{i},\sigma}\sum_{\alpha=1}^{m-1}\hat{G}^\dagger_{\alpha,\mathbf{i},\sigma}\hat{G}_{\alpha,\mathbf{i},\sigma},\qquad C_{g,2}=2N_c\sum_{\alpha=1}^{m-1}z_\alpha,$$

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

Importance of different U_n values:

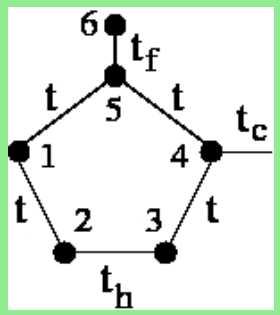


Let us consider for example:
$t = 1.0$, $t_c = 0.5$, $t_h = -1.1$, $t_f = 1.2$, $\epsilon_1 = \epsilon_4 = -2.5$, $\epsilon_2 = \epsilon_3 = -2.0$, $\epsilon_5 = \epsilon_6 = -2.1$, $N_c = 2$.
One has: $E_{int} = \sum_i U_i \langle \hat{d}_i \rangle$

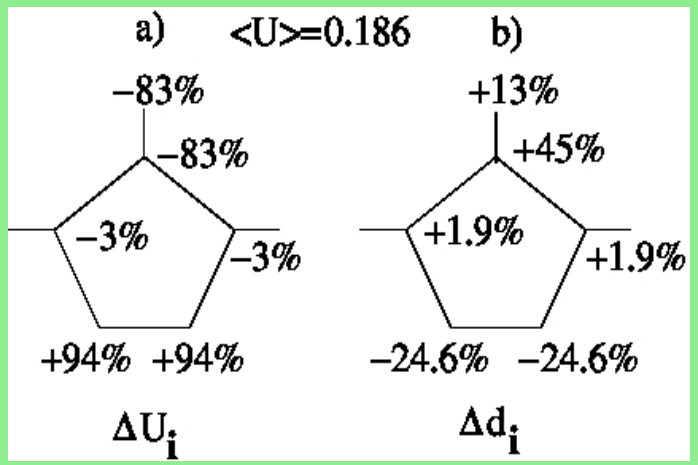


Redistribution of the double occupancy $\langle \hat{d}_i \rangle = \langle \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} \rangle$

Importance of different U_n values:

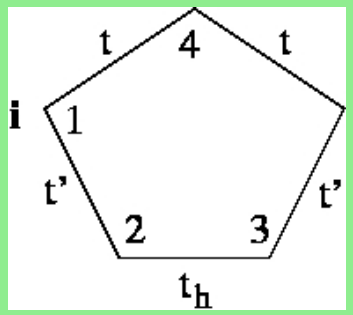


Let us consider for example:
$t = 1.0$, $t_c = 0.5$, $t_h = -1.1$, $t_f = 1.2$, $\epsilon_1 = \epsilon_4 = -2.5$, $\epsilon_2 = \epsilon_3 = -2.0$, $\epsilon_5 = \epsilon_6 = -2.1$, $N_c = 2$.

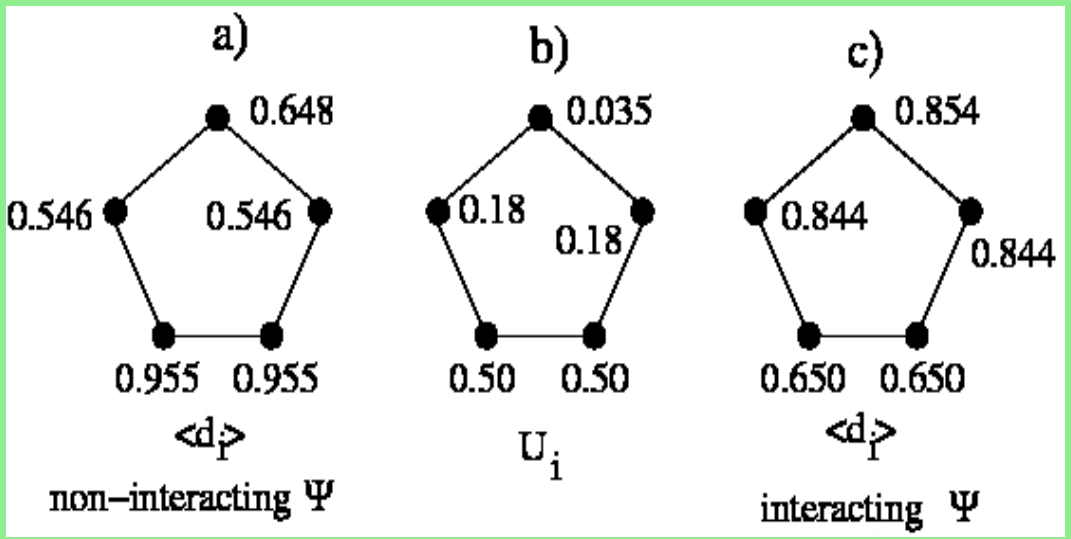


Redistribution of the double occupancy $\langle \widehat{d}_i \rangle = \langle \widehat{n}_{\mathbf{i},\uparrow} \widehat{n}_{\mathbf{i},\downarrow} \rangle$

External bonds, antennas, and ϵ_n not matter:

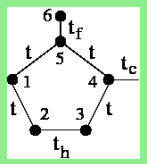


Let us consider for example:
$t = 1.0,\ t' = 1.0,\ t_h = -1.1,$
$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = 0,\ N_c = 2.$
One has: $E_{int} = \sum_i U_i \langle \hat{d}_i \rangle$



Redistribution of the double occupancy $\langle \hat{d}_i \rangle = \langle \hat{n}_{\mathbf{i},\uparrow} \hat{n}_{\mathbf{i},\downarrow} \rangle$

The huge δE_{int} decrease drives the transition:



One considers $U_n \neq 0$, uses $t = 1$ units, and calculate in percents $\delta E_\nu = (E_\nu - E_{0,\nu})/|E_{0,\nu}|$, $\nu = kin, int, g$.

$E_{0,kin}, E_{0,int}, E_{0,g}$ deduced from $|\Psi_{0,g}\rangle$ as trial wave function

E_{kin}, E_{int}, E_g deduced from the $|\Psi_g\rangle$ exact ground state

$E_{0,kin} = -52.597, \quad E_{0,int} = 2.055, \quad E_{0,g} = -50.541,$

$E_{kin} = -51.223, \quad E_{int} = 0.664, \quad E_g = -50.558,$

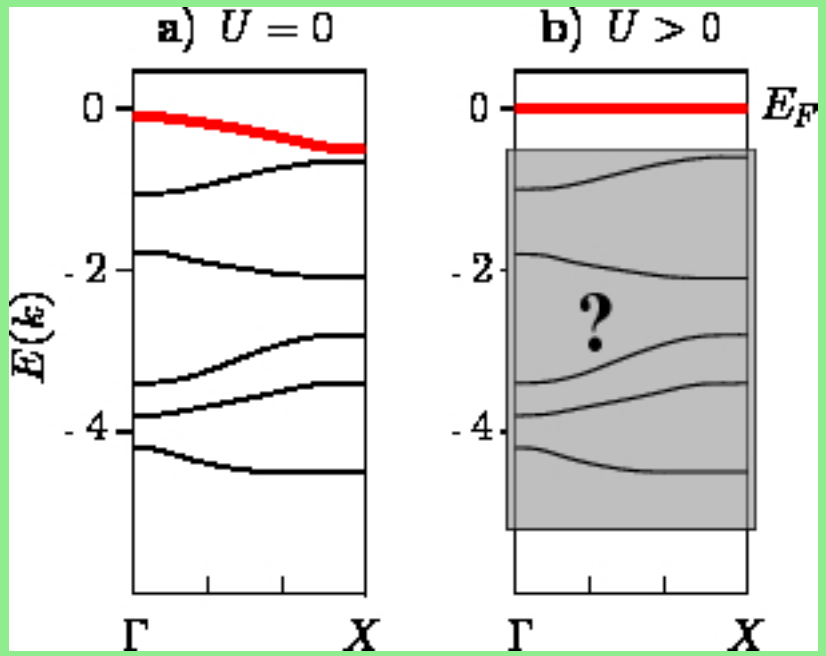
$\delta E_{kin} = +2.6\%, \quad \delta E_{int} = -69.5\%, \quad \delta E_g = -0.03\%.$

IN CONCLUSIONS:

- **The huge decrease in E_{int} alone drives the transition,**
- **This to be possible, the system quenches E_{kin},**
- **The quench of $E_{kin} \Rightarrow$ the effective flat band emerges.**

Pentagon Chains

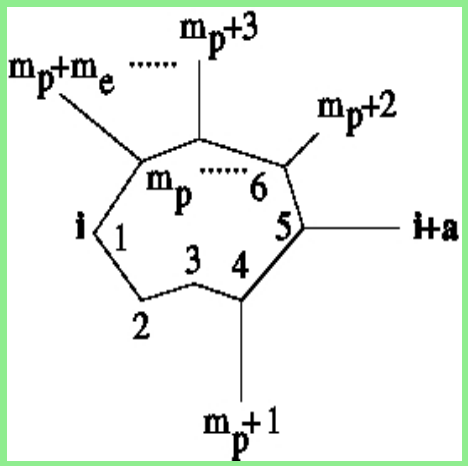
Comparison of the $U = 0$ and $U > 0$ cases



The exact behavior inside the shaded region is exactly not known. (Z.G,A.K,D.V, Phys.Rev.Lett. 2010)

$|\Psi_g\rangle$: 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).

More general chain case



The unit cell at i of the general chain: One has $m = m_p + m_e$ sites, where the m_p sites are included into a closed polygon, and m_e represents the number of external sites connected to the polygon. a is the Bravais vector.

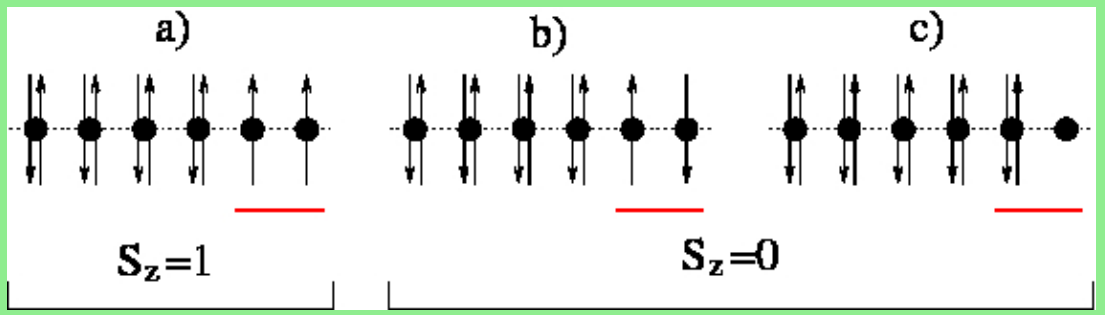
In $\mathcal{D}$, effective (U_n created) upper flat band appears:

$$\hat{H} = \hat{P}_I + \hat{P}_{II} + E_g, \;\; \hat{P}_I = \hat{H}_{kin} + C, \;\; \hat{H}_{kin} = -\sum_{\mathbf{i},\sigma} \sum_{\alpha=1}^{m-1} \hat{G}^{\dagger}_{\alpha,\mathbf{i},\sigma} \hat{G}_{\alpha,\mathbf{i},\sigma},$$

$$H_{kin} = \sum_{\mathbf{k},\sigma} \sum_{\gamma=1}^{m} \xi_{\gamma}(\mathbf{k}, \{U_n\}) \hat{C}^{\dagger}_{\gamma,\mathbf{k},\sigma} \hat{C}_{\gamma,\mathbf{k},\sigma}, \qquad \xi_{\gamma=m}(\mathbf{k}, \{U_n\}) = constant.$$

$$|\Psi_g\rangle = [\prod_{\mathbf{i}} (\prod_{n=1}^{m} \hat{c}^{\dagger}_{\mathbf{i}+\mathbf{r}_n,\sigma}) (\prod_{\alpha=1}^{m-1} \hat{G}^{\dagger}_{\alpha,\mathbf{i},-\sigma})]|0\rangle, \qquad N = (2m-1)N_c.$$

Ferromagnetism appears as a half metal



Half filled upper band:
$N_c = 2, N_b = 6, N = 22,$
$N_\wedge = 12,\ N_{Max} = 24,$
$N_{\uparrow,\downarrow} = 10$, **It remains:**
2 electrons, 2 sites

WHY FERROMAGNETISM ?

1) The decrease of E_{int} means also the reduction of $N_{\uparrow,\downarrow}$,
2) If $\hat{H}|\phi\rangle = E|\phi\rangle$ and $|b)\rangle \in |\phi\rangle$, $\Rightarrow$ also $|c)\rangle \in |\phi\rangle$,
3) Consequently $N_{\uparrow,\downarrow}(S_z = 0) > N_{\uparrow,\downarrow}(S_z = 1)$,
4) Hence the strong $\delta E_{int} << 0$ leads to ferromagnetism.

WHY ONE SPIN UP ELECTRON ON ALL SITES ?

1) Only configuration a) contributes to the Ferro phase,
2) If a) holds $\Rightarrow$ one has 1 $\uparrow$ electron on all sites.

Mechanism: Summary

- Different $U_{\rm j} > 0$ on different type of sites offers a supplementary possibility for a strong decrease of E_{int}.

- This is done by a redistribution of the site dependent double occupancy $D_{\rm j}$ such to have high $D_{\rm j}$ where $U_{\rm j} > 0$ is small and vice versa.

- For $D_{\rm j} \sim 0$ the mechanism not works, that is why high concentration is needed.

- To take advantage of the huge E_{int} decrease possibility, the transition is driven exclusively by a $\delta E_{int} << 0$.

- This to be possible (i.e. to afford to concentrate only on the decrease of E_{int}), the system quenches E_{kin}, roughly at the value present in the non-interacting case.

- The kinetic energy quench provides the effective upper flat band (Note: bare flat bands are not present).

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: the case of the pentagon, and a general chain.
- The physical mechanism leading to the effective flat band has been described in details (different U_n, quench of E_{kin}, huge $\delta E_{int} << 0$, redistribution of $\langle \hat{d}_{\mathrm{j}} \rangle$).

Financial Support

I kindly acknowledge the financial support of:

- OTKA-K-100288 (Hungarian Research Funds for Basic Research),
- TAMOP-4.2.2/A-11/1/KONV-2012-0036 (Hungarian Development Funds for Research Universities cofinanced by EU),
- TAMOP 4.2.4. A/2-11-1-2012-0001 National Excellence Program elaborating and operating an inland student and researcher personal support system. This project was subsidized by the European Union and co-financed by the European Social Fund.
- Alexander von Humboldt Foundation.

University of Debrecen:

Main Building: Inner yard

Main University Library

THANKS FOR YOUR KIND ATTENTION !