Detection and chemical tailoring of entanglement in antiferromagnetic spin clusters

February 4^{th} 2015, ***Bilbao***

Outline

- **Molecular Nanomagnets**

    Spin Hamiltonians

- **Entanglement detection**

    Exchange energy as an entanglement witness

- **Spin-pair entanglement modulation**

    Homometallic and heterometallic rings : Cr_8, Cr_7M and $Cr_{2n}M_2$

    Exchanged coupled dimers

- **Multi-spin entanglement**

    Energy as a witness of multi-spin entanglement

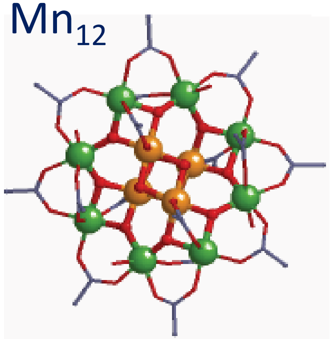
    Homometallic and heterometallic rings

- **Conclusions**

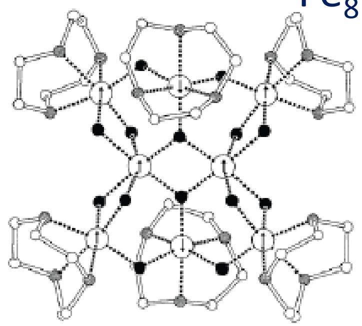
Molecular Spin Clusters: Single Molecule Magnets

high spin ground state

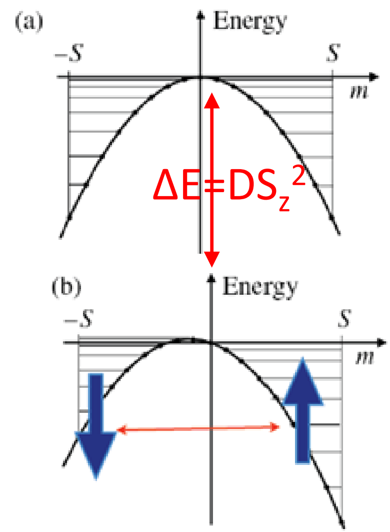
Mn$_{12}$



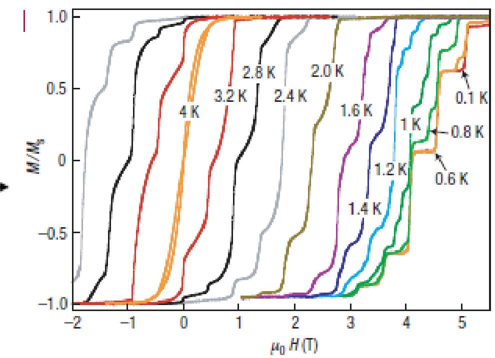
Fe$_8$



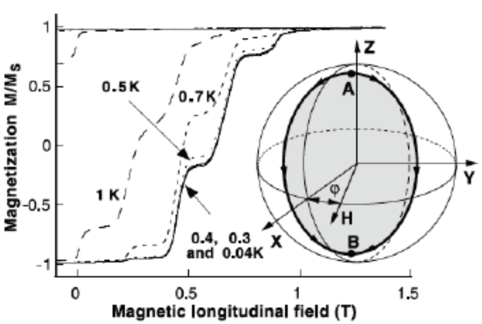
8 Mn^{3+}+ 4 Mn^{4+} 8 Mn^{3+}+ 4 Mn^{4+}

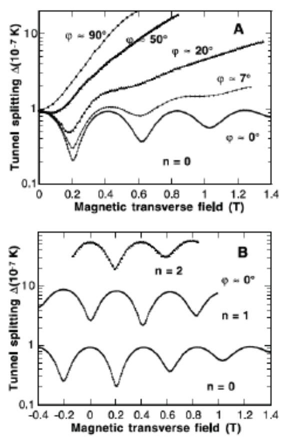


quantum tunneling of the magnetization (low T)

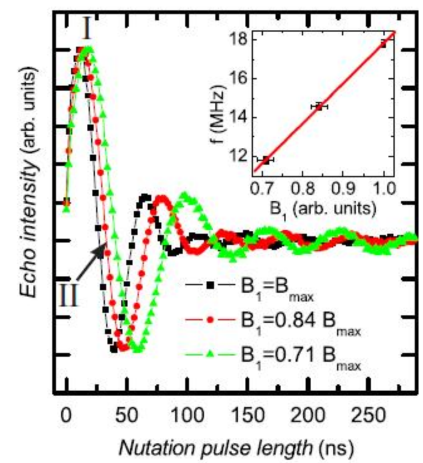


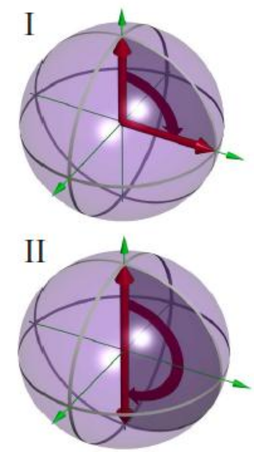
quantum phase interference





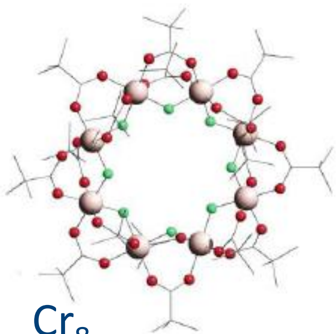
quantum oscillations



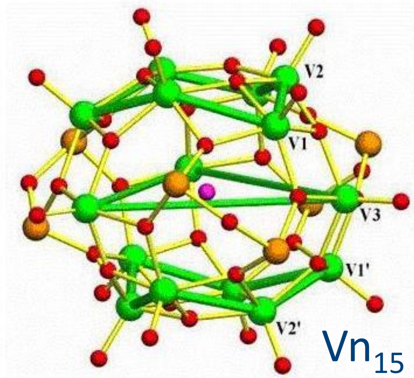


Thomas et al, Nature 383, 145 (1996).
Sangregorio et al, Phys. Rev. Lett. 78, 4645 (1997).
Schelgel et al., Phys. Rev. Lett. 101, 147203 (2003).

Molecular Spin Clusters: AF molecules



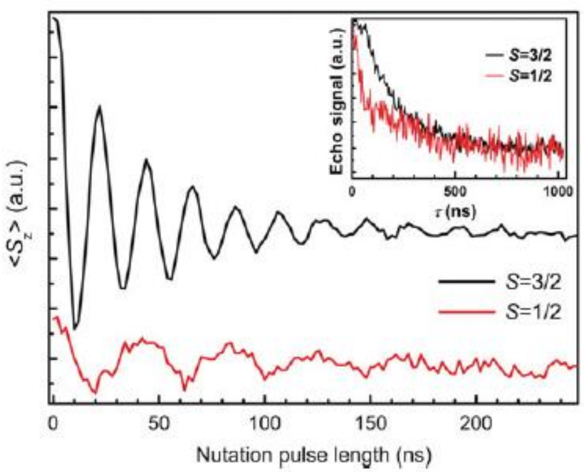
Cr_8



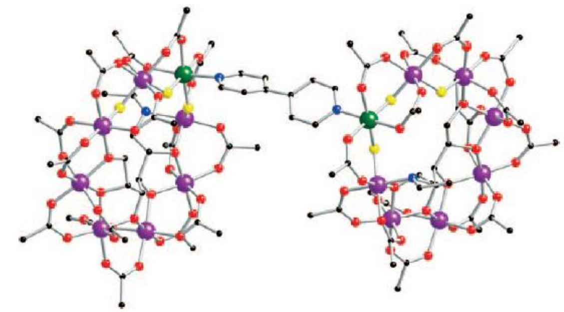
highly correlated

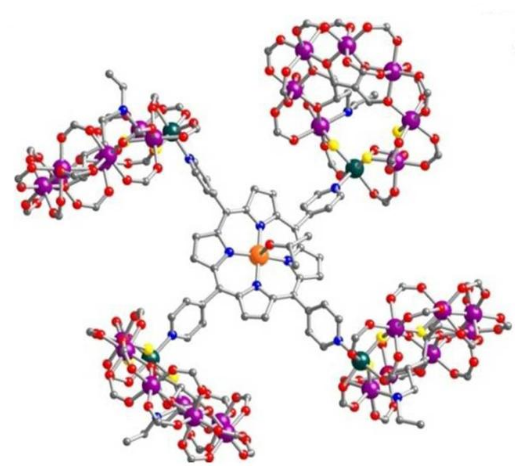
low spin ground state

quantum oscillations



chemical engineering





Bertaina et al, Nature 453, 203 (1996).
Timco et al. Angew. Chem. Int. Ed. 47, 9681 –9684 (2008).
Timco et al., Chem. Soc. Rev. 40, 3067–3075 (2011)

Spin Hamiltonians

$$H = \sum_{i=1}^{N} J_{i,i+1}\mathbf{s}_i \cdot \mathbf{s}_{i+1} + \sum_{i=1}^{N}\left(d_i s^2{}_{i,z} + \frac{1}{2} e_i (s^2{}_{i,+} - s^2{}_{i,-}) \right) + \sum_{i<j} \mathbf{s}_i \cdot \bar{D}_{ij} \cdot \mathbf{s}_j$$

- Direct **diagonalization** of the Hamiltonian (dimension $(2s_i+1)^N$)

  Irreducible Tensor Operator (ITO) formalism

  block matrix (exploiting symmetries, conservation of S and M)

  non-local basis: successive coupling scheme is adopted

$$| S_1 S_2 (\tilde{S}_2) S_3 (\tilde{S}_3) \ldots S_{N-1} (\tilde{S}_{N-1}) S_N SM >=| (\tilde{S}) SM >$$

- Reduced **density matrix** at **finite temperature** in the local basis

$$\rho = \frac{1}{Z} e^{-H/k_B T} \qquad | m_1, m_2, \ldots, m_N >$$

J.J. Borras-Almenar et al, Inorg. Chem. 38, 6081 (1999)

Entanglement Detection

An observable ***W*** is an **entanglement witness** if:

$$\langle W \rangle \quad \geq W^{th} \quad \text{for all separable states } \rho_s$$

$$W^{th} = \inf_{\psi \text{ is separable}} \langle \psi | W | \psi \rangle$$

✓ knowledge of ρ is not required

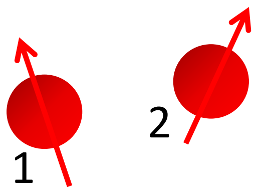
✓macroscopic properties are informative of microscopic quantum correlations

✓ thermal entanglement

✓each witness is selective for a specific kind of entanglement

Exchange energy as a witness in AF systems

$$H = J\mathbf{s}_1 \cdot \mathbf{s}_2$$



Factorizable state

$$|\psi\rangle = |\varphi_1\rangle \otimes |\varphi_2\rangle \Rightarrow \langle H\rangle = J\langle\varphi_1|\mathbf{s}_1|\varphi_1\rangle \cdot \langle\varphi_2|\mathbf{s}_2|\varphi_2\rangle \geq -Js^2$$

M.R. Dowling, A. C. Doherty and S. D. Bartlett, Phys. Rev. A 70, 062113 (2004).
G. Toth, Phys. Rev. A 71, 010301 (2005).
C. Brukner and V. Vedral , arXiv quant-ph:0406040 (2004).

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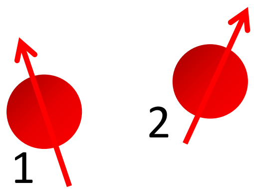

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$$\langle H \rangle < -Js^2 \quad \Rightarrow \text{ spin-pair entanglement}$$

Singlet

$$|\psi\rangle_S \qquad \Rightarrow \langle H \rangle = -Js^2 - Js$$

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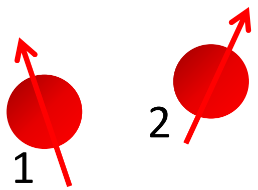

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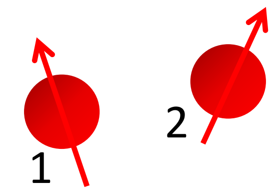

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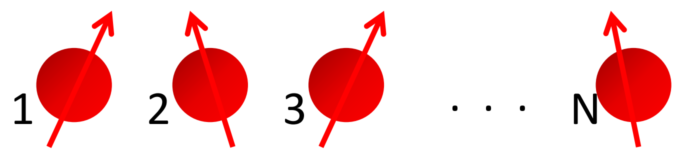

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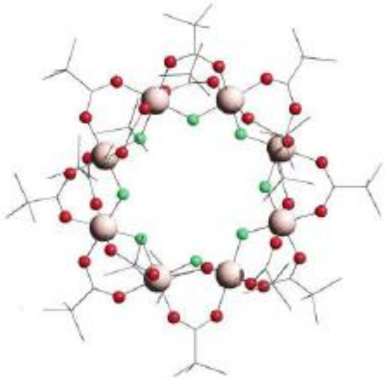
G. Toth, Phys. Rev. A 71, 010301 (2005).
C. Brukner and V. Vedral , arXiv quant-ph:0406040 (2004).

Spin pair entanglement modulation

I. Siloi and F. Troiani, Phys. Rev. B 86,224404 (2012)
G. Lorusso, V. Corradini, A. Ghirri, R. Biagi, U. del Pennino, I. Siloi, F. Troiani, G. Timco, R.E.P. Winpenny and M. Affronte, Phys. Rev. B 86, 184424 (2012)

Homometallic rings: Cr_8



$$H = J\sum_{i=1}^{N} \mathbf{s}_i \cdot \mathbf{s}_{i+1}$$

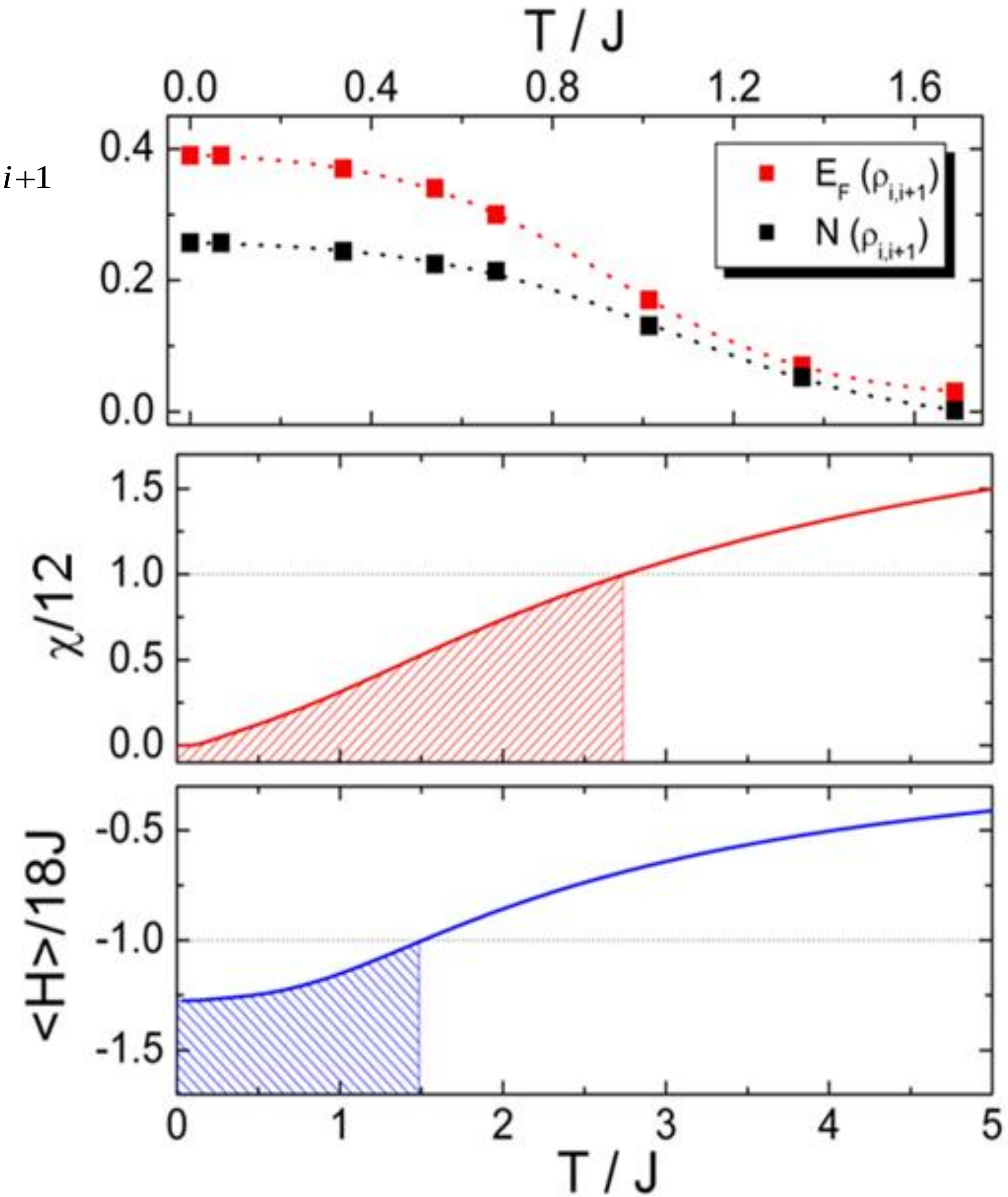
$$\Delta \approx 0.559J$$

$$J \simeq 17K$$

spin-pair entanglement @ finite temperature

$$N(\rho_{ij}) > 0, \quad T < 1.58\,J$$

$$\langle H \rangle < -18J, T < 1.51\,J$$



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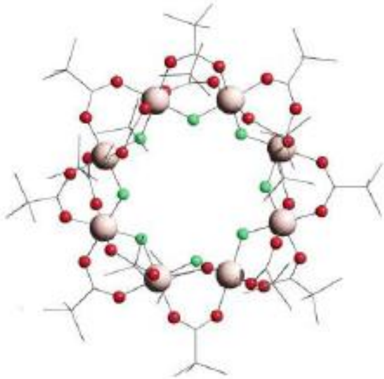

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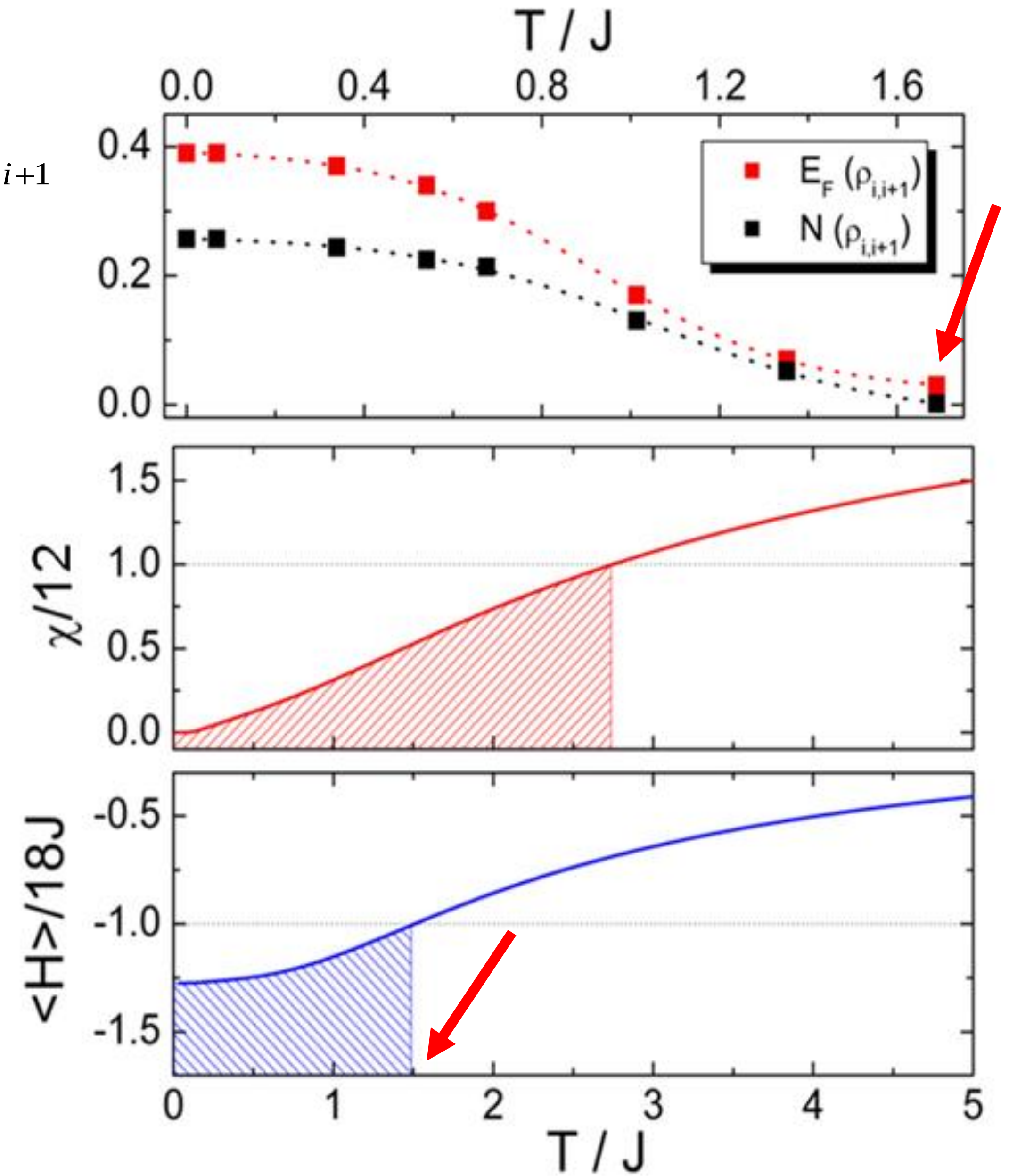

spin-pair entanglement
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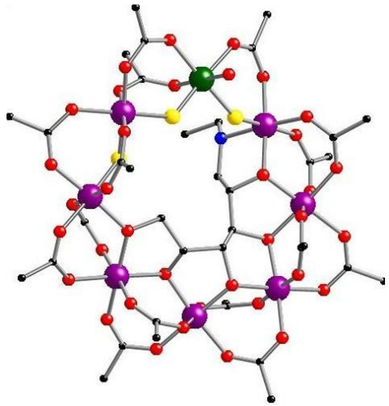
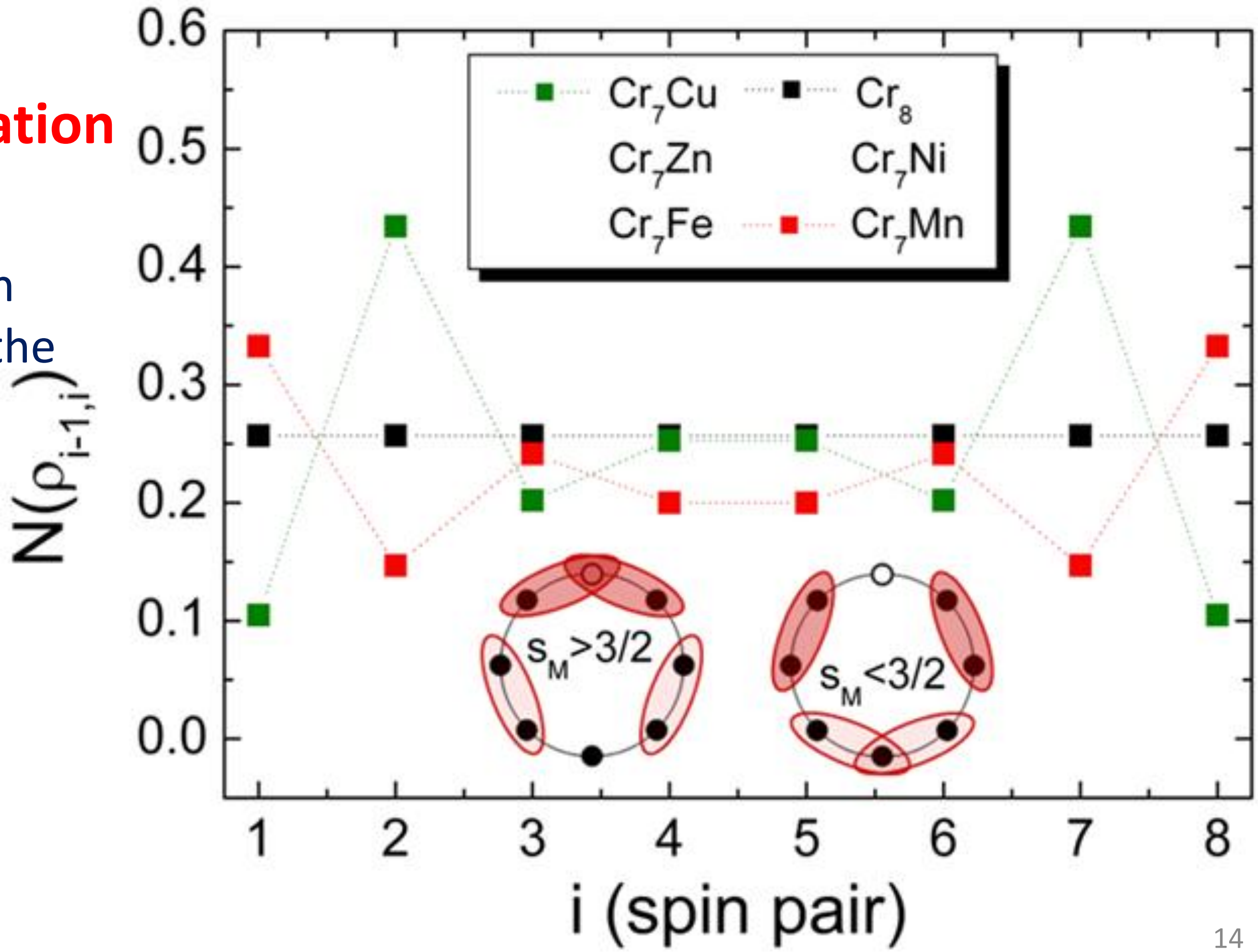
Heterometallic rings: Cr_7M



entanglement modulation @ T=0

- oscillations damped with increasing distance from the impurity
- each pair displays spin impurity dependence
- competition between neighboring pairs

	Zn	Cu	Ni	Cr	Fe	Mn
s_M	0	1/2	1	3/2	2	5/2
S	3/2	1	1/2	0	1/2	1



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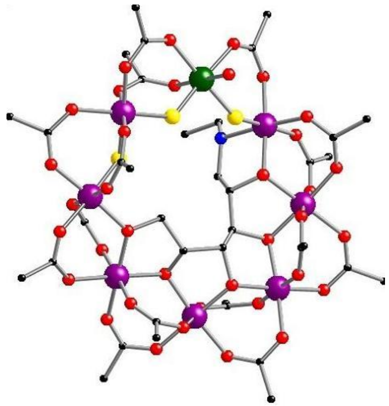

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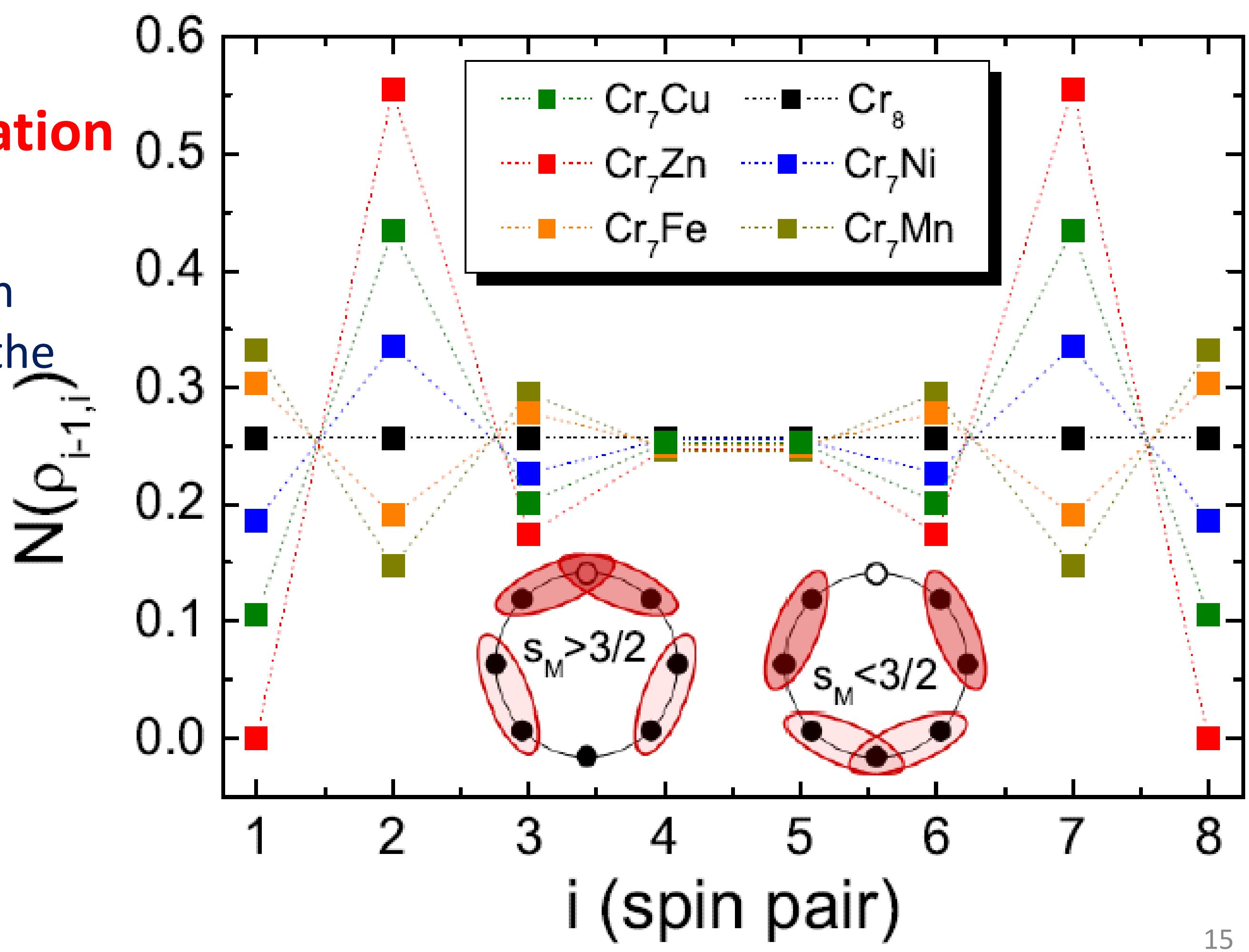
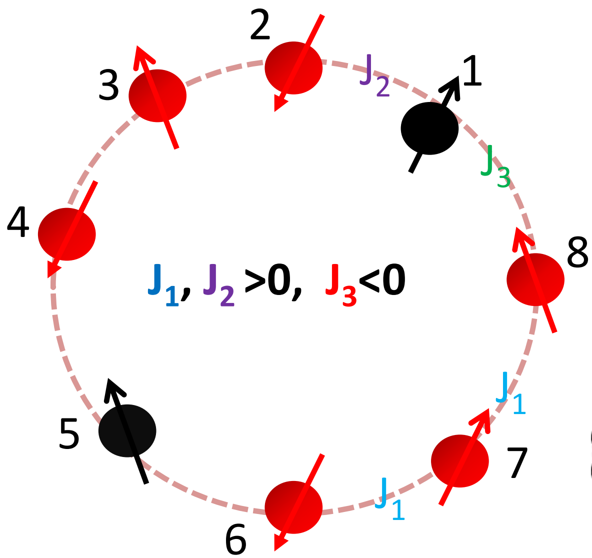
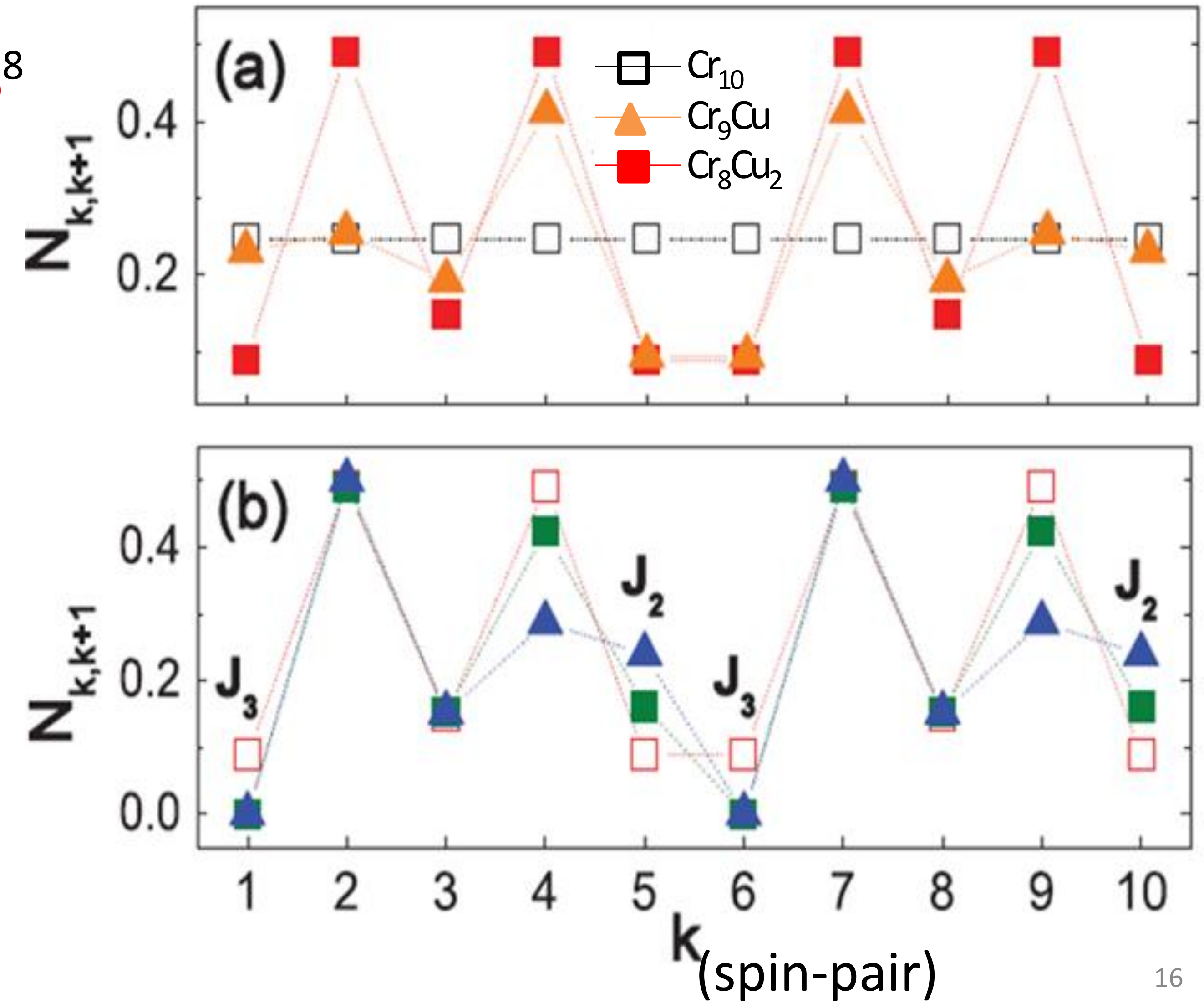


Heterometallic rings: $Cr_{2n}Cu_2$

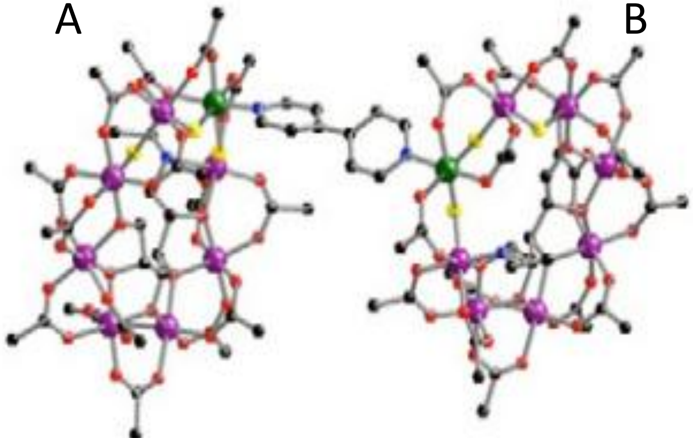


combined modulations@ T=0



- spin impurities combine modulations on spin-pair entanglement
- small antiferromagnetic coupling acts as small spin impurity

Exchanged coupled dimer

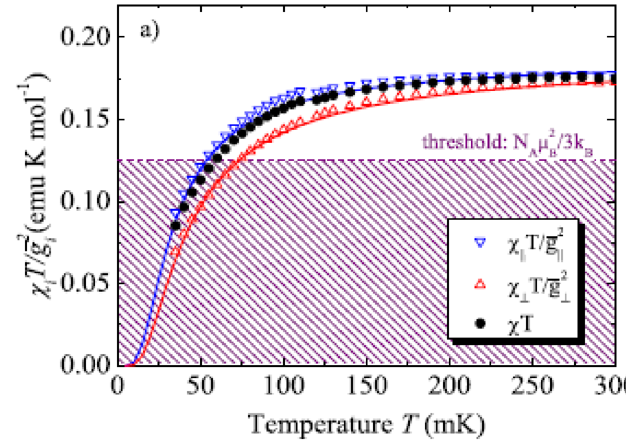


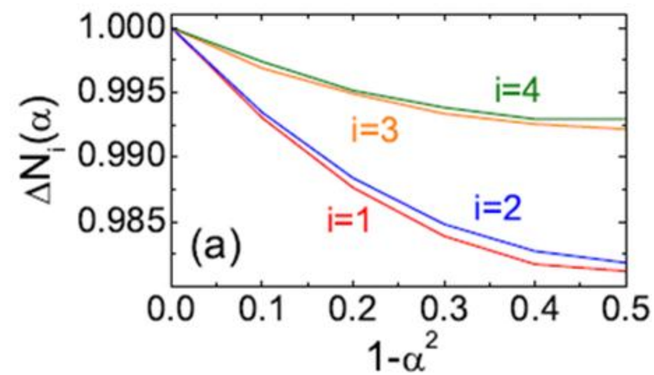
$S_A=1/2$ $S_B=1/2$

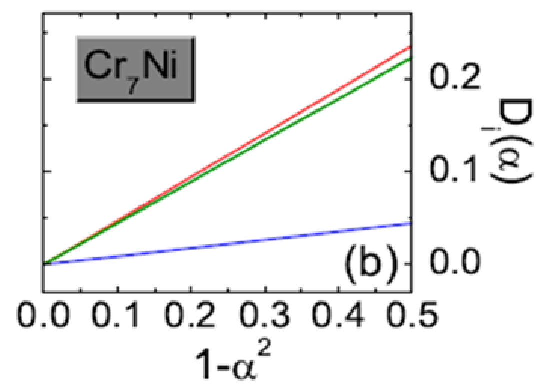
$$\left|\Psi^{Ni}_{AB}(\alpha)\right\rangle = \alpha\left|\Uparrow,\Downarrow\right\rangle - (1-\alpha^2)^{1/2}\left|\Downarrow,\Uparrow\right\rangle$$

$$\rho^{A}_{ij}(\alpha) = \alpha^2 \rho^{\Uparrow}_{ij} + (1-\alpha^2)\rho^{\Downarrow}_{ij}$$

$$N\Big(\sum_i p_i \rho_i\Big) \le \sum_i p_i N(\rho_i)$$





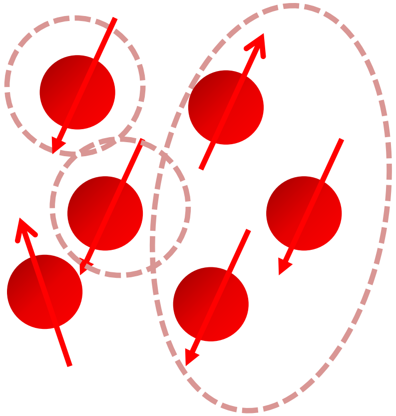


Candini et al., Phys. Rev. Lett. 104, 037203 (2010).

Multi-spin entanglement

F. Troiani and I. Siloi, Phys. Rev. A 86, 032330 (2012)
I. Siloi and F. Troiani, Eur. J. Phys. B (Special Issue JEMS2012) 86 (2), 1-6 (2013)
I. Siloi and F. Troiani, Phys. Rev. A 90, 042328 (2014)

k-spin entanglement



$$\left|\psi^k\right\rangle = \left|\varphi_{n_1}\right\rangle \otimes \left|\varphi_{n_2}\right\rangle \otimes \ldots \otimes \left|\varphi_{n_p}\right\rangle$$

$$\sum_i n_i = N \qquad \max\{n_i\} = k$$

Energy as a witness of k-spin entanglement

spin-pair entanglement

$\langle H \rangle < E_2$

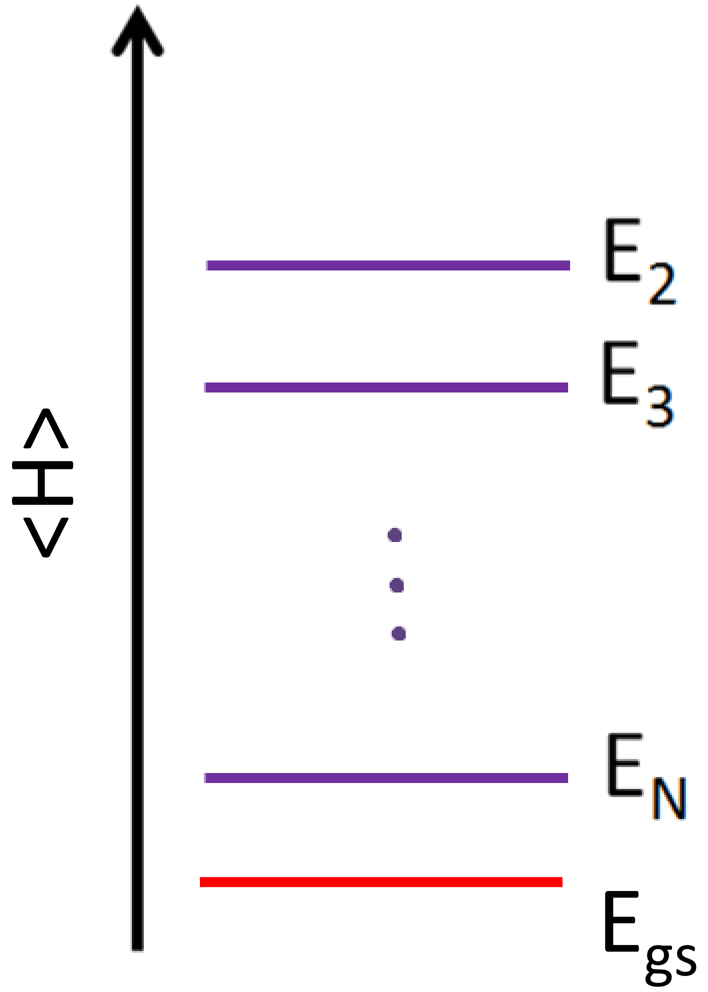
3-spin entanglement

$\langle H \rangle < E_3$

⋮

N-spin entanglement

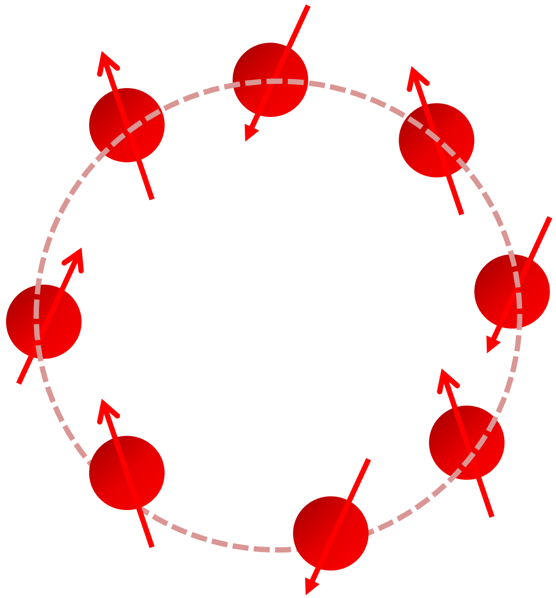
$\langle H \rangle < E_N$



O. Guhne, G. Toth and H. J. Briegel, New J. Phys. 7,229 (2005)

O. Guhne and G. Toth , Phys. Rev A 73, 052319 (2006)

Energy as a witness of k-spin entanglement



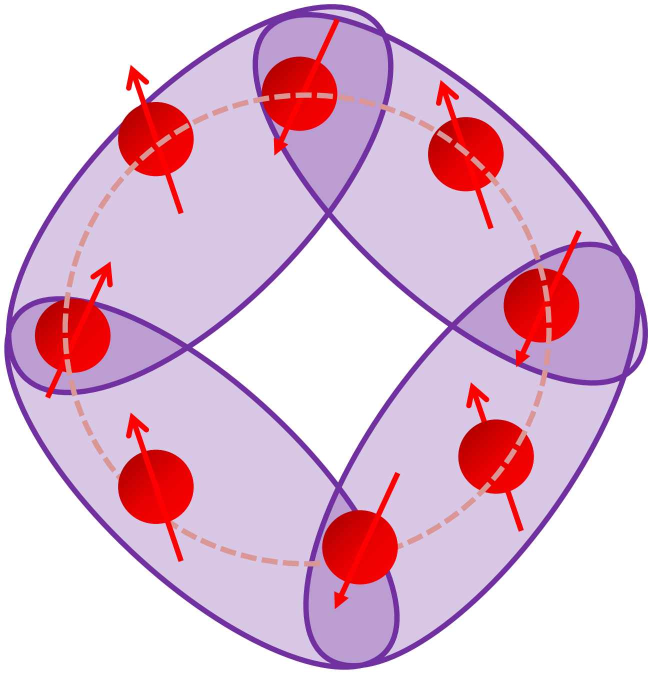
$$H = H_{123} + H_{345} + H_{567} + H_{678}$$

$$\langle H_{ijk} \rangle \geq E_3$$

fully separable or biseparable

$$\langle H \rangle > 4E_3$$

Energy as a witness of k-spin entanglement



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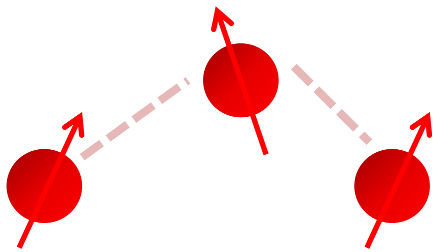
$$\langle H \rangle > 4E_3$$

3-spin entanglement

$$\langle H \rangle < 4E_3$$

Example: 3-spi n entanglement



$$H = \mathbf{s}_1 \cdot \mathbf{s}_2 + \mathbf{s}_2 \cdot \mathbf{s}_3$$

$$E^{bs} = \langle \Phi_{bs} | H | \Phi_{bs} \rangle = \langle \varphi_1 | \mathbf{s}_1 | \varphi_1 \rangle \cdot \langle \varphi_{23} | \mathbf{s}_2 | \varphi_{23} \rangle + \langle \varphi_{23} | \mathbf{s}_2 \cdot \mathbf{s}_3 | \varphi_{23} \rangle$$

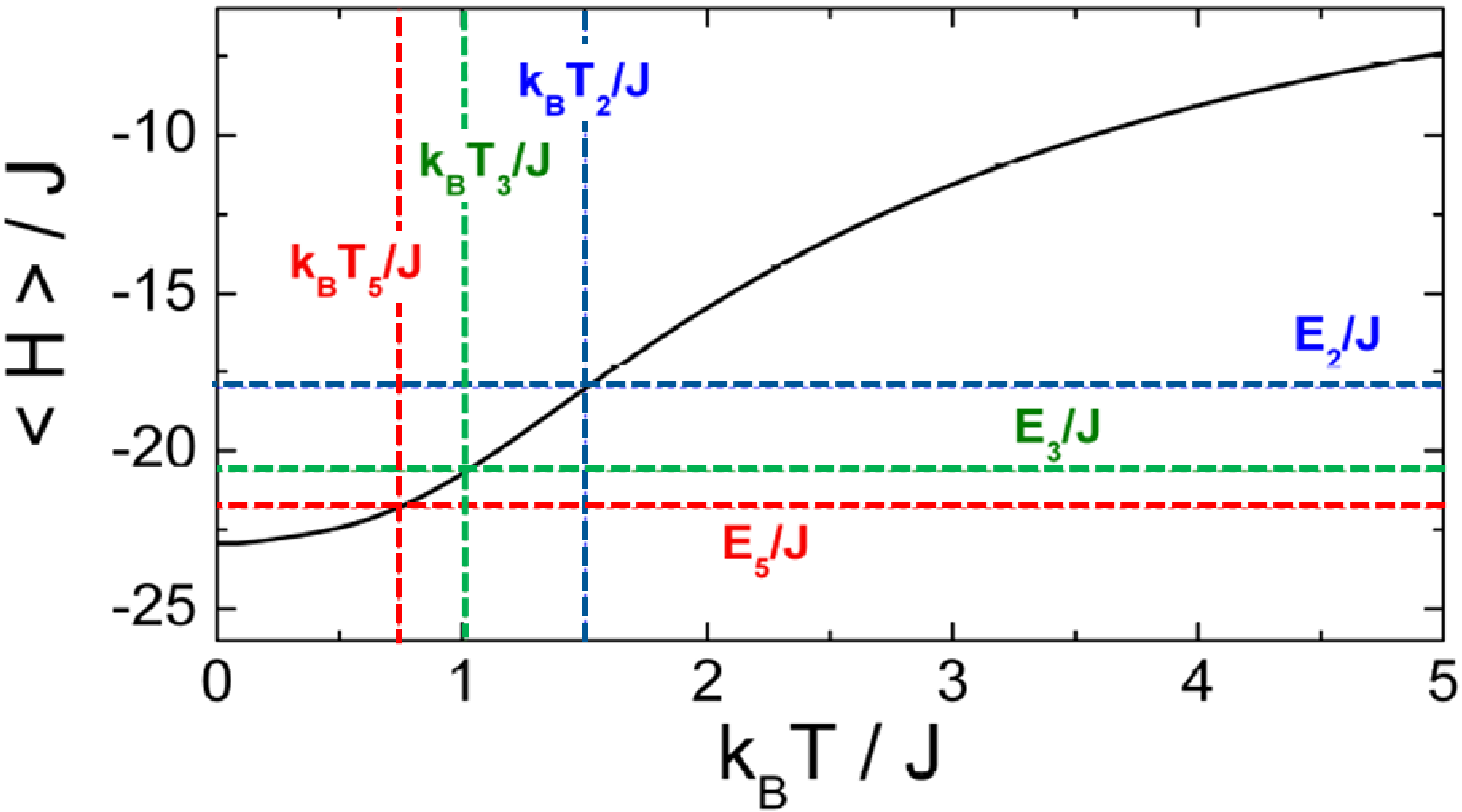
biseparable $|\Phi_{bs}\rangle = |\phi_1\rangle \otimes |\phi_{23}\rangle$

$$E^{bs} = \langle H_{eff} \rangle = \langle -s_1 s_2{}^z + \mathbf{s}_2 \cdot \mathbf{s}_3 \rangle$$

fully separable $E^{fs} = -s_2(s_1 + s_3)$

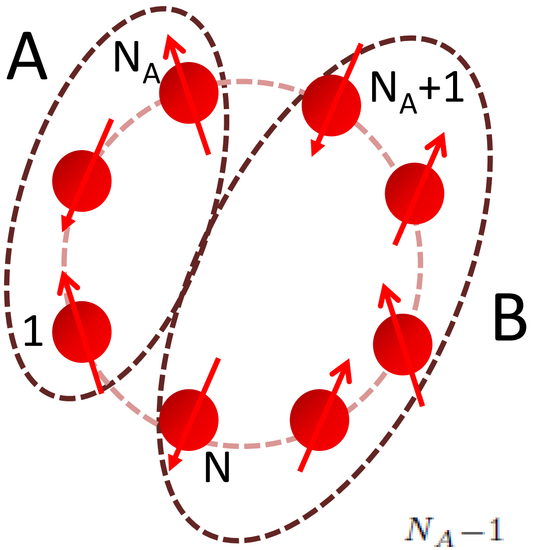
$$E < E^3 = E^{bs} = \langle -s_1 s_2{}^z + \mathbf{s}_2 \cdot \mathbf{s}_3 \rangle$$

Homometallic ring: Cr_8



- spin-pair entanglement $T<$**T_2=1.51 J**
- 3-spin entanglement $T<$**T_3=1.02 J**
- 5-spin entanglement $T<$**T_5=0.72 J**

k-spin entanglement in spin rings



$$H = J\sum_{i=1}^{N} \mathbf{s}_i \cdot \mathbf{s}_{i+1}$$

$$|\Psi_{bs}\rangle = |\Psi_A\rangle \otimes |\Psi_B\rangle$$

$$E_{bs} = \min_{N_A, N_B} E_{bs}(N_A, N_B)$$

$$H = H_A + H_B + H_{AB}$$

$$H_A = \sum_{i=1}^{N_A-1} \mathbf{s}_i \cdot \mathbf{s}_{i+1}, \; H_B = \sum_{i=N_A+1}^{N-1} \mathbf{s}_i \cdot \mathbf{s}_{i+1} \quad H_{AB} = \mathbf{s}_{N_A} \cdot \mathbf{s}_{N_A+1} + \mathbf{s}_N \cdot \mathbf{s}_1$$

$$\begin{aligned} \langle\Psi_{bs}|H|\Psi_{bs}\rangle &= \langle\Psi_A|H_A|\Psi_A\rangle + \langle\Psi_B|H_B|\Psi_B\rangle \\ &+ \langle\Psi_A|\mathbf{s}_{N_A}|\Psi_A\rangle \cdot \langle\Psi_B|\mathbf{s}_{N_A+1}|\Psi_B\rangle \\ &+ \langle\Psi_A|\mathbf{s}_1|\Psi_A\rangle \cdot \langle\Psi_B|\mathbf{s}_N|\Psi_B\rangle. \end{aligned}$$

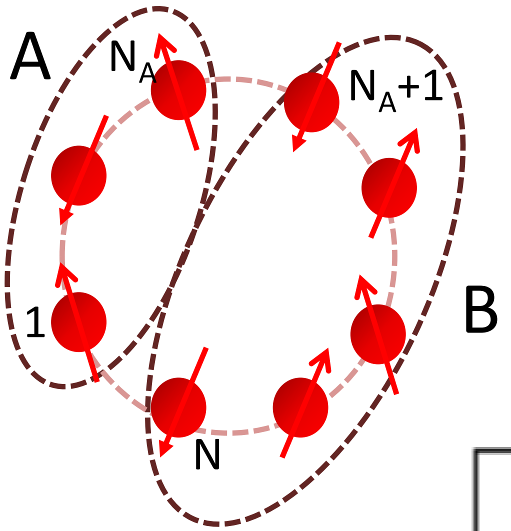
$$\tilde{H}_A(z_B, z'_B) = H_A + z_B \cdot s_{N_A} + z'_B \cdot s_1$$

$$\tilde{H}_B(z_A, z'_A) = H_B + z_A \cdot s_{N_A+1} + z'_A \cdot s_N$$

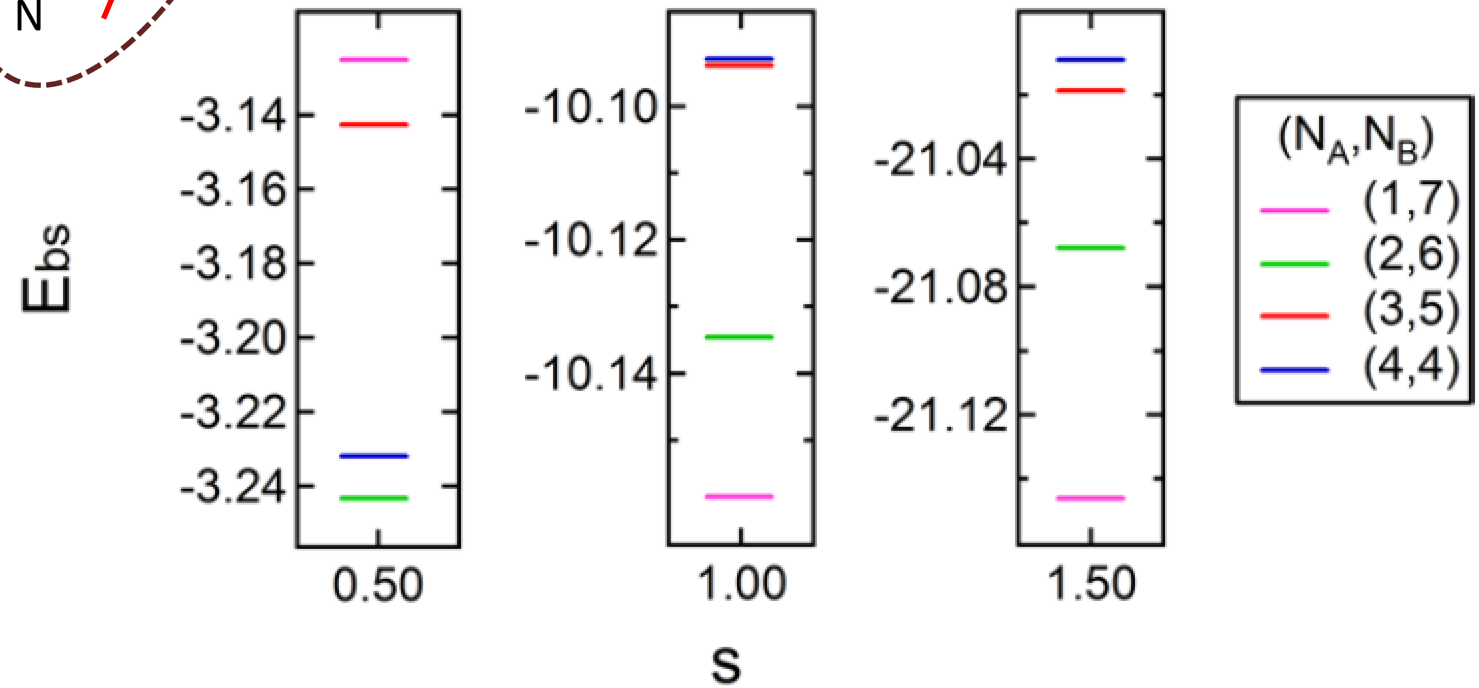
$$z_A \equiv \left\langle s_{N_A} \right\rangle \quad z'_A \equiv \left\langle s_1 \right\rangle$$

$$z_B \equiv \left\langle s_{N_{A+1}} \right\rangle \quad z'_B \equiv \left\langle s_N \right\rangle$$

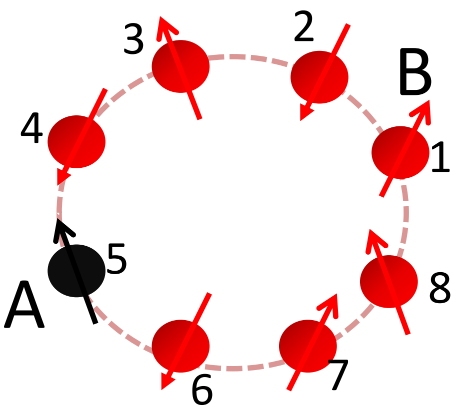
k-spin entanglement in spin rings



$$E_{bs} = \min_{N_A, N_B} E_{bs}(N_A, N_B)$$



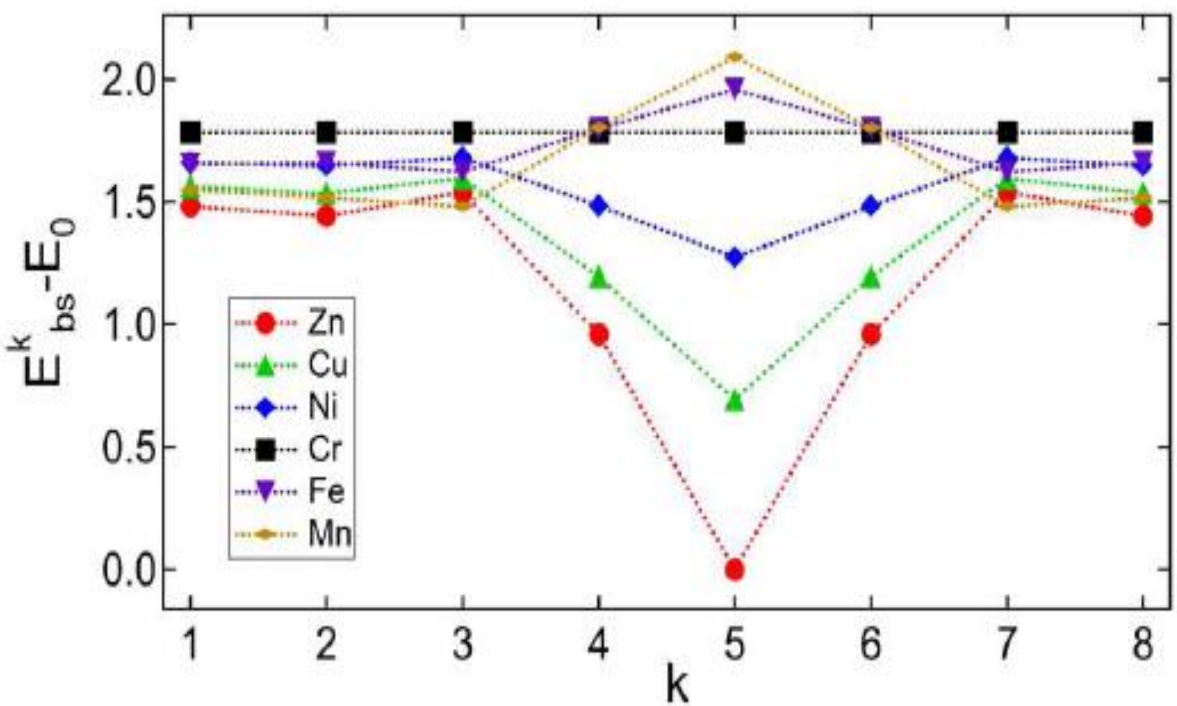
Heterometallic rings: Cr_7M

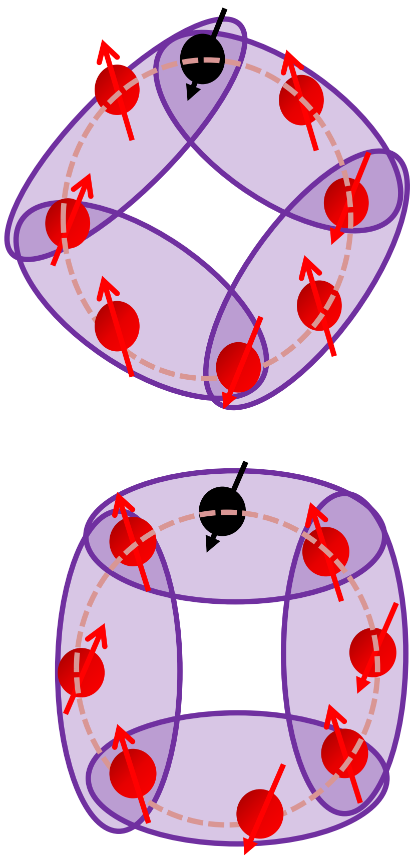


$$(N_A, N_B) = (1, 7)$$

Inequivalent ways of including the defect into the 3-spin terms

$$\tilde{H}_B(z_A = s_k) = H_B + s_k(s_{z,k-1} + s_{z,k+1})$$





Conclusions

- **chemical substitutions** induce strong **spatial modulation** of spin-pair entanglement
- **modulation** at finite temperature is detected by **spin-pair correlation function**
- **exchange** coupled **dimers**: local spins and collective spins entanglement coexist
- **exchange energy** is a witness also of **k-spin entanglement**
- **single spin separariblity criteria**: access to **local features** through global observable

Heterometallic rings: Cr_7M

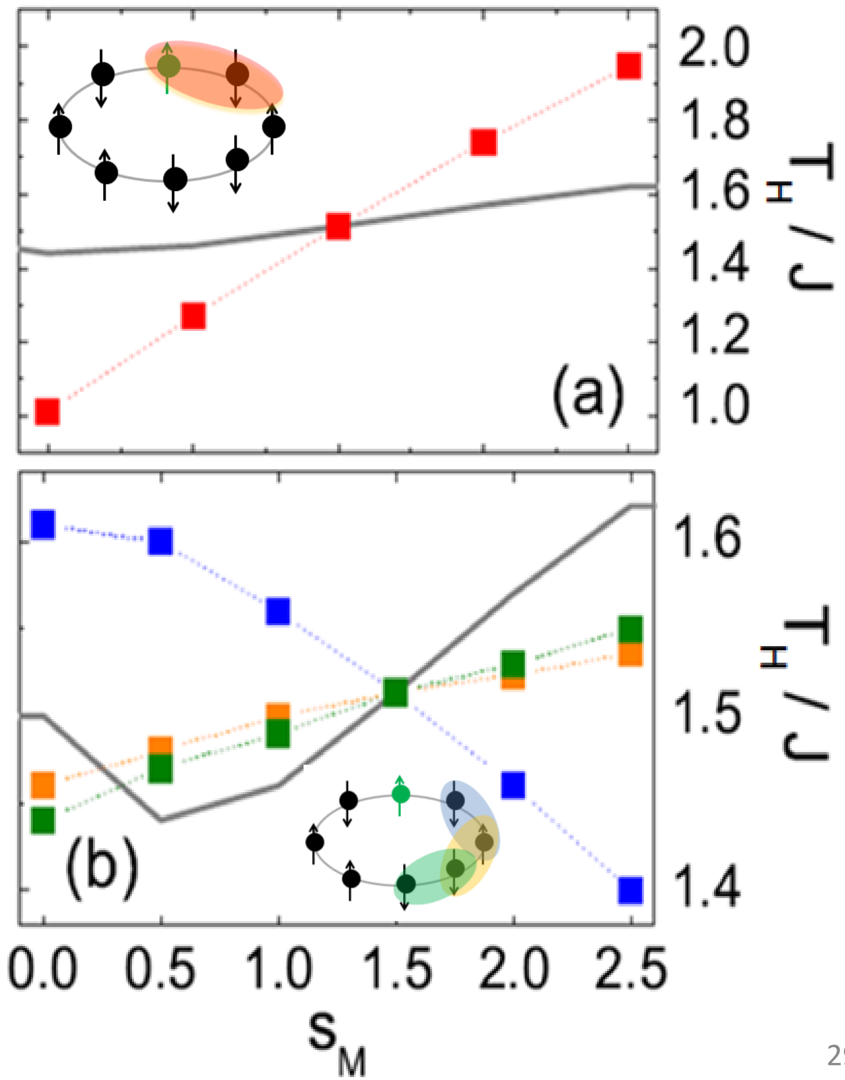
finite temperature

- spatial modulations revealed by **local witnesses**

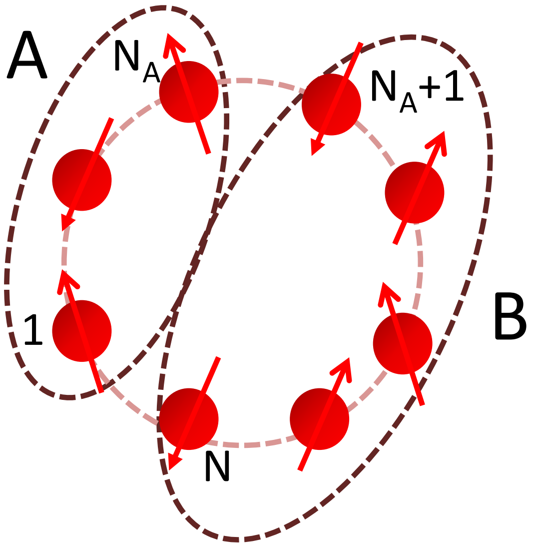
$$\langle \mathbf{s}_i \cdot \mathbf{s}_{i+1} \rangle < -s_i s_{i+1}$$

- **threshold temperatures** identified by global energy witness

$$\langle H \rangle < -(N-2) J s_{Cr}^{\;2} - 2 J s_{Cr} s_M$$



N-spin entanglement in spin rings



$$\tilde{H}_A(\mathbf{z}_B, \mathbf{z}'_B) = H_A + \mathbf{z}_B \cdot \mathbf{s}_{N_A} + \mathbf{z}'_B \cdot \mathbf{s}_1$$

$$\tilde{H}_B(\mathbf{z}_A, \mathbf{z}'_A) = H_B + \mathbf{z}_A \cdot \mathbf{s}_{N_A+1} + \mathbf{z}'_A \cdot \mathbf{s}_N$$

$$\mathbf{z}_A \equiv \langle \mathbf{s}_{N_A} \rangle \qquad \mathbf{z}'_A \equiv \langle \mathbf{s}_1 \rangle$$

$$\mathbf{z}_B \equiv \langle \mathbf{s}_{N_A+1} \rangle \qquad \mathbf{z}'_B \equiv \langle \mathbf{s}_N \rangle$$

$$\mathbf{z}'_A = \eta \mathbf{z}_A, \ \ \mathbf{z}'_B = \eta \mathbf{z}_B \quad (\eta = \pm 1)$$

$$\cos\theta_\alpha \equiv \frac{\mathbf{z}_\alpha \cdot \mathbf{z}'_\alpha}{|\mathbf{z}_\alpha||\mathbf{z}'_\alpha|} \neq (-1)^{N_\alpha+1} \qquad Z_\alpha \equiv ||\mathbf{z}_\alpha| - |\mathbf{z}'_\alpha|| > 0,$$

$$(\mathbf{z}_B, \mathbf{z}'_B) \xrightarrow{\tilde{H}_A} (\bar{\mathbf{z}}_A, \bar{\mathbf{z}}'_A) \xrightarrow{\tilde{H}_B} (\bar{\bar{\mathbf{z}}}_B, \bar{\bar{\mathbf{z}}}'_B)$$