

# **Magnetism in Conjugated Polymers**

**S. Ramasesha**

**ramasesh@sscu.iisc.ernet.in**

**Solid State and Structural Chemistry Unit**

**Indian Institute of Science**

**Bengaluru 560012**

**Frustrated Magnetism – Jawaharlal Nehru University**

**February 09-13, 2015**

# **Plan of the talk**

**1. Models for Organic Magnetism**

**2. Model Hamiltonian for Conjugated Carbon Systems**

**3. Density Matrix Renormalization Group (DMRG) Method**

**4. Determining Spin of the ground state**

**5. Results for fused ring systems**

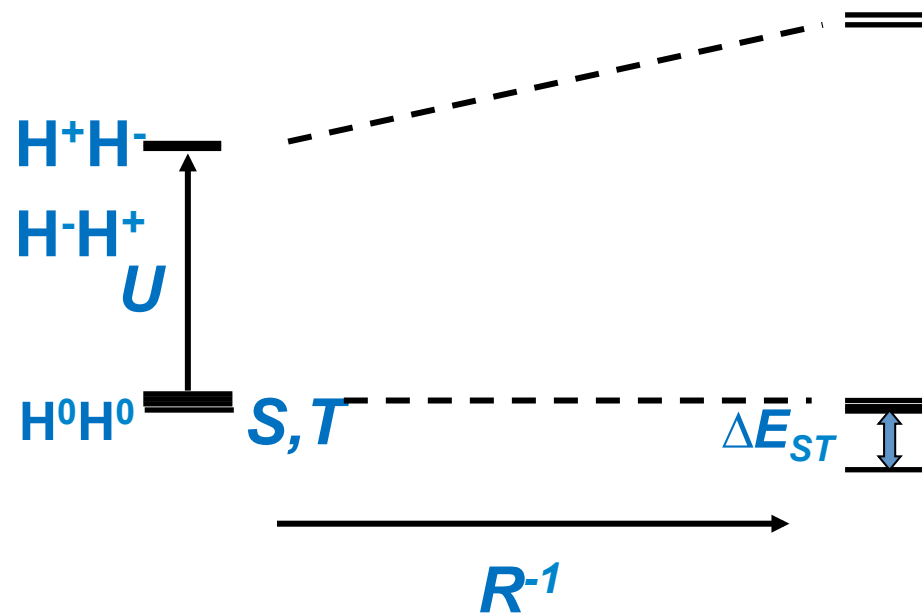
## Why is Molecular Magnetism a Challenge

- ✓ Hund's rule weakly obeyed due to spread of MOs.
- ✓ Degenerate MOs not usually found in molecules.
- ✓ Unpaired spins make molecules very reactive.
- ✓ Three theoretical models suggest ways of designing molecular magnets.

Two are due to McConnell.

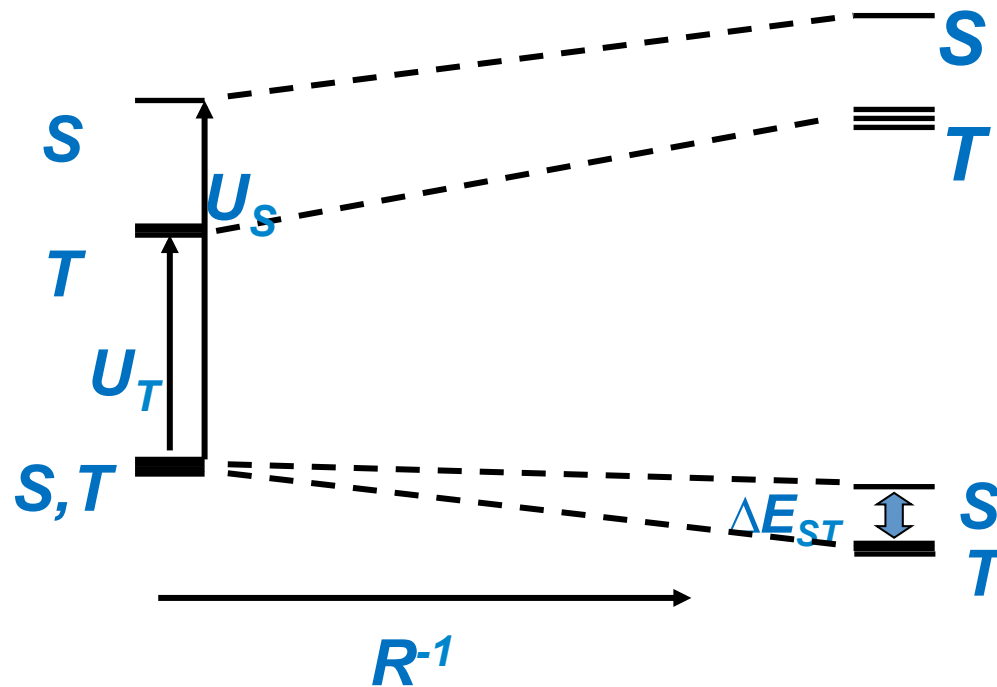
Third due to Mataga and Ovchinnikov.

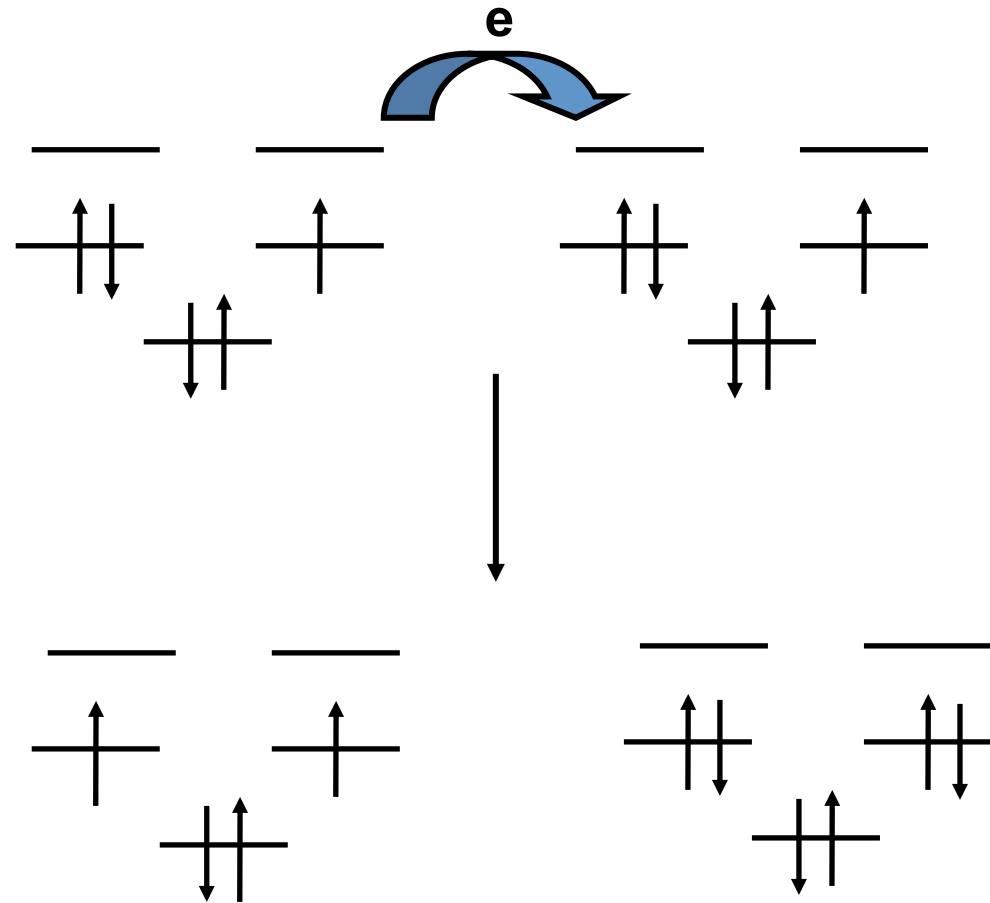
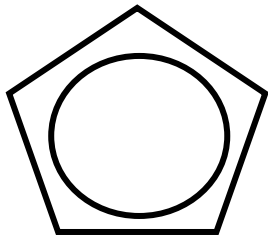
# McConnel Mechanism



# Anderson Kinetic Exchange

# McConnel Mechanism (1967)

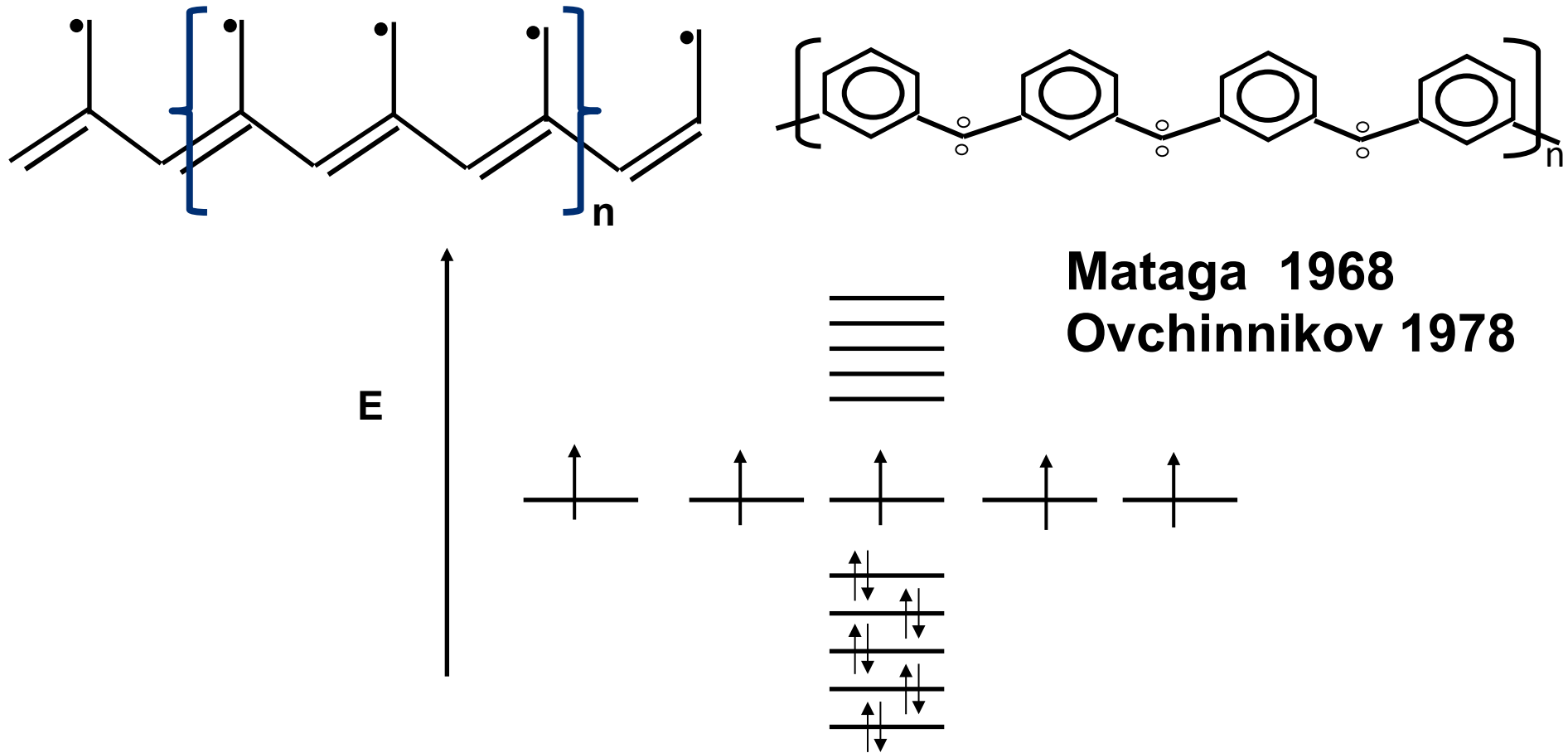




**Does not work as (i) phase space for singlet delocalization is bigger and (ii) in the crystal molecular degeneracy lifted.**

**B. Sinha and S. R, Phys. Rev. B 48, 16410 (1993).**

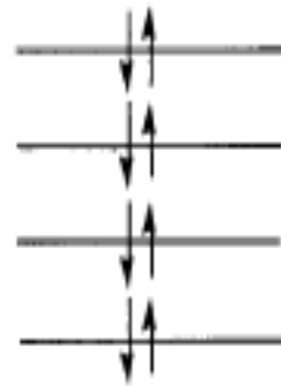
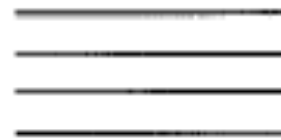
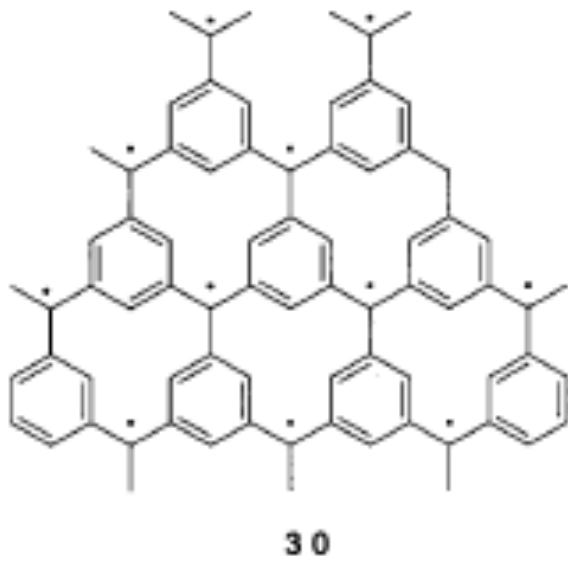
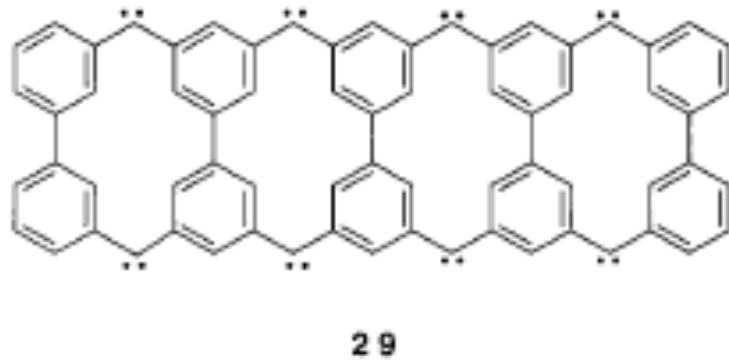
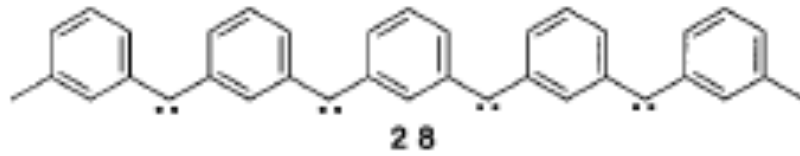
# Mataga Ovchinnikov Models



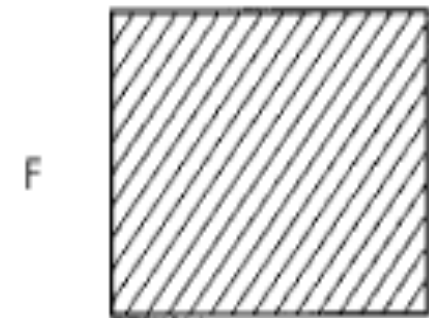
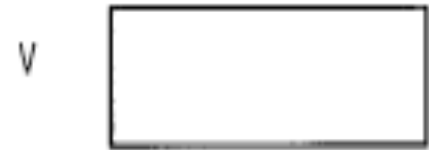
The high spin ground state is not stable to Peierls' type of distortions.

S. R, B. Sinha and I.D.L. Albert, Phys. Rev. B 42, 9088 (1990).

# Mataga Polymers (1968)



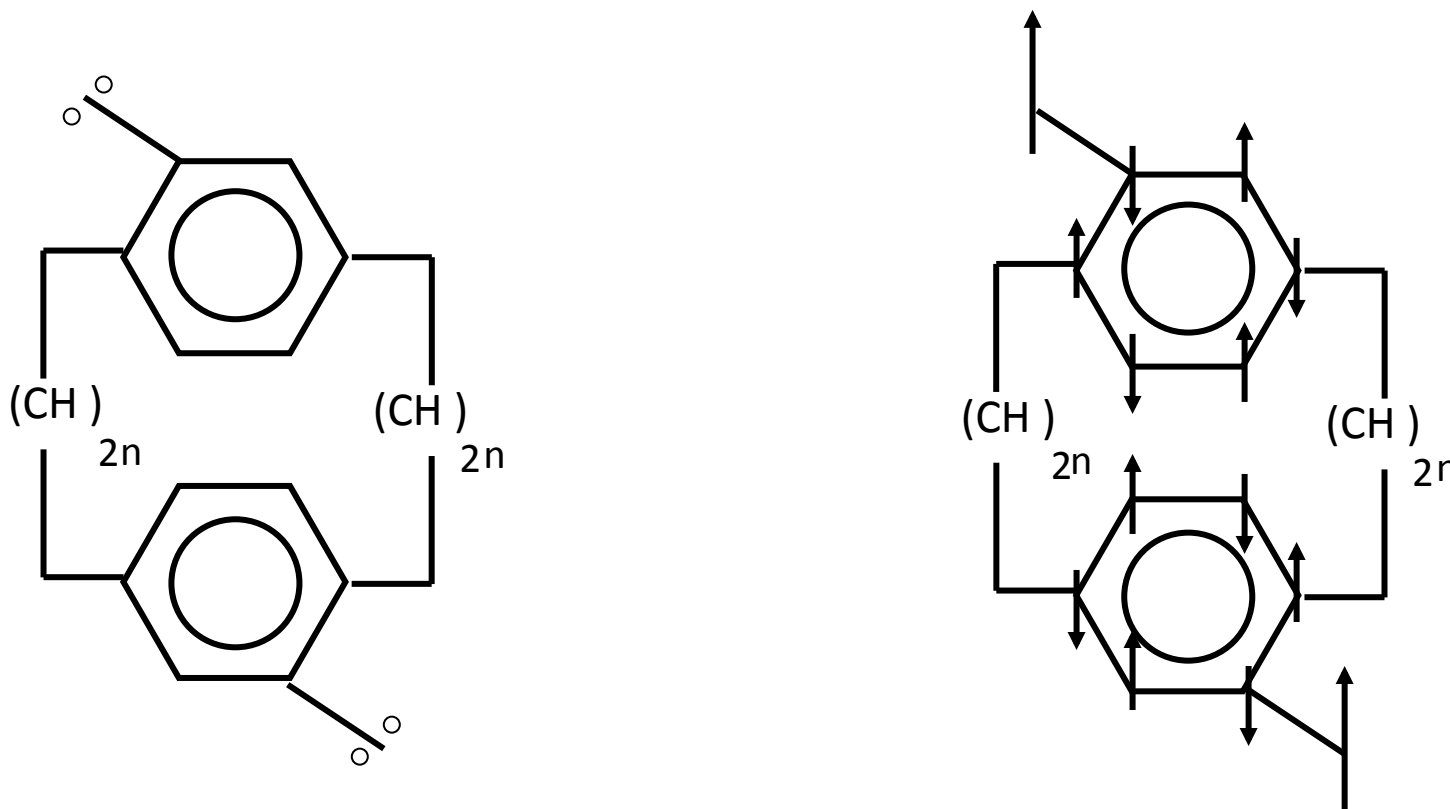
(a)



(b)

## McConnell's second mechanism (1963)

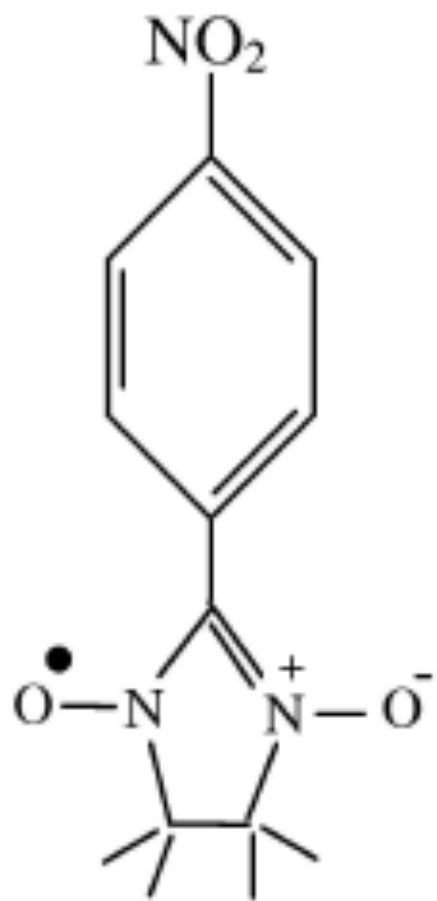
In a molecule with two radicals, if opposite spin densities are aligned on top of each other, the radical spins will have parallel alignment.



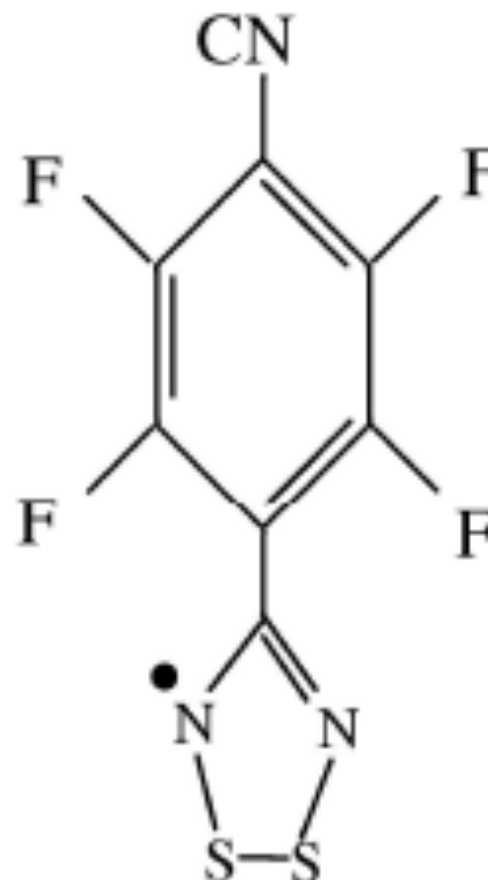
Bhabadyuti Sinha and S. R, Chem. Phys. Lett., 182, 180 (1991).



## Magnetism observed in $\gamma$ -para nitropheny nitronyl nitroxide ( $\gamma$ -NPNN) in 1991



$\gamma$ -NPNN  $T_c = 0.65\text{K}$



p-NC(C<sub>6</sub>F<sub>4</sub>)(CNSSN)  $T_c = 35.5\text{K}$

# Frustrated Systems

**Is it possible to use frustration in organic systems to obtain high spin ground state?**

**It is known in molecular magnetism that frustration leads to intermediate spin ground state eg  $\text{Mn}_{12}\text{Ac}$  And  $\text{Fe}_8$  high nuclearity complexes.**

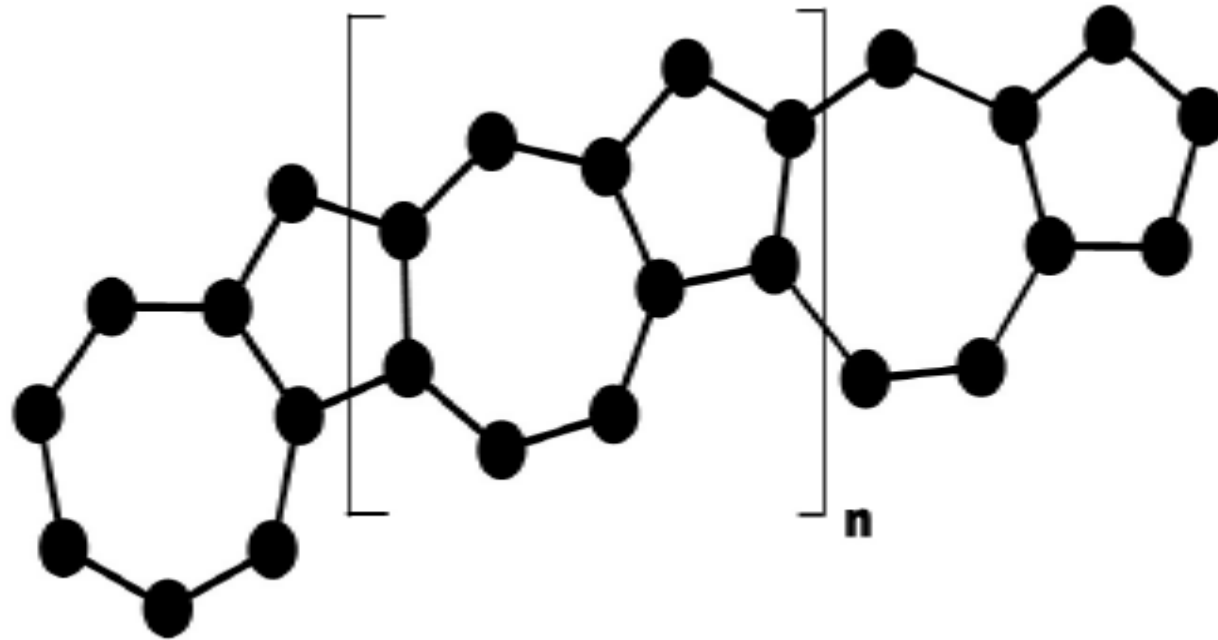
**It is also known that frustration leads to lower spin gaps.**

**Can we use the same principle in organic systems?**

**Is it possible to build systems with large frustration leading to high spin ground state?**

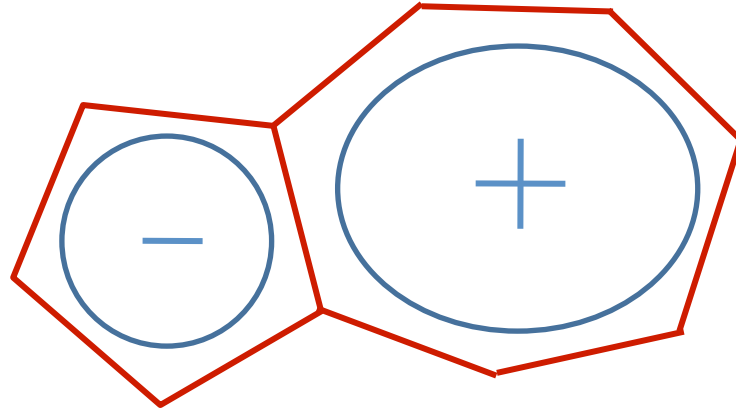
If we introduce geometric frustration in the rings, then spin gaps are expected to decrease.

Question: Can we lower the spin gap further if we fuse five and seven members alternately?



The primary unit in such a systems is azulene which consists of fused seven and five membered rings

## Properties of Azulene in Hückel or Noninteracting Model



This system will have a dipole moment as the Hückel  $4n+2$  rule for aromatic stability favors a positive charge on the seven membered ring and a negative charge on the five membered ring.

Question: Can we simultaneously have a large dipole moment and a high spin ground state in larger systems?

# Modeling Conjugated Carbon Systems

## Interacting One-Band Models

- One-band tight binding model

$$H_o = \sum_{\langle ij \rangle} t_{ij} (a_{i\sigma}^\dagger a_{j\sigma} + H.c.) + \sum_i \alpha_i n_i$$

- Explicit electron – electron interactions essential for realistic modeling

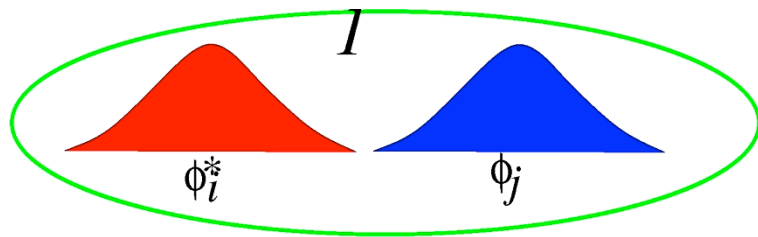
$$H_{Full} = H_o + \frac{1}{2} \sum_{ijkl} [ij|kl] (E_{ij}E_{kl} - \delta_{jk}E_{il})$$

$$E_{ij} = \sum_{\sigma} a_{i,\sigma}^\dagger a_{j,\sigma}$$

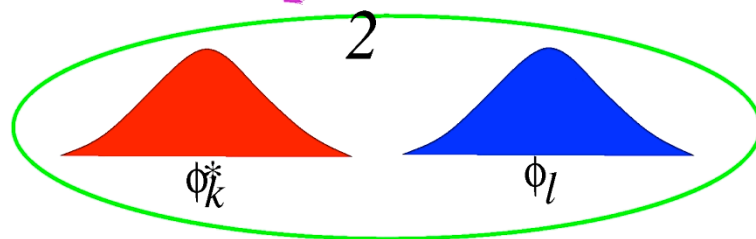
$$[ij|kl] = \int \phi_i^*(1) \phi_j(1) (e^2/r_{12}) \phi_k^*(2) \phi_l(2) d^3r_1 d^3r_2$$

This model requires further simplification to enable routine solvability.

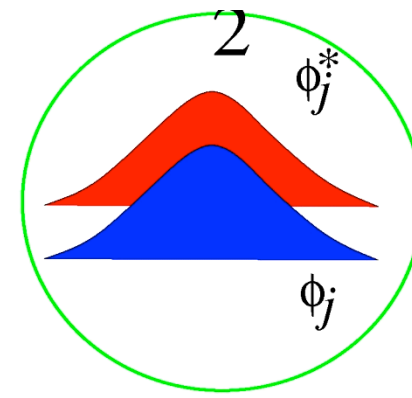
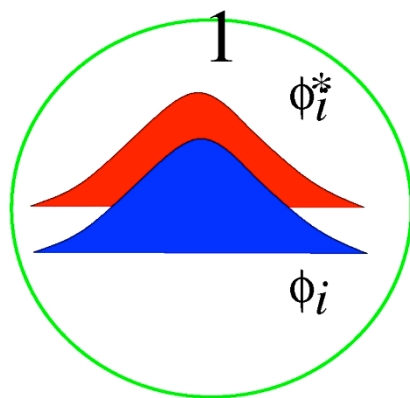
# Zero Differential Overlap (ZDO) Approximation



$$[ij|kl] = \int \phi_i^*(1) \phi_j(1) (e^2/r_{12}) \phi_k^*(2) \phi_l(2) d^3r_1 d^3r_2$$



$$[ij|kl] = [ij|kl] \delta_{ij} \delta_{kl}$$



# Hubbard Model (1964)

- Hückel model + on-site repulsions

$$[ii|jj] = 0 \text{ for } i \neq j;$$

$$[ii|jj] = U_i \text{ for } i=j$$

$$\hat{H}_{Hub} = H_o^{\wedge} + \sum_i U_i n_i (\hat{n}_i - 1)/2$$

- In large  $U/t$  limit, Hubbard model gives antiferromagnetic Heisenberg Spin-1/2 model

$$\hat{H} = \sum_i J (\hat{S}_i \cdot \hat{S}_{i+1} - 1/4)$$
$$J = 2z t^2 / U$$

# Pariser-Parr-Pople (PPP) Model (1953)

$[ii|jj]$  parametrized by  $V(r_{ij})$

$$H_{PPP} = H_{Hub} + \sum_{i>j} V(r_{ij}) (n_i - z_i) (n_j - z_j)$$

$z_i$  are local chemical potentials.

➤ Ohno parametrization:

$$V(r_{ij}) = \{ [ 2 / ( U_i + U_j ) ]^2 + r_{ij}^2 \}^{-1/2}$$

➤ Mataga-Nishimoto parametrization:

$$V(r_{ij}) = \{ [ 2 / ( U_i + U_j ) ] + r_{ij} \}^{-1}$$



**The Hamiltonian for N carbon atoms spans a Fock space of dimensionality  $4^N$ .**

**Routine Exact Diagonalization of the Hamiltonian matrix is viable for  $N \leq 18$  sites (# of triplets for 18 sites and 18 electrons is 901,931,939).**

**For larger systems, one needs approximate methods.**

**For quasi-one-dimensional models, most accurate method is the density matrix renormalization group (DMRG) method.**

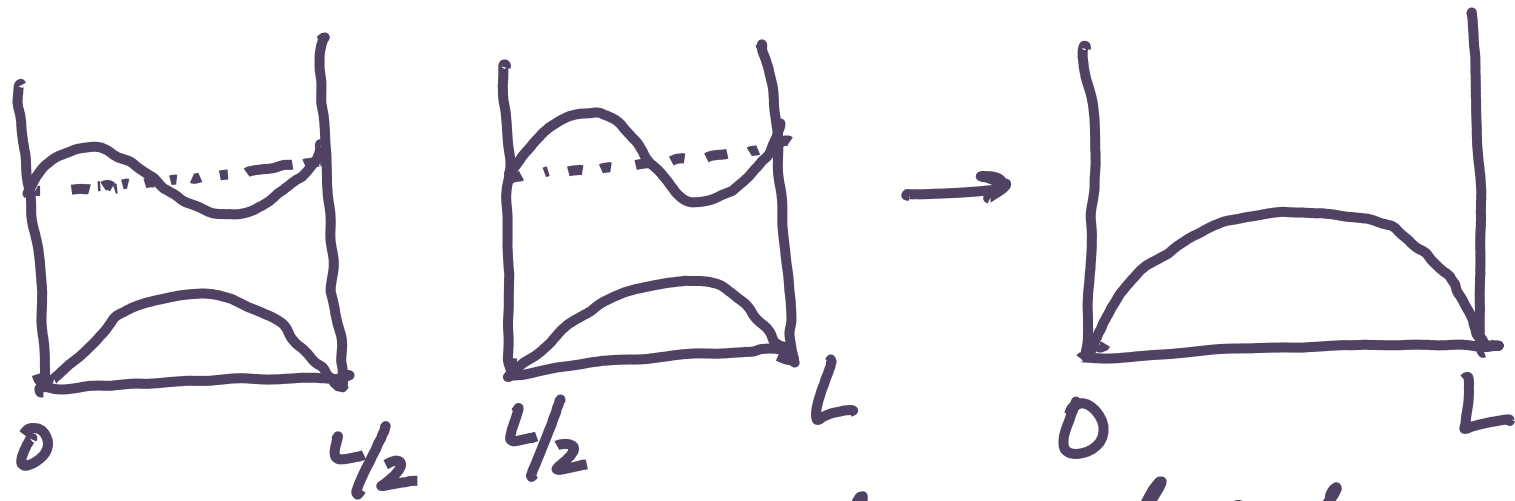
**We have shown that the method is highly accurate for PPP models, even though it is a long-range Interacting model.**

# Approximate Methods

- Restricted CI methods
- Coupled Cluster methods
- Quantum Monte Carlo methods
- Renormalization Group Methods
  - Energy eigenvalue based methods
  - Density matrix eigenvalue based methods.

# Renormalization Group Method

Construct the Hilbert space of the augmented system using direct product of the Fock spaces of the subsystems.



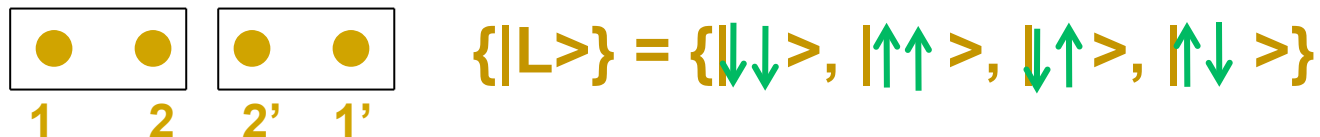
Using energy based truncation always gives a state with a node in the augmented system.

## Density matrix based methods.

- Natural orbital basis: eigenfunctions of one particle density matrix with large densities (density matrix eigenvalues) were used as orbitals for CI calculations.
- DMRG uses eigenstates of many-body density matrices to span the Fock space of the many-particle subsystem. Besides it also uses a renormalization procedure to extend the system size.

# Implementation of DMRG Method

- Diagonalize a small system of say 4 sites with two on the left and two on the right



$$H = S_1 \cdot S_2 + S_2 \cdot S_{2'} + S_{2'} \cdot S_{1'} \quad |\psi_G\rangle = \sum_L \sum_R C_{LR} |L\rangle |R\rangle$$

The summations run over the Fock space dimension  $L$

- Renormalization procedure for left block

Construct density matrix  $\rho_{L,L'} = \sum_R C_{LR} C_{L'R}$

\* Diagonalize density matrix  $\rho |\mu_\lambda\rangle = \mu_\lambda |\mu_\lambda\rangle,$

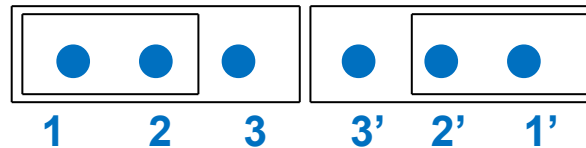
Construct renormalization matrix

$$O_L = [\mu_1 \mu_2 \cdots \mu_m] \text{ is } L \times m; m < L$$

- Repeat this for the right block

\*  $\rho$  is block diagonal in number and  $M_s$  sectors.

- $\tilde{H}_L = O_L H_L O_L^\dagger$  ;  $H_L$  is the unrenormalized  $L \times L$  left-block Hamiltonian matrix, and  $\tilde{H}_L$  is renormalized  $m \times m$  left-block Hamiltonian matrix.
- Similarly, necessary matrices of site operator of left block are renormalized.
- The process is repeated for right-block operators with  $O_R$
- The system is augmented by adding two new sites



- The Hamiltonian of the augmented system is given by

- **Hamiltonian matrix elements in fixed DMEV Fock space basis**
- **Obtain desired eigenstate of augmented system**
- **New left and right density matrices of the new eigenstate**
- **New renormalized left and right block matrices**
- **Add two new sites and continue iteration**

## Calculation of Properties

From the DMRG eigenstate, we may want to compute quantities such as site spin and charge densities,

$\langle S_i^z \rangle$  and  $\langle n_i^z \rangle$ . Since we have a matrix representation of these operators

$$\langle S_i^z \rangle = \sum_{\mu, \sigma, \sigma', \mu'} \sum_{\nu} (S_i^z)_{\mu\nu} C_{\mu\sigma'\mu'} C_{\nu\sigma\sigma'}$$

and similarly the site charge densities.



Calculating expectation values of product of site operators on two different sides of the chain is also straightforward

$$\langle S_i^z S_j^z \rangle = \sum_{\mu\sigma\sigma'\mu'} \sum_{\nu\nu'} (S_i^z)_{\mu\nu} (S_i^z)_{\mu'\nu'}$$

$\times C_{\mu\sigma\sigma'\mu'} C_{\nu\sigma\sigma'\nu'}$ ; assuming

normalized eigenstates.

This is not accurate for two site operators on the same side of the chain

In cases where we need to evaluate expectation values such as  $\langle \delta_i^z \delta_j^z \rangle$ , both  $i$  and  $j$  on the same side of the chain, we compute the matrix representation of the product operator on its first occurrence and renormalize the product from there on and we get

$$\langle \delta_i^z \delta_j^z \rangle = \sum_{\mu\sigma\sigma'\mu'} \langle \delta_i^z \delta_j^z \rangle_{\mu\sigma} C_{\mu\sigma\sigma'\mu'} C_{\sigma\sigma'\mu'}$$

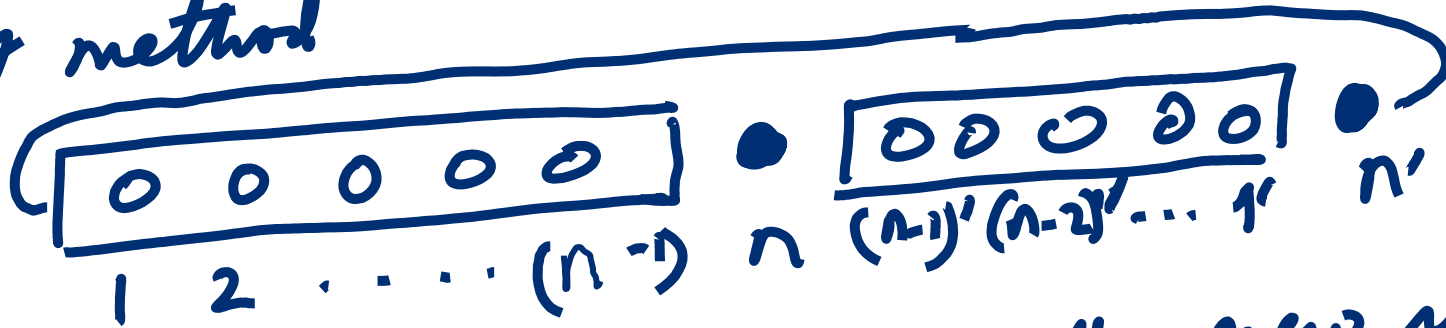
## Targeting excited states

If we need an excited state say the first excited state  $|\Psi_1\rangle$ , we can target it by constructing the density matrix from  $|\Psi_1\rangle$  at each step and using their eigenvectors to span the Fock space of the system.

To simultaneously target say  $|\Psi_0\rangle, |\Psi_1\rangle, \dots, |\Psi_p\rangle$ , we can use an average density matrix  $P_{av} = \sum_{i=0}^p w_i \rho_i$ . This is useful for comparable accuracy of all the states.

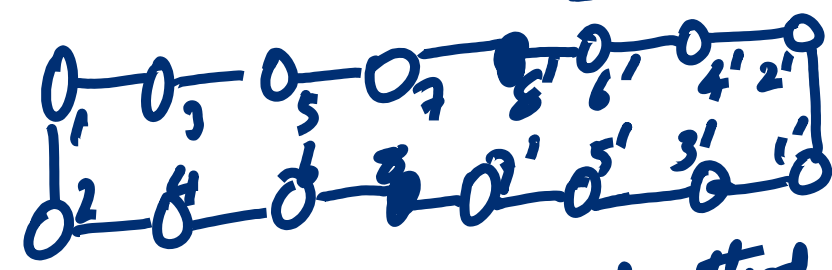
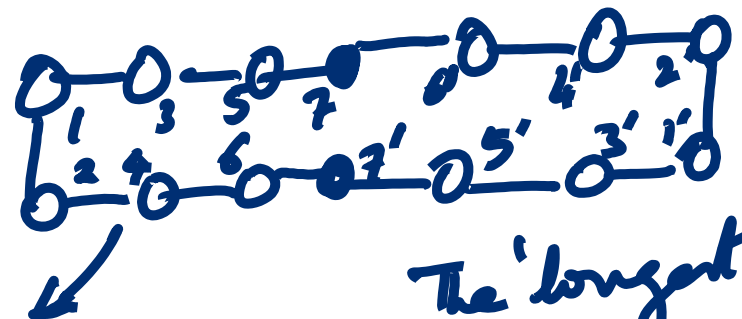
# Implementing Cyclic Boundary Conditions

Early method



cbc involves bonds between the new sites  $n$  ( $n'$ ) and the first site  $1$  ( $1'$ ). These are terribly inaccurate.

Present method:



The 'longest bond' is only two sites removed and the method is very accurate.

# Finite system DMRG

If the goal is a system of  $2N$  sites, density matrices employed enroute were those of smaller systems.

The DMRG space constructed would not be the best

This can be remedied by resorting to finite DMRG technique

After reaching final system size, sweep through the system like a zipper

While sweeping in any direction (left/right), increase corresponding block length by 1-site, and reduce the other block length by 1-site

$$(0) P_L^{N/2-1}$$

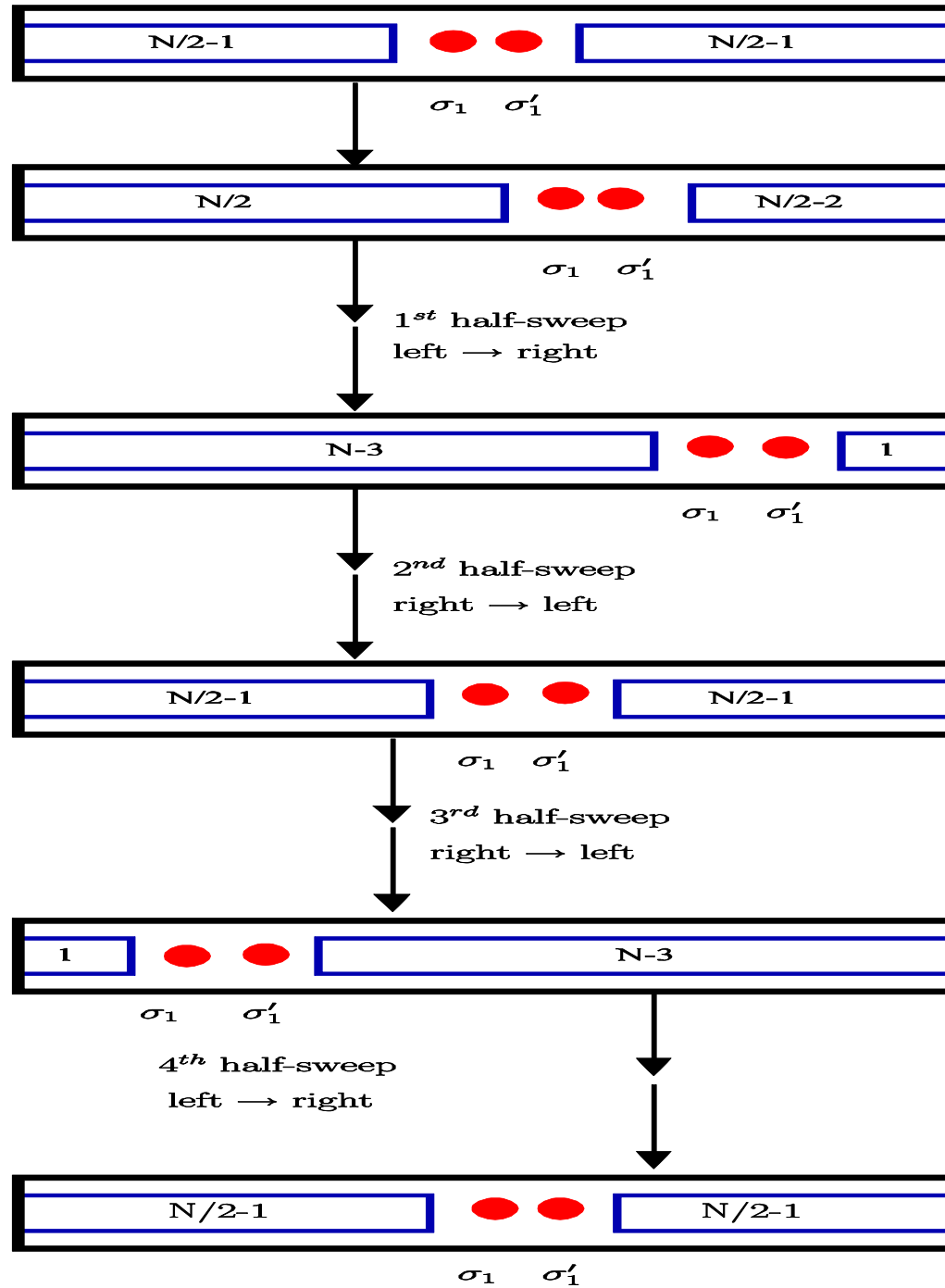
$$(1) P_L^{N/2}$$

$$(2) P_L^{N-3}$$

$$(3) P_L^{N/2-1}$$

$$(4) P_L^1$$

$$(5) P_L^{N/2-1}$$



$$(0) P_R^{N/2-1}$$

$$(1) P_R^{N/2-2}$$

$$(2) P_R^1$$

$$(3) P_R^{N/2-1}$$

$$(4) P_R^{N-3}$$

$$(5) P_R^{N/2-1}$$

# The DMRG Technique - Summary

- **DMRG method involves iteratively building a large system starting from a small system.**
- **The eigenstate of superblock consisting of system and surroundings is used to build density matrix of system.**
- **Dominant eigenstates ( $\sim 10^3$ ) of the density matrix are used to span the Fock space of the system.**
- **The superblock size is increased by adding new sites.**
- **Very accurate for one and quasi-one dimensional systems such as Hubbard, Heisenberg spin chains and polymers**

# DMRG and Matrix Product States

DMRG wavefunction at the end of right sweep



$$\bar{\Psi} = \sum_{\nu^{(N-1)}, \sigma_N} A_{\nu^{(N-1)}, \sigma_N}^{(N-1)} |\nu^{(N-1)}, \sigma_N\rangle$$

$$|\nu^{(N-1)}\rangle = \sum_{\nu^{(N-2)}, \sigma_{N-1}} A_{\nu^{(N-1)}, \nu^{(N-2)}, \sigma_{N-1}}^{(N-2)} |\nu^{(N-2)}, \sigma_{N-1}\rangle$$

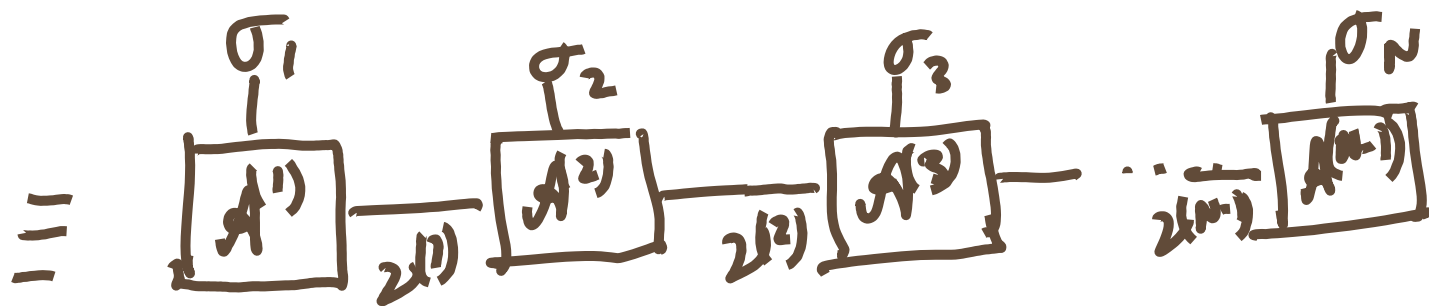
$$\bar{\Psi} = \sum_{\nu^{(N-2)}} \sum_{\nu^{(N-1)}} \sum_{\sigma_{N-1}} \sum_{\sigma_N} A_{\nu^{(N-1)}, \sigma_N}^{(N-1)} A_{\nu^{(N-1)}, \nu^{(N-2)}, \sigma_{N-1}}^{(N-2)} |\nu^{(N-2)}, \sigma_{N-1}, \sigma_N\rangle$$



Continuing

$$\Psi = \sum_{\sigma_1, \sigma_2, \dots, \sigma_N} \sum_{\chi^{(1)}, \chi^{(2)}, \dots, \chi^{(N-1)}}$$

$$A^{(1)}_{\chi^{(1)}, \sigma_1} A^{(2)}_{\chi^{(2)}, \chi^{(1)} \sigma_2} \dots A^{(N-1)}_{\chi^{(N-1)}, \sigma_N} |\sigma_1, \sigma_2, \dots, \sigma_N\rangle$$



Matrix Product States (MPS)

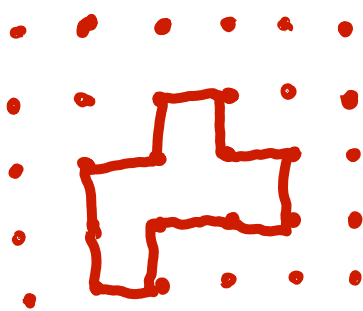
# Entanglement Entropy and the Area Law.

$$P_i |M_i\rangle = M_i |M_i\rangle$$

$$S = - \sum_{\alpha} p_{\alpha} \log_2 p_{\alpha}$$

Area Law

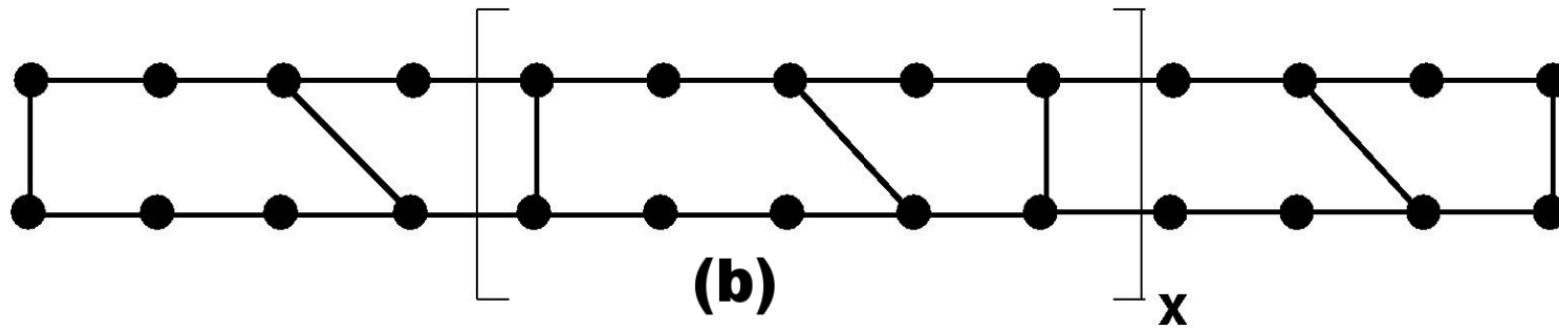
$S \sim$  Area between system and environment.



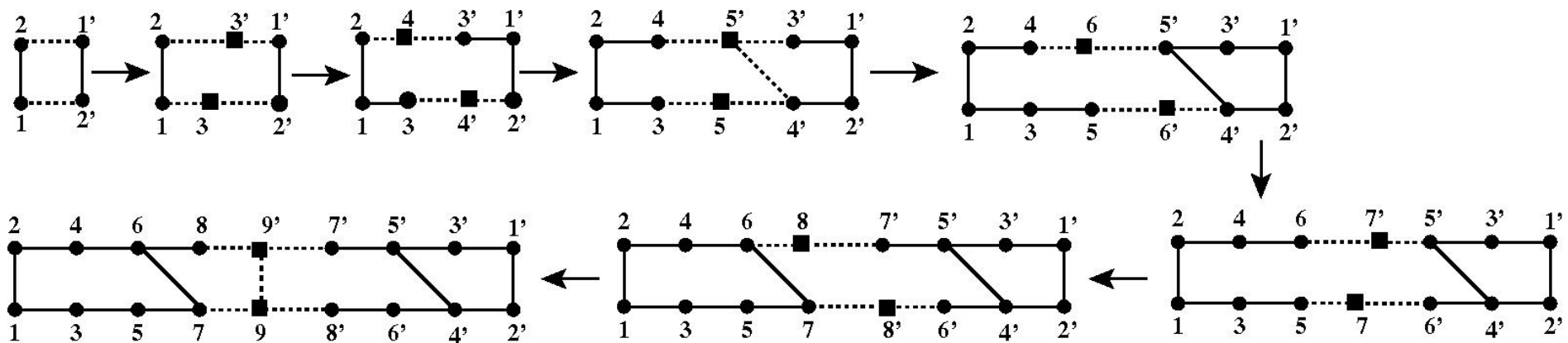
DMRG cut-off  $m \sim e^{aS}$

Hence DMRG most accurate for 1-D systems. At criticality, there are log corrections to  $S$  leading to higher cut-off for desired accuracy.

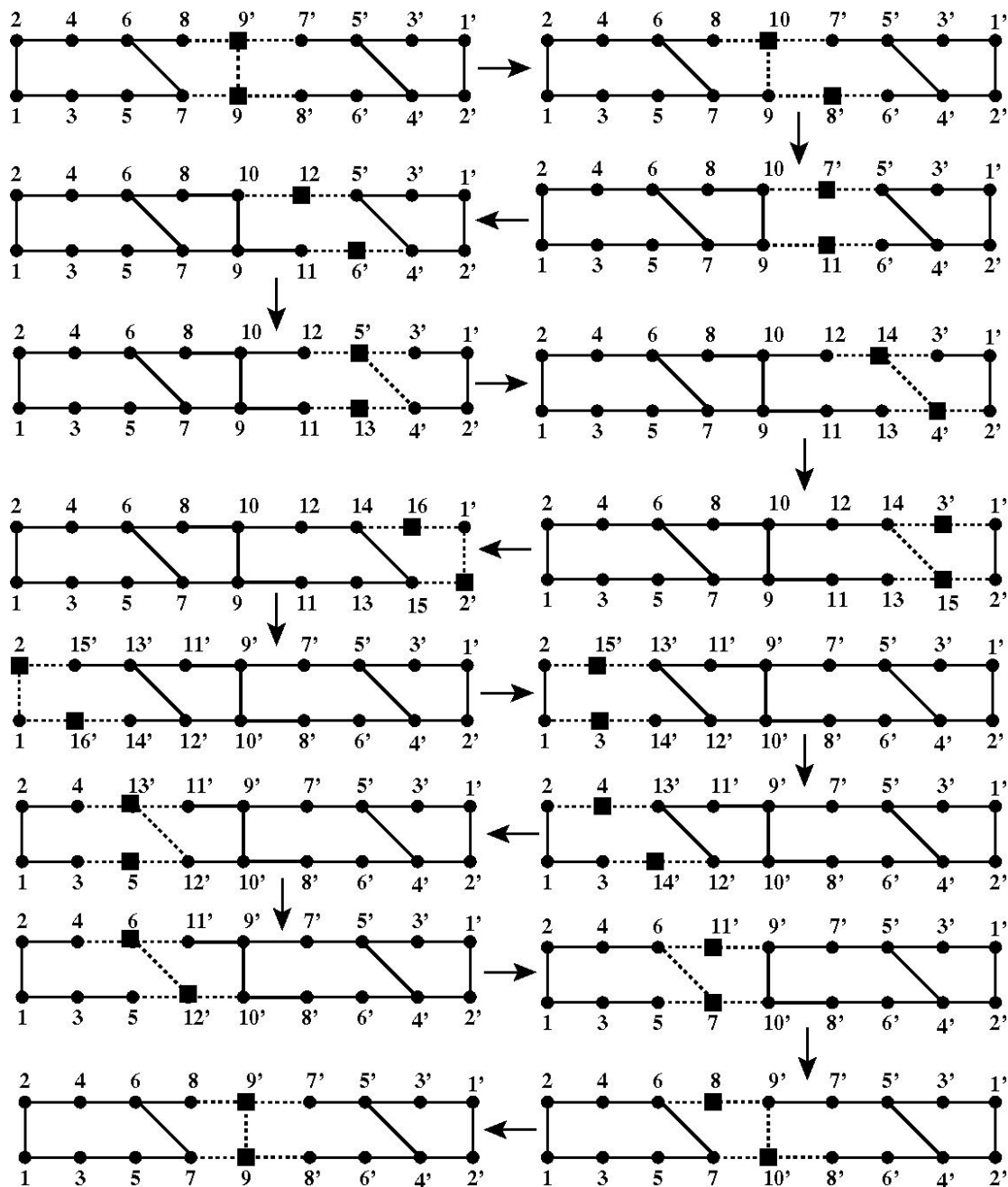
# **DMRG Studies of Fused Azulenes**



## Topological representation of fused azulenes



## infinite DMRG scheme for building fused azulene



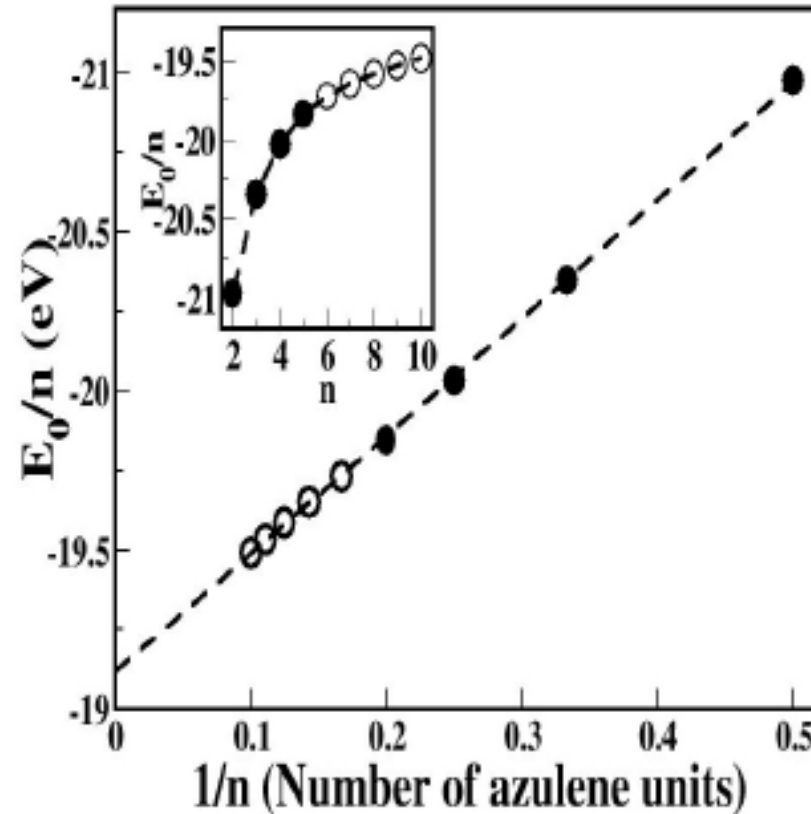
Finite DMRG build up  
of the fused azulene  
structure

**The DMRG results were compared against noninteracting model results and a cut-off of  $m=400$  was used in all Calculations.**

Accuracy of DMRG calculation for ground state energy with different  $m$  (number of density matrix eigenvectors) against exact Hückel MO results for fused azulene with 3 azulene units.

Number of sites	Exact Hückel MO ground state energy (in eV)	Ground state energy using finite DMRG (in eV)
26 (3 fused azulenes)	-85.598	-85.590 ( $m=200$ ) -85.596 ( $m=300$ ) -85.597 ( $m=400$ ) -85.598 ( $m=500$ )

## Ground state energy per site shows smooth extrapolation To the thermodynamic limit



(●) is  $S = 0$  ground state and (○) is  $S = 1$  ground state.

Extrapolated Ground state energy per azulene unit is  $-19.117$  eV.

## Determining spin of the ground state

DMRG calculations are carried out in a given  $M_S$  sector

We calculate lowest eigenvalue in the  $M_S = 0$  space

The spin of the state can be  $S = 0, 1, 2, \dots$

We also calculate the lowest eigenvalue in the  $M_S = 1$  space

if  $E_{\text{lowest}}(M_S = 0) < E_{\text{lowest}}(M_S = 1)$ , ground state spin is 0

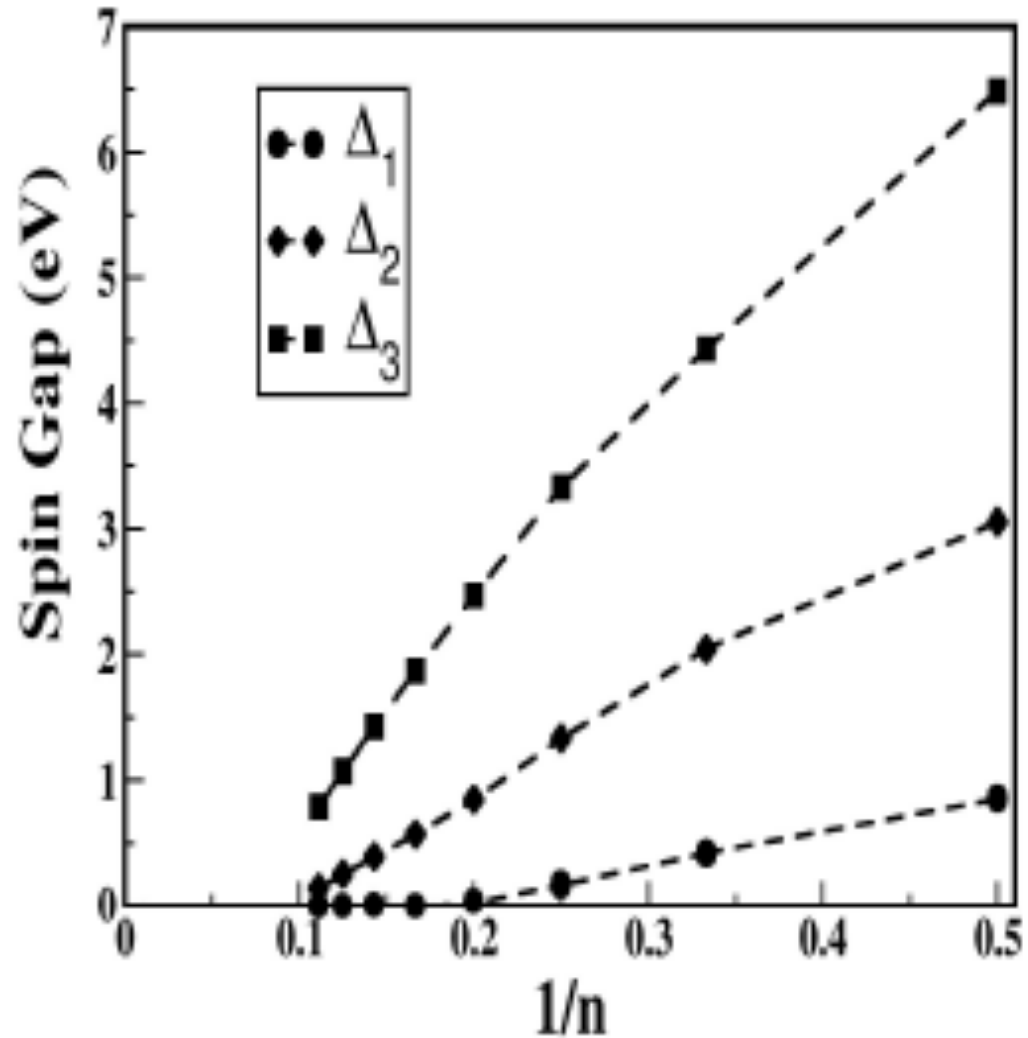
if  $E_{\text{lowest}}(M_S = 0) = E_{\text{lowest}}(M_S = 1)$ , ground state spin is  $\geq 1$

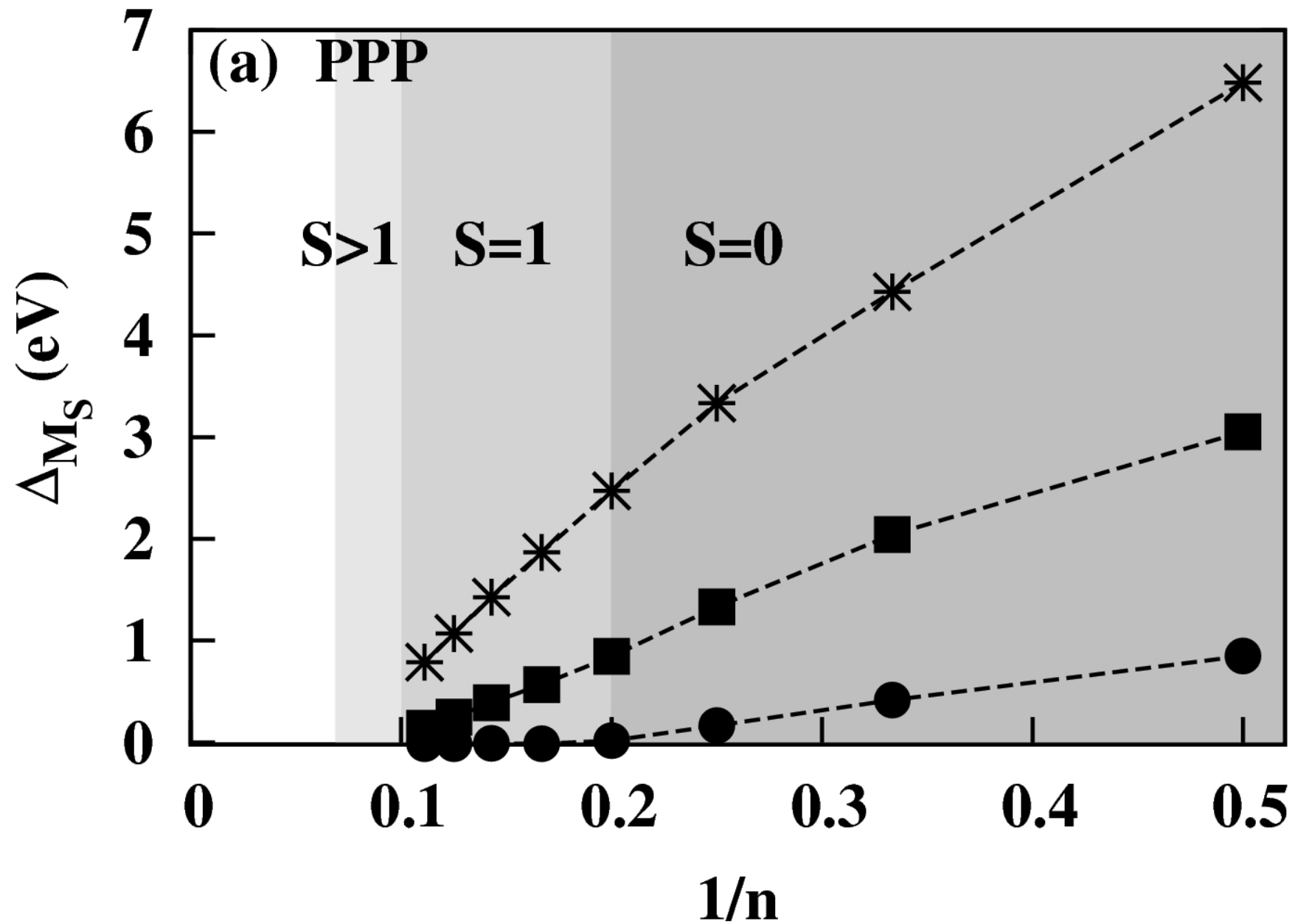
We calculate the lowest eigenvalue in the  $M_S = 2$  space

if  $E_{\text{lowest}}(M_S = 0) = E_{\text{lowest}}(M_S = 1) < E_{\text{lowest}}(M_S = 2)$ , then  
the ground state spin is 1



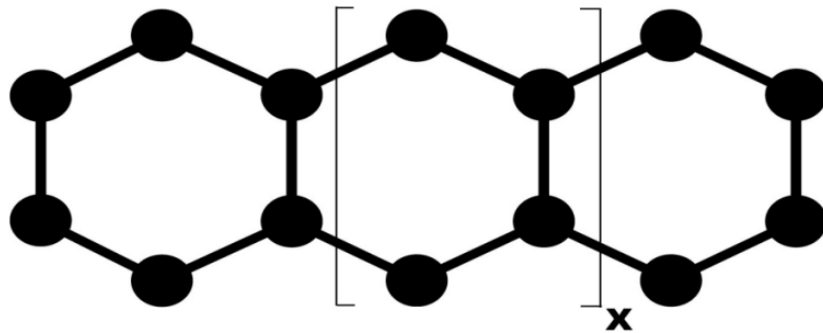
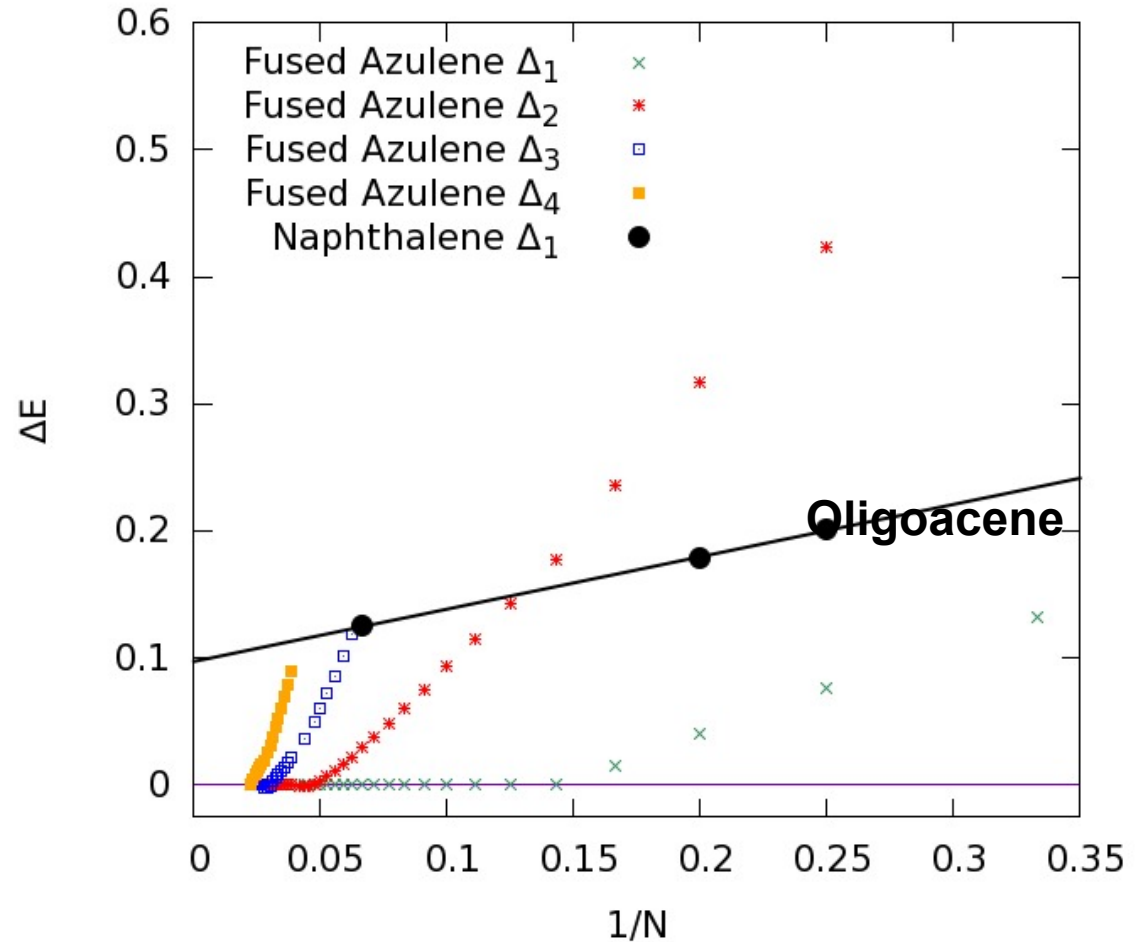
We studied spin gaps,  $\Delta_n = E_{\text{lowest}}(M_S = 0) - E_{\text{lowest}}(M_S = n)$ ,  
for fused systems with different sizes



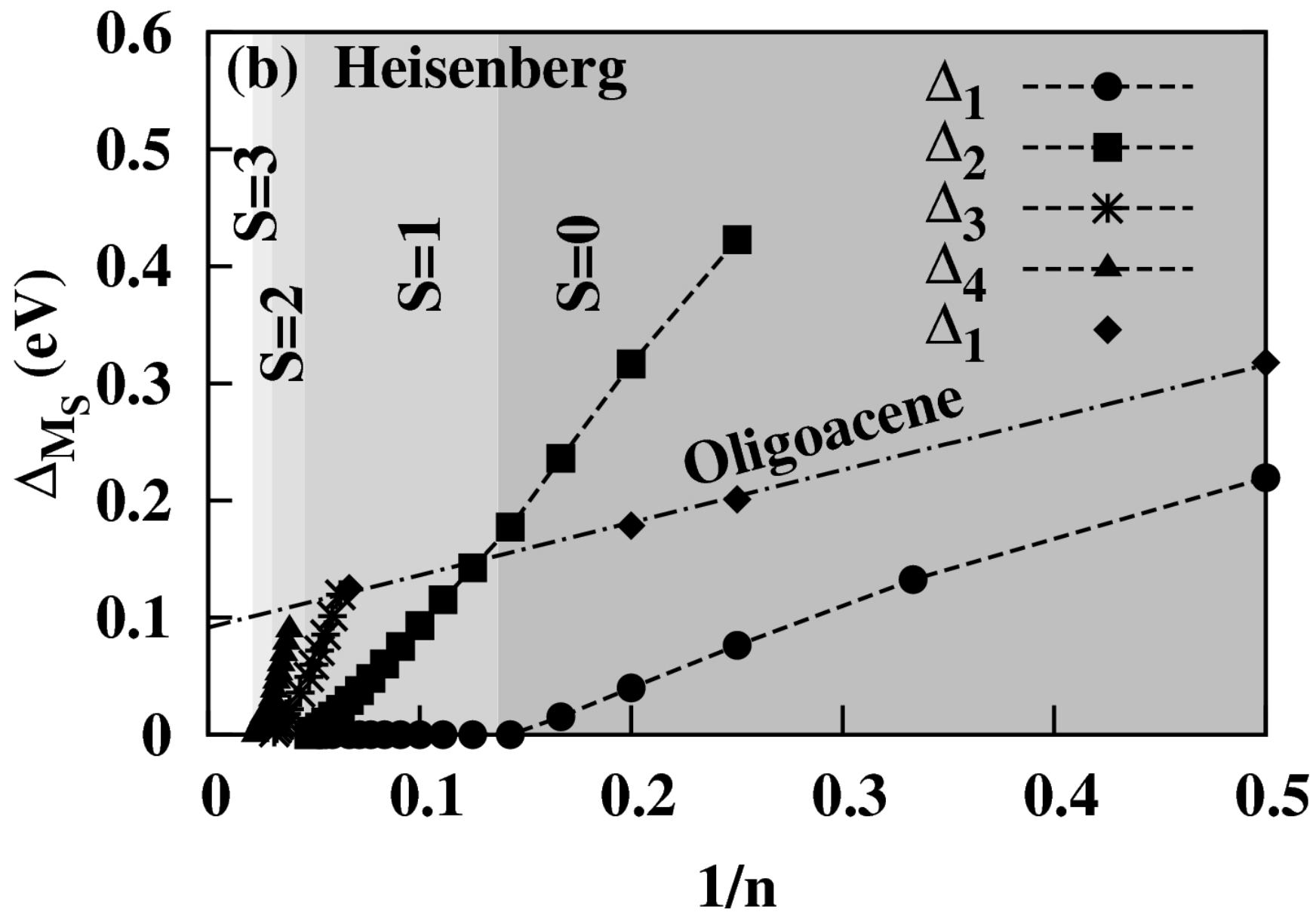


The result also holds for large  $U/t = 20$  as well as for spin  $- \frac{1}{2}$  antiferromagnetic Heisenberg model.

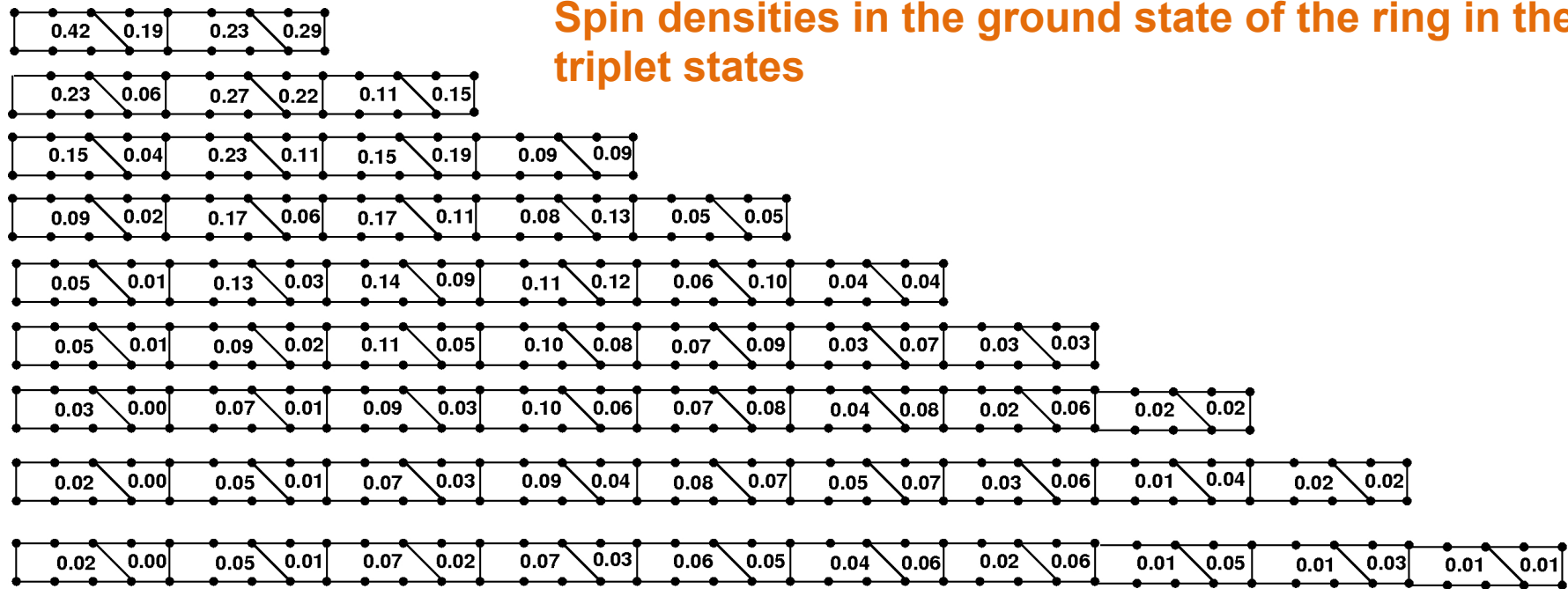
The spin model shows many more crossovers as we can study larger systems.



oligoacenes



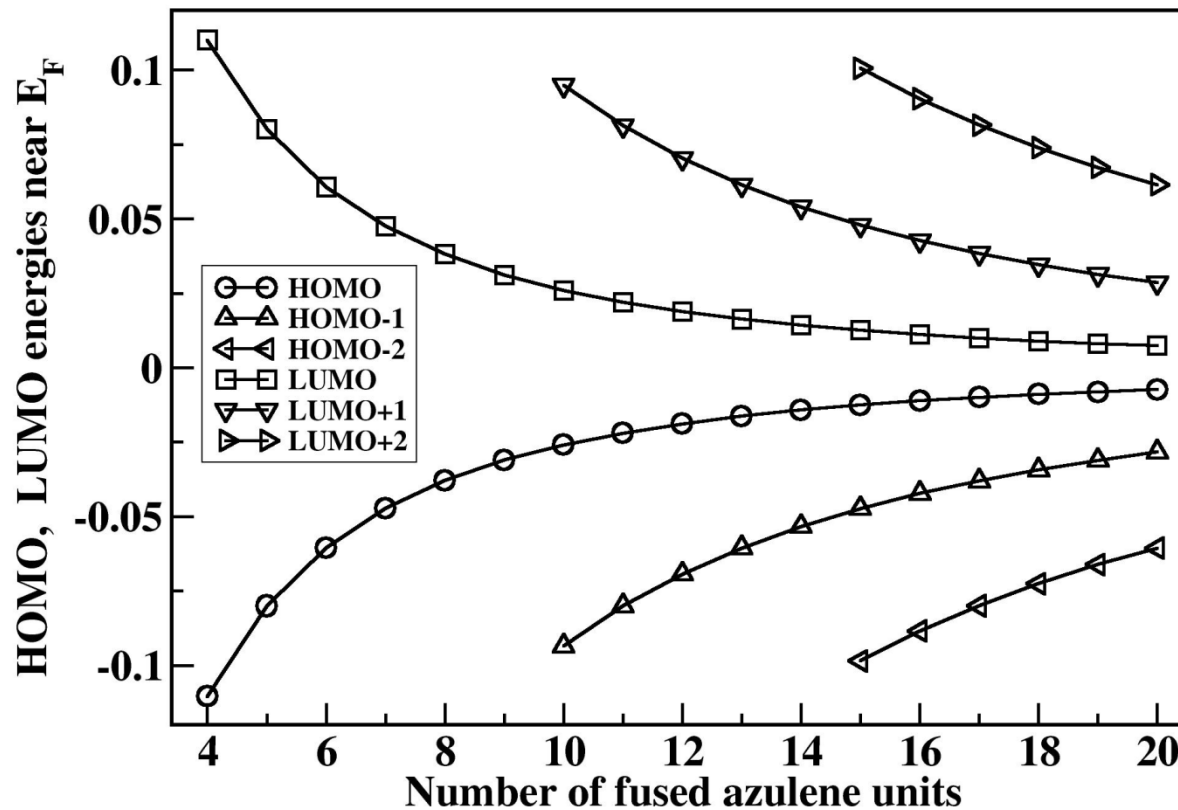
## Spin densities in the ground state of the ring in the triplet states



The spin densities are smeared over the ring

The bond orders  $\frac{1}{2} \langle \sum_{\sigma} a_{i,\sigma}^{\dagger} a_{j,\sigma} + H.C. \rangle$   
 in the ground state are nearly uniform in the interior.  
 Implies Peierls' distortion is not favored.

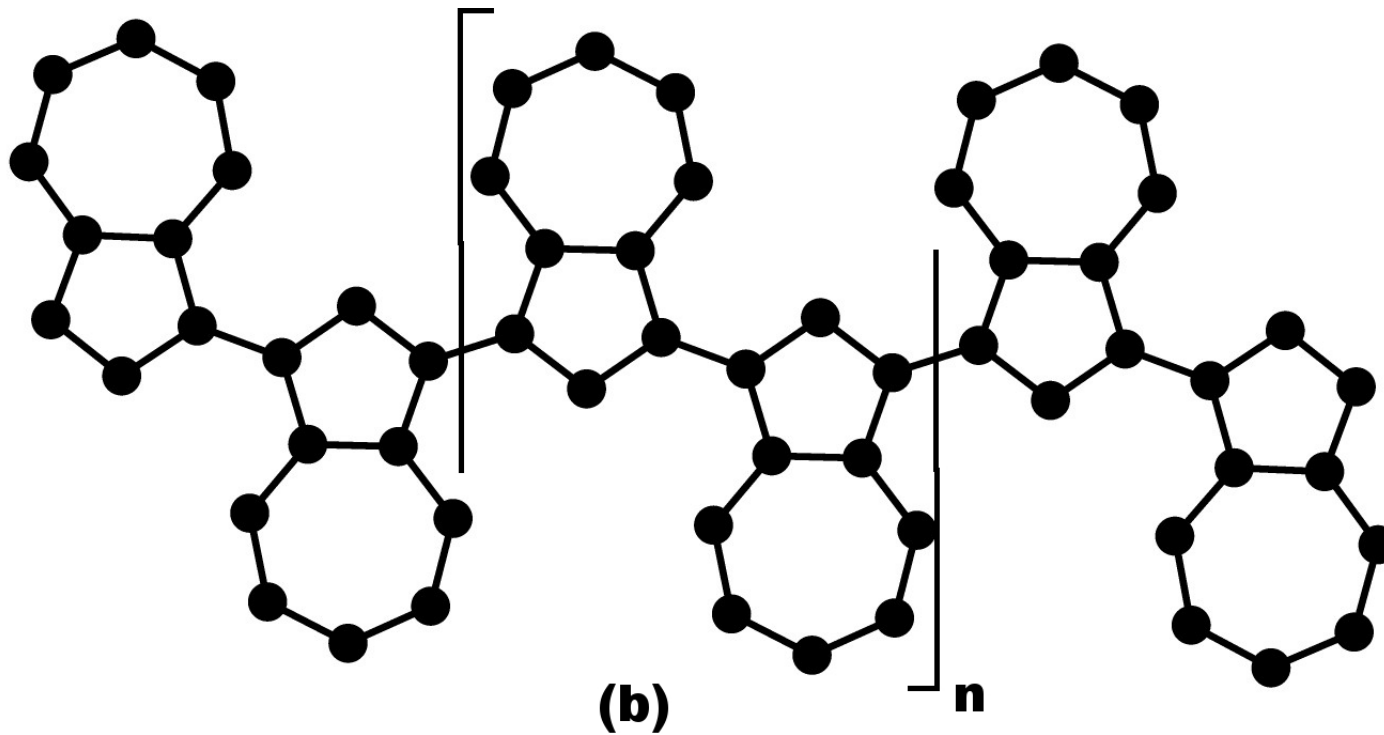
Is the high spin ground state due to degenerate Partially Occupied Molecular Orbitals (flat band ferromagnetism)?



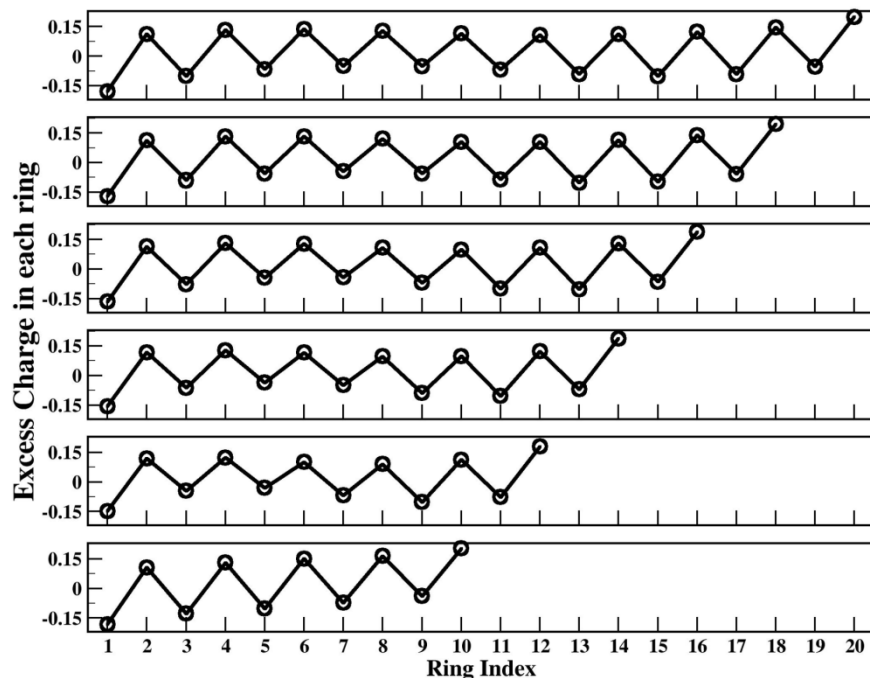
Energies of MOs near the Fermi level as a function of size

Do we need extended range frustration for the ground state spin to cascade with systems size?

DMRG studies on polyazulenes yield singlet ground state at all system sizes with spin gap extrapolating to  $\sim 1.08$  eV.

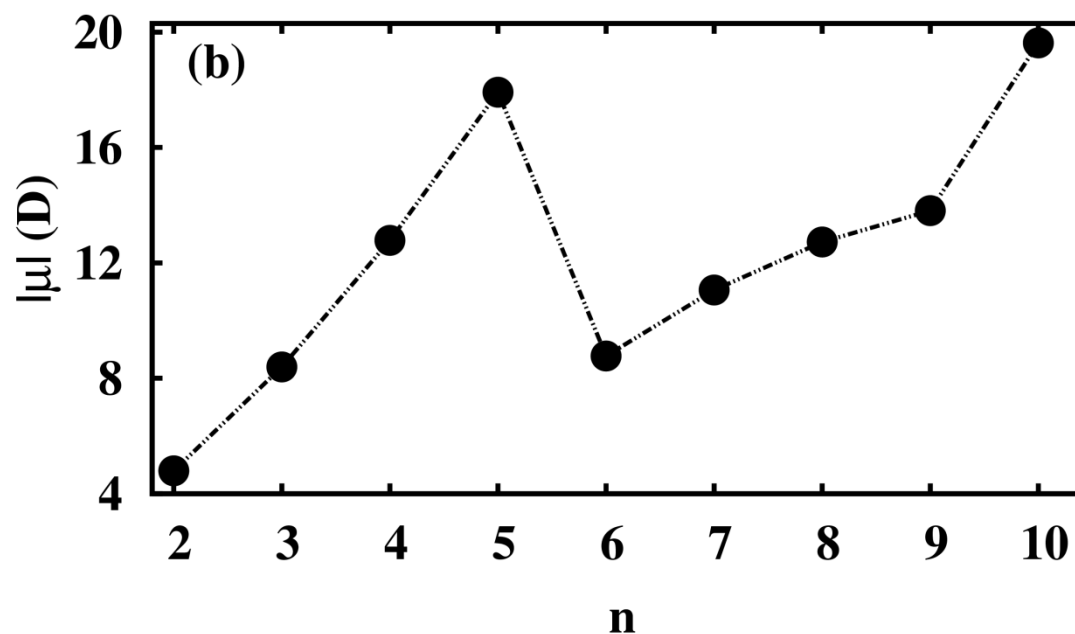


All-trans polyazulene



**Ground state charge density in the rings. Seven site rings are positively charged and five site rings are negatively charged**

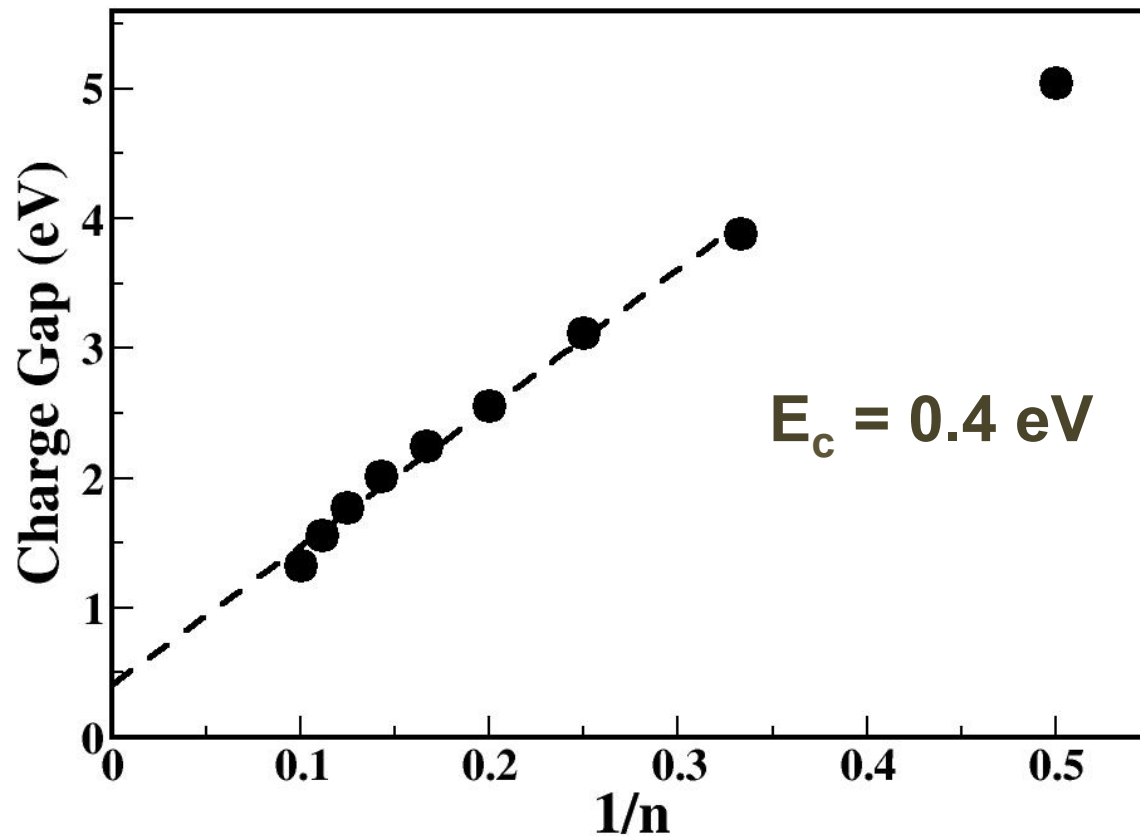
**Dipole moment in the ground state as a function of oligomer size.**



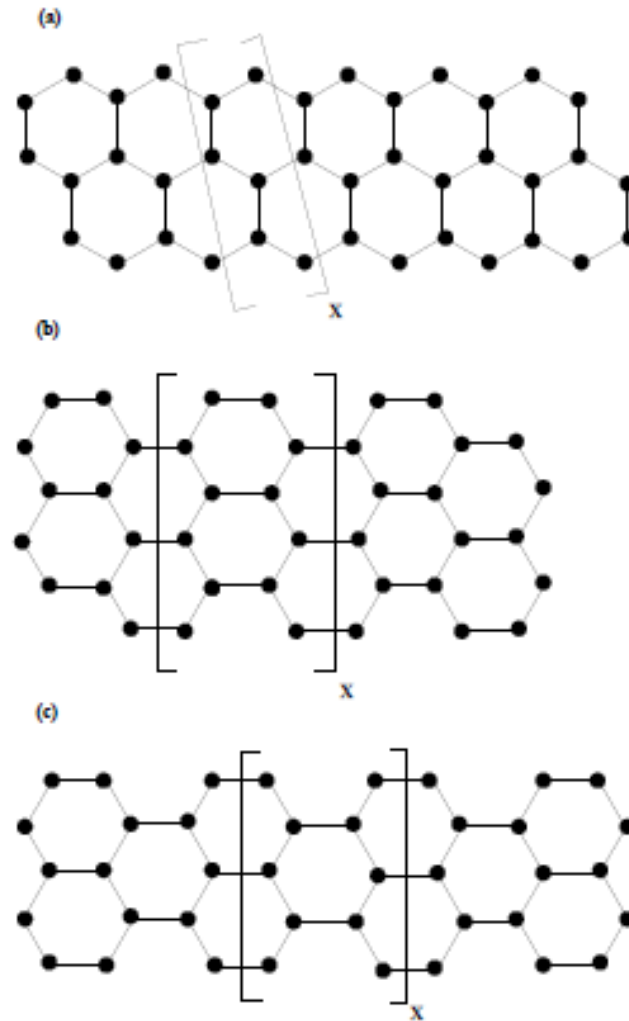


$$\text{Charge gap } E_C = \lim_{N \rightarrow \infty} [E(N, P^+) + E(N, P^-) - 2 E(N, P)]$$

Measures the energy for disproportionation of two long neutral chains into two well separated oppositely charged chains



# Carbon Nano Ribbons



*Figure 5.1: Geometrical structure of (a) zigzag and (b) armchair fused naphthalene systems and (c) polyperylene system. To retain  $C_2$  symmetry in the calculations, we have calculated the properties after augmenting the system by two naphthalene units in (b).*

## Spin Gaps in the Systems

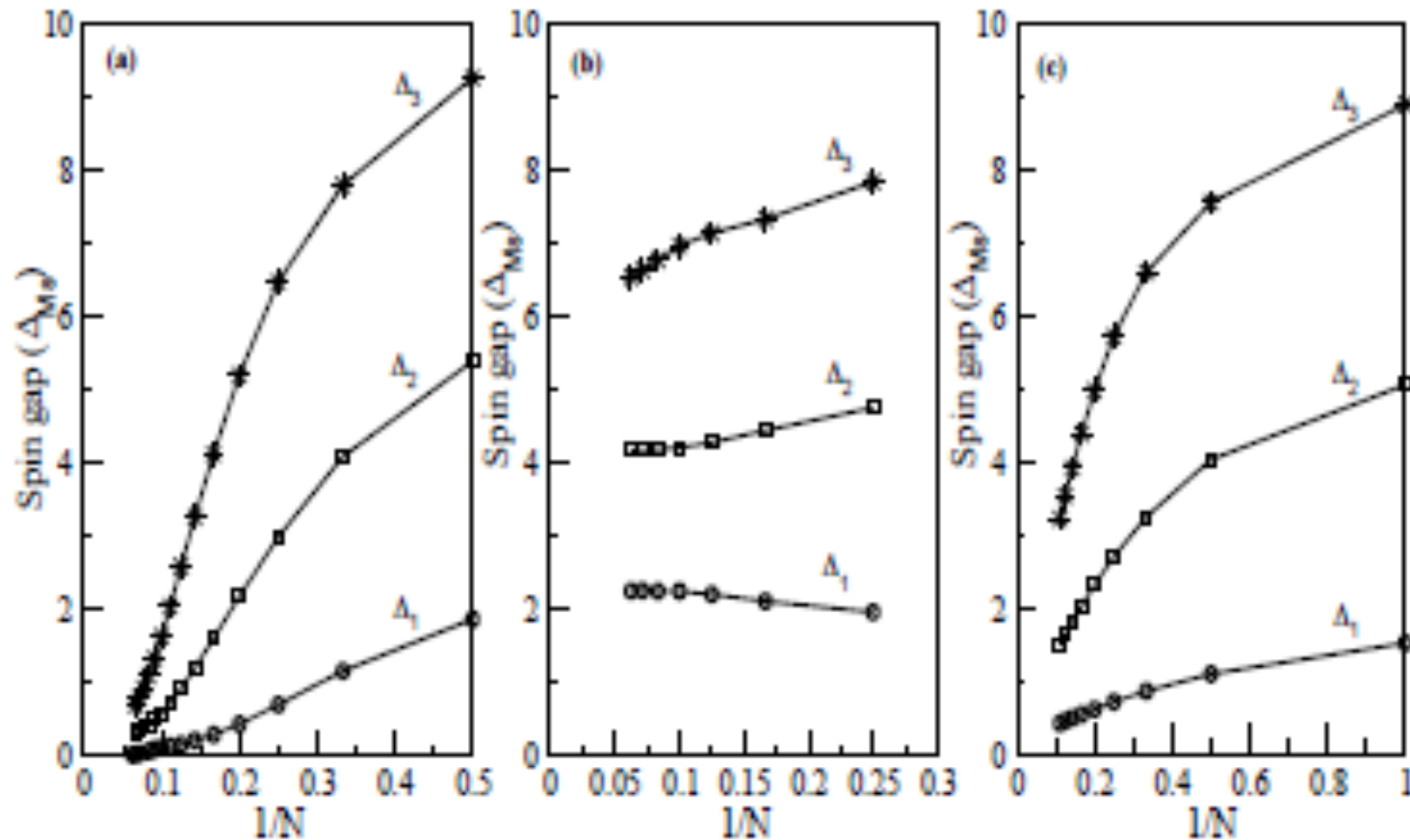


Figure 5.5: Spin gaps as a function of the inverse of number of units for (a) zigzag and (b) armchair fused naphthalene and (c) polyperylene systems within the PPP model. In the figure  $\Delta_1 = E(M_S = 1) - E(M_S = 0)$ ,  $\Delta_2 = E(M_S = 2) - E(M_S = 0)$  and  $\Delta_3 = E(M_S = 3) - E(M_S = 0)$ ,

# **Acknowledgments**

**Dr. Shaon Sahoo**  
**Mr. Durga Prasad G.V.M.L.**  
**Mr. Suryoday Prodhan**  
**Dr. C. Raghu,**  
**Dr. Manoranjan Kumar**  
**Dr. Simil Thomas,**  
**Dr. Tirthankar Dutta,**  
**Prof. Diptiman Sen**  
**Prof. H.R. Krishnamurthy**

**Thank You**