Title: Quantum chemistry methods to study strongly correlated systems â€“ from variational to machine learning approaches

Speakers: Debashree Ghosh

Series: Machine Learning Initiative

Date: May 09, 2023 - 9:00 AM

URL: https://pirsa.org/23050035

Abstract: Polyaromatic hydrocarbons (PAHs) such as acenes have long been studied due to its interesting optical properties and low singlet triplet gaps. Earlier studies have already noticed that use of complete valence active space is imperative to the understanding of its qualitative and quantitative properties. Since complete active space based methods cannot be applied to such large active spaces, we have used density matrix renormalization group (DMRG) based approaches. Further small modification to the PAH topology shows interesting new phases of behaviour in its optical gaps. We have understood the effect of these effects based on spin frustration due to the presence of odd membered rings. In this talk, I will discuss these observations from molecular and model Hamiltonian perspectives.Further developments based on artificial neural network based configuration interaction for strongly correlated systems will also be discussed.5 The similarities between the ANNs and the MPS wavefunctions will be leveraged for 2D systems.

Zoom link: https://pitp.zoom.us/j/92159136836?pwd=ZFJBcXZ3R3czSUcxcThOci9ueStBZz09

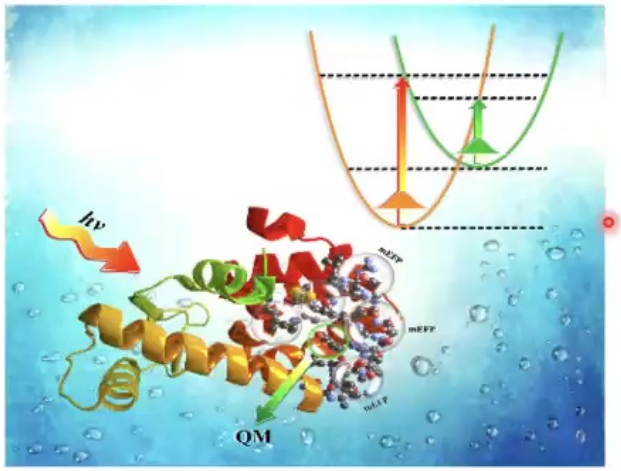
Machine learning the configuration space for strongly correlated quantum chemistry

Debashree Ghosh

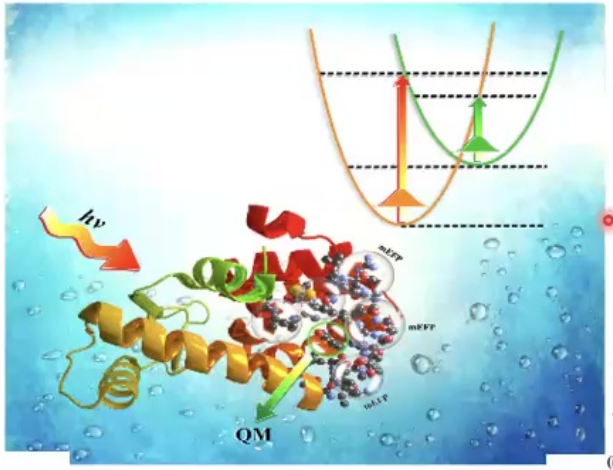
School of Chemical Sciences

Indian Association for the Cultivation of Science

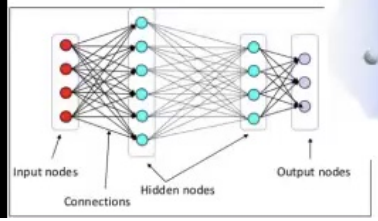
Hybrid QMMM for excited states

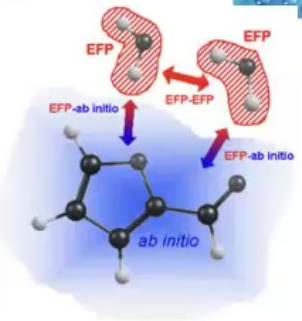


Hybrid QMMM for excited states

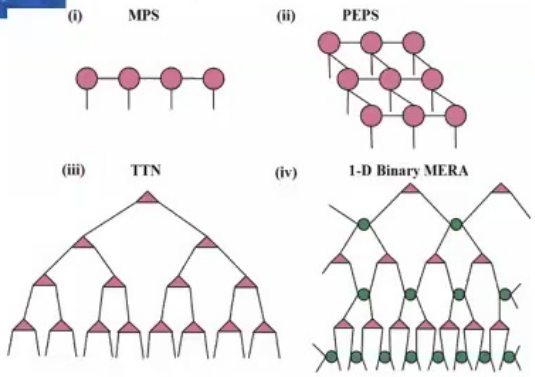


Fragment based and Machine learning based polarizable FF

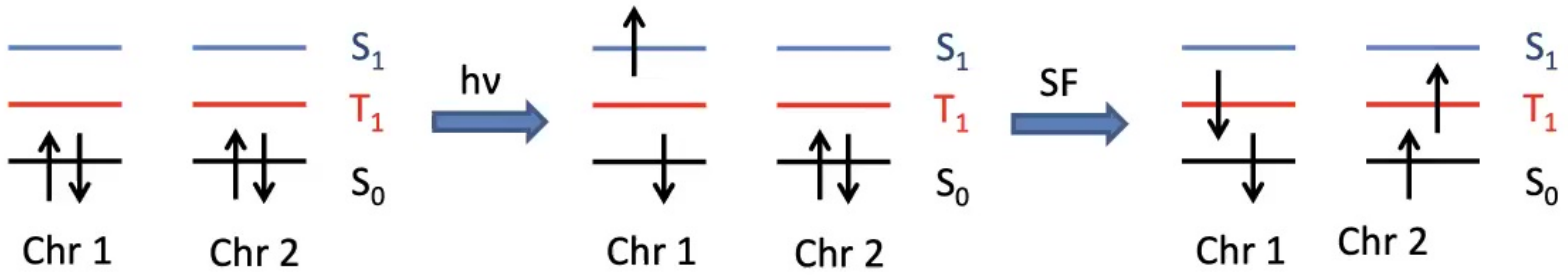


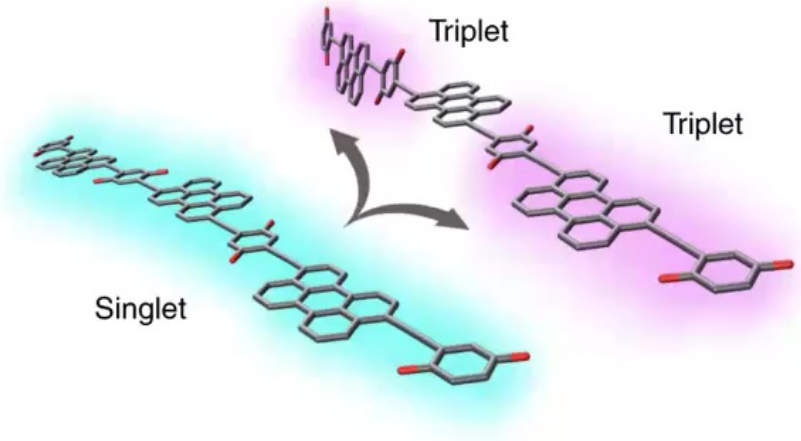


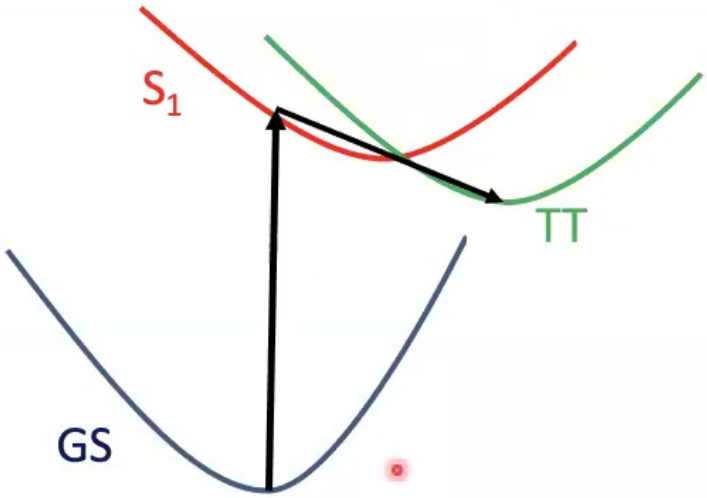
Strong correlation and tensor product states



Energy - Singlet fission



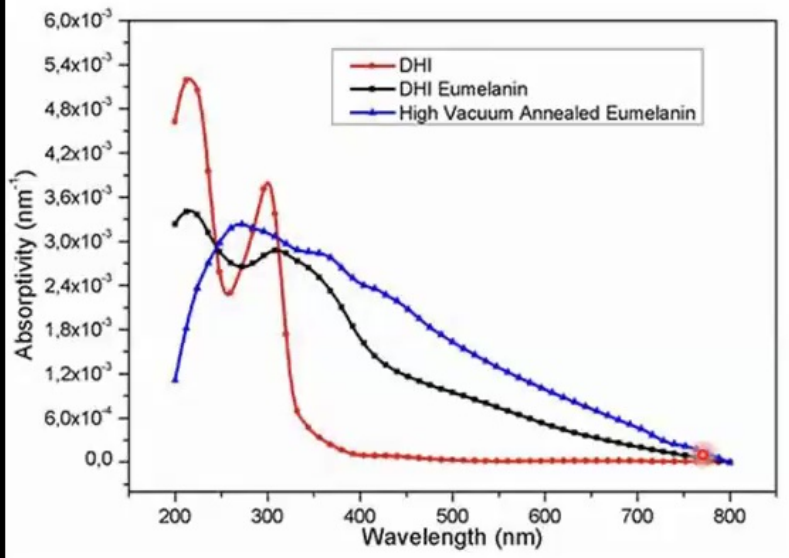




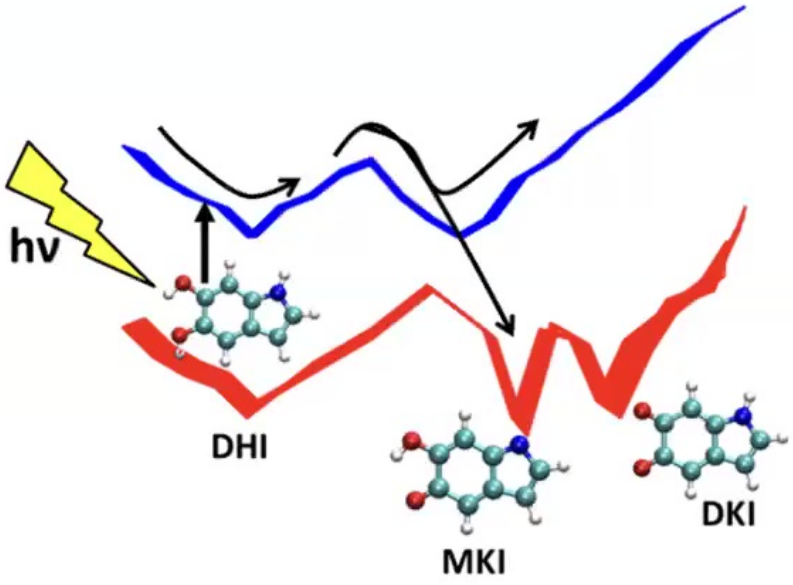
Mechanism and electronic structure of states involved in singlet fission

Santra, Ray, **DG**, J Phys Chem Lett (2022)

Biology - photoprotection



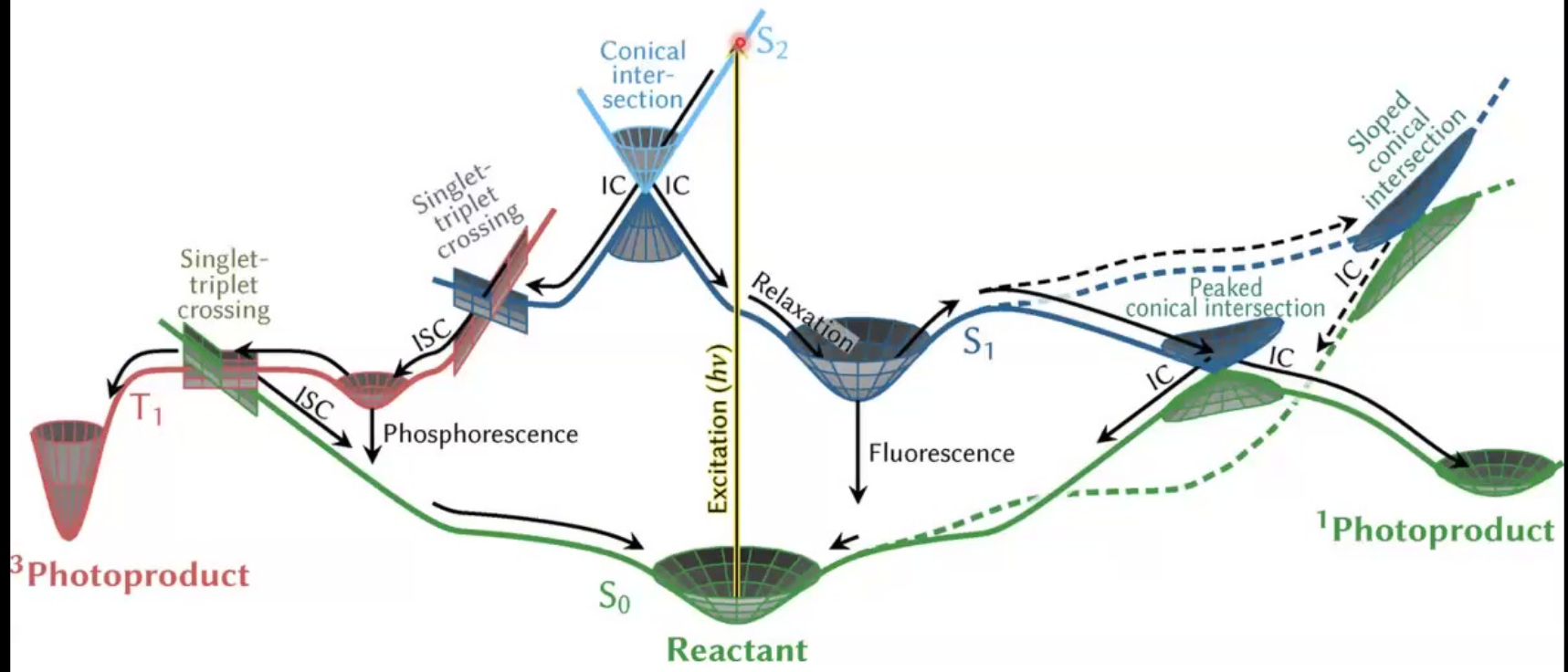
Understanding the monotonic and featureless spectra of melanin



What happens to melanin once it absorbs UV-vis light?

DG, WIREs – Comp. Mol. Sci. , (2021)
Chen…, Beuhler, Nature Comm (2014)

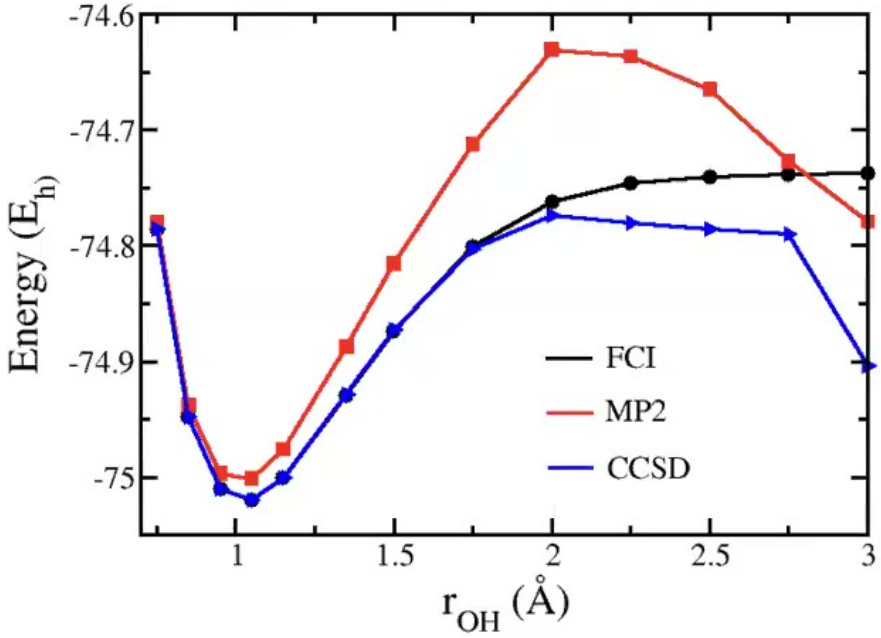
Excited state processes

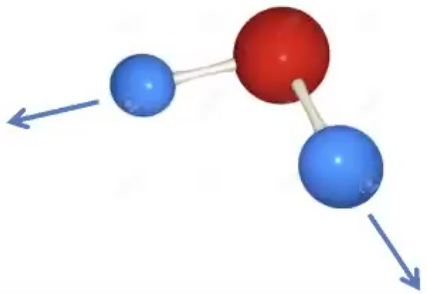


Rapidly evolving field that relates spectroscopy with electronic structure theory and molecular dynamics for electronic excited states

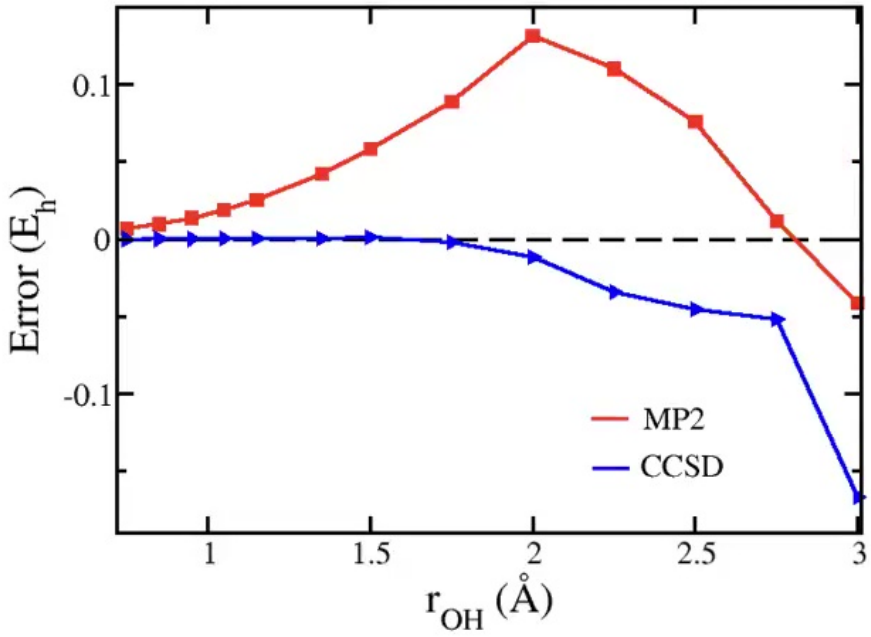
Mai, Gonzalez, Angew Chem, (2020)

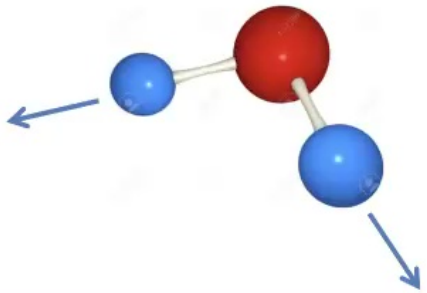
Failure



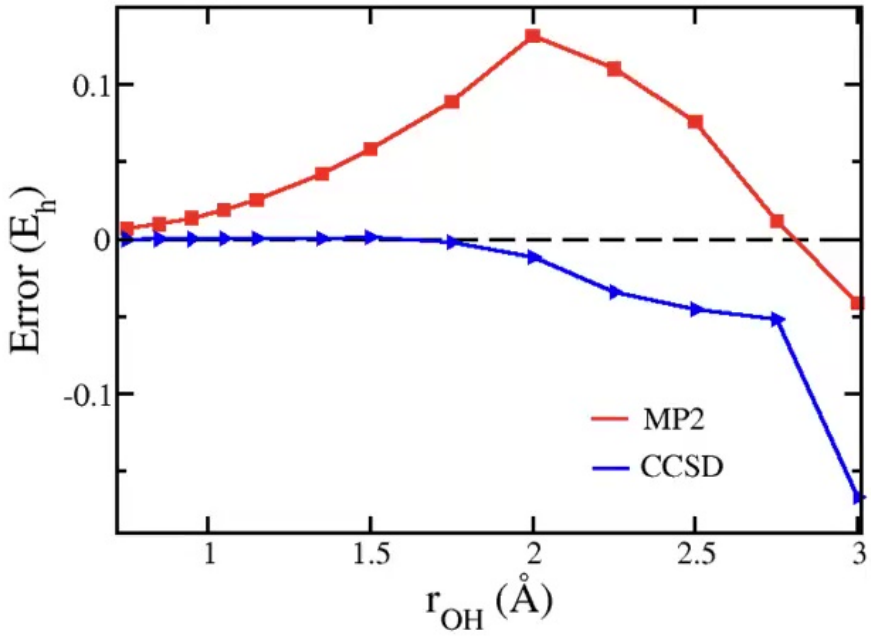


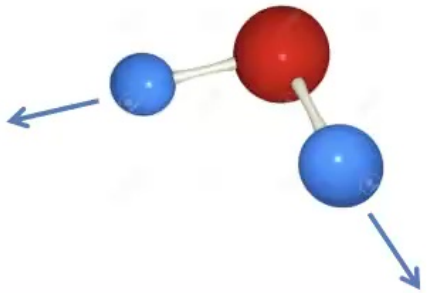
Failure





Failure

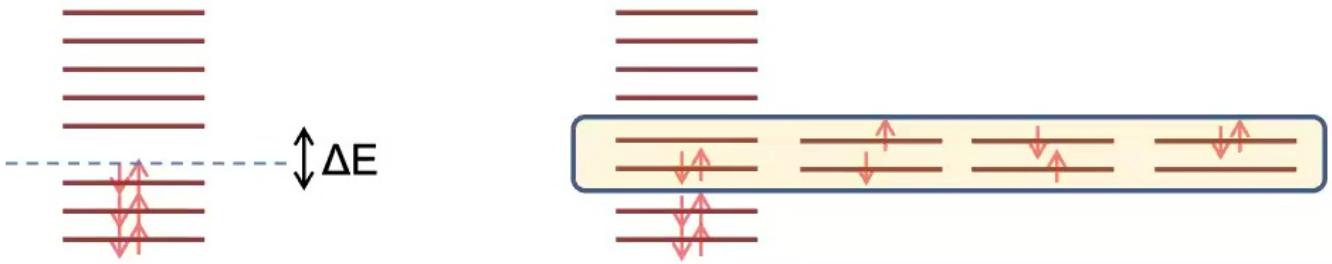




This effect shows up in :

- Excited states
- Di-, tri-radicals
- Transition metal complexes
- Polyenes, graphene etc
- Metal clusters

Multireference

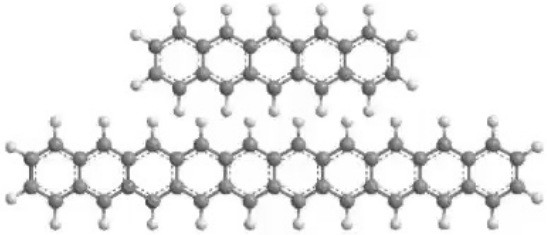


Single reference
Aufbau principle

Multireference or multiconfiguration

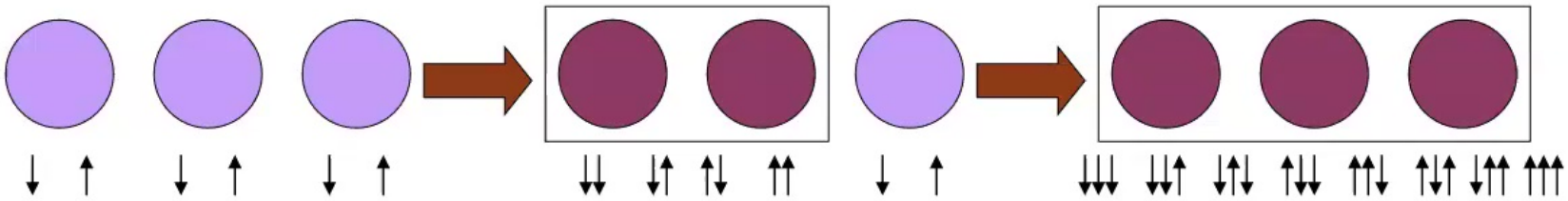
- Multiple electronic configurations across the valence space
- Instead of single molecular orbital occupation

Challenges in ST gap computation



- CSFs in the active (valence) space is an exponentially scaling problem.
- CSF space is large ~10^{33} for 30 π orbitals with 30 electrons
- For a matrix diagonalization of this size, one requires to perform 10^{99} operations.
- Comparison – No of atoms in universe is 10^{82}

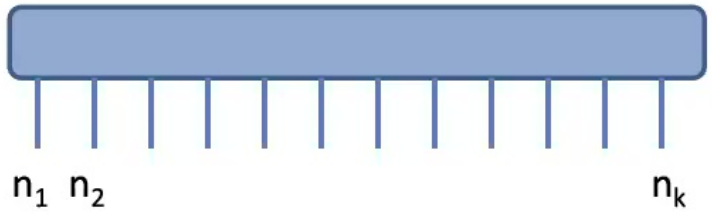
Exponential Hilbert space



2^N or d^N

Thus, the exact wavefunction can be written as a many dimensional tensor

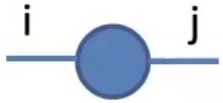
$$|\Psi_{FCI}\rangle = \sum_{n_1 n_2 n_3 \ldots} \Psi^{n_1 n_2 n_3 \ldots n_k} \, | n_1 n_2 n_3 \ldots . n_k \rangle$$



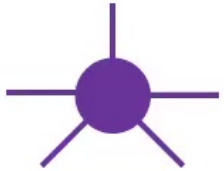
Matrix product state

Real / complex value

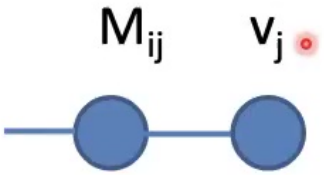
Vector



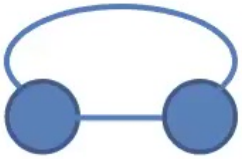
Matrix



Tensor



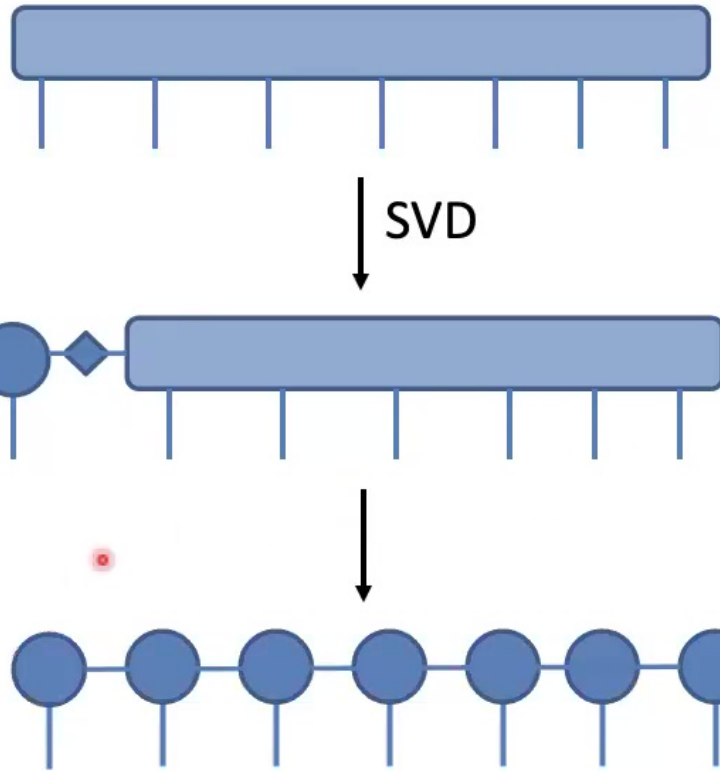
$$\sum_j M_{ij} v_j$$



Trace

Matrix Product State ansatz

$$\sum_{n_1 n_2 n_3 \ldots} \Psi^{n_1 n_2 n_3 \ldots n_k} \, | n_1 n_2 n_3 \ldots n_k \rangle$$



d^N

Verstraete, Garcia-Ripoll, Cirac, PRL, (2004)
Kliesch, Gross, Eisert, PRL (2014)

Matrix Product State ansatz

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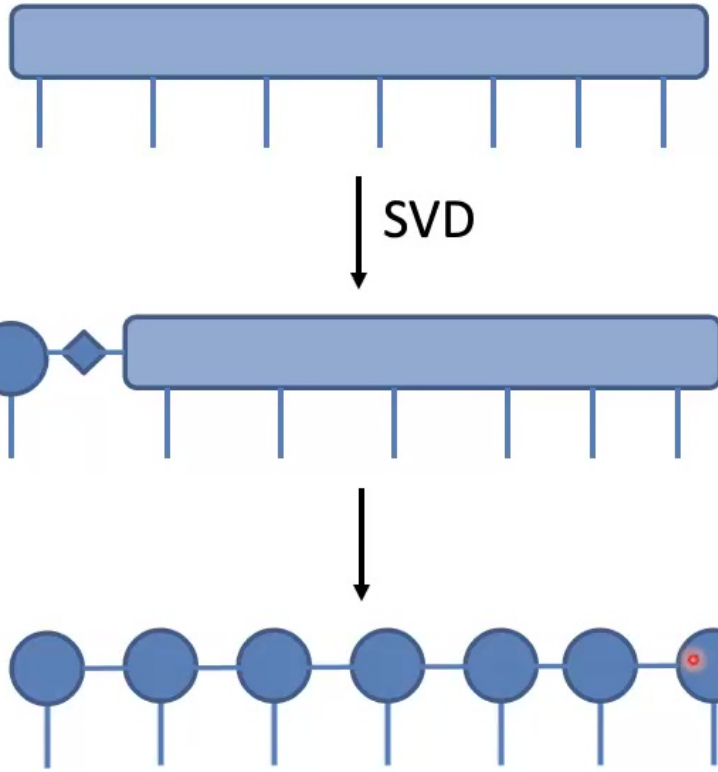


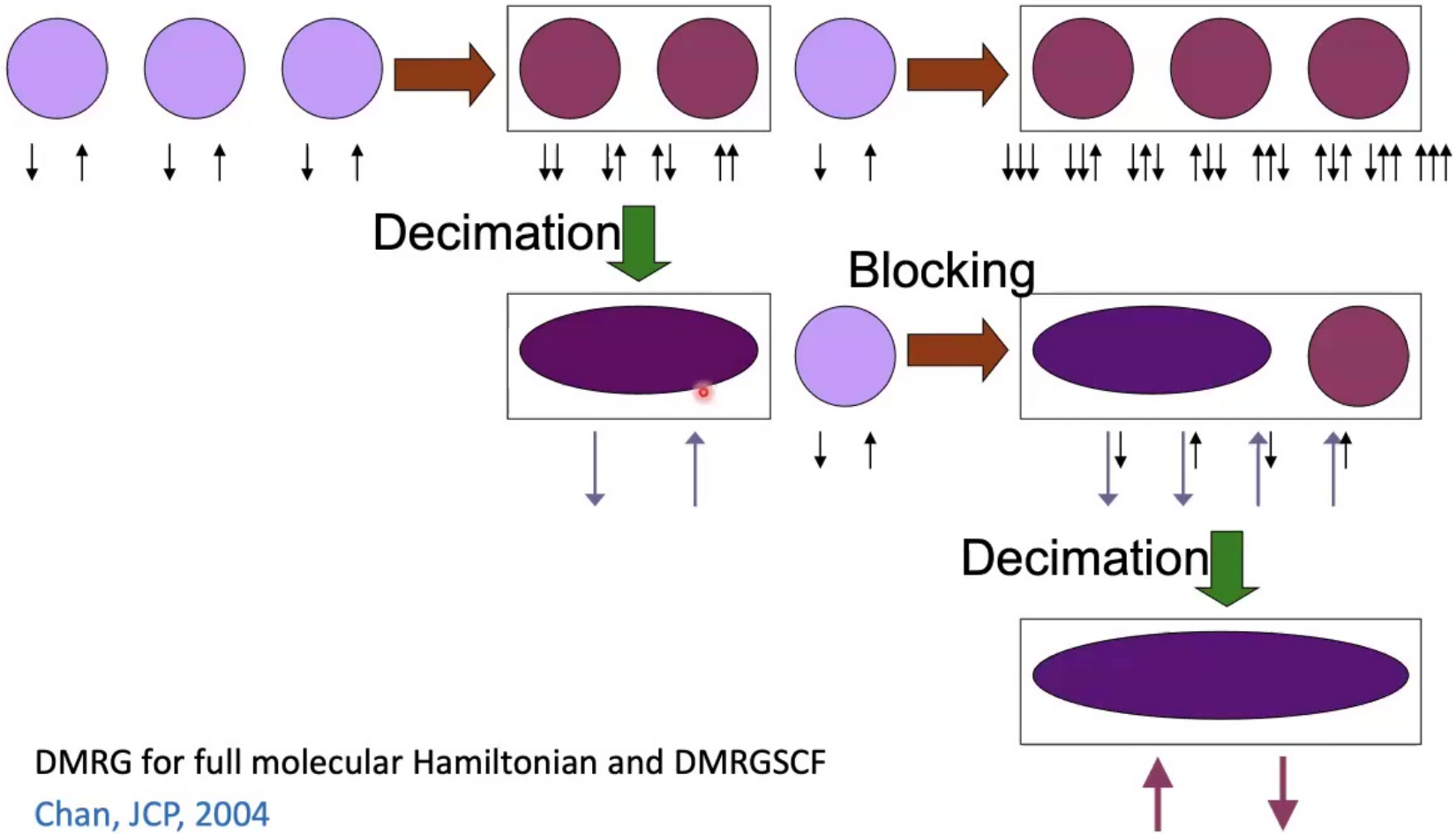
d^N

Exponential saving!

NdM^2

Verstraete, Garcia-Ripoll, Cirac, PRL, (2004)
Kliesch, Gross, Eisert, PRL (2014)

Density Matrix Renormalization group



DMRG for full molecular Hamiltonian and DMRGSCF

Chan, JCP, 2004

Ghosh et al, JCP, 2008

Matrix product states

$$|\Psi_{FCI}\rangle = \sum_{n_1 n_2 n_3} \Psi^{n_1 n_2 n_3} |n_1 n_2 n_3\rangle$$

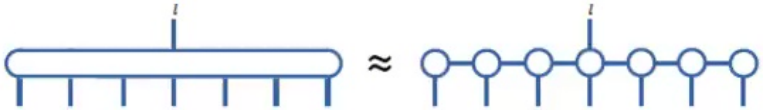
$$|n\rangle = \{|0\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\}$$

4^n scaling !

$$\Psi^{n_1 n_2 n_3} \approx A^{n_1} A^{n_2} A^{n_3}$$

No correlation between sites(orbitals).
Mean field approximation (HF)

- DMRG simply gives us a good algorithm to determine these matrix product states.
- As long as the dimension of the matrix products is small this gives a general ansatz that is economical.



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$$\Psi^{n_1 n_2 n_3} \approx \sum_{i_1 i_2 i_3} A^{n_1}_{i_1 \; i_1} A^{n_2}_{i_2 \; i_2} A^{n_3}_{i_3}$$

Correlation between two sites.
Auxiliary indices.
Product of matrices (MPS).

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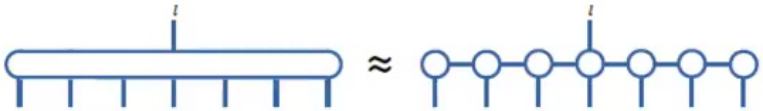
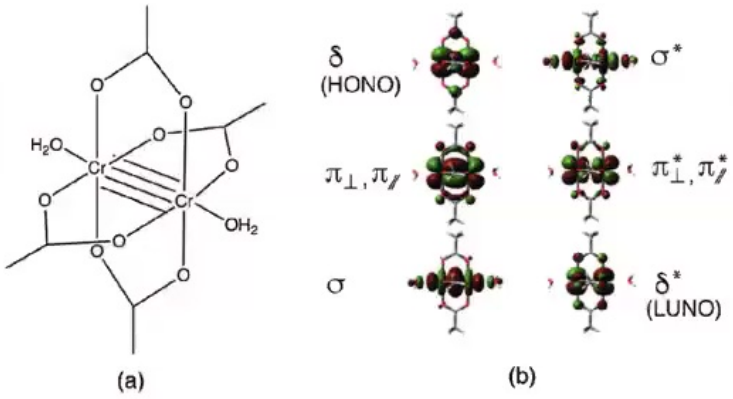
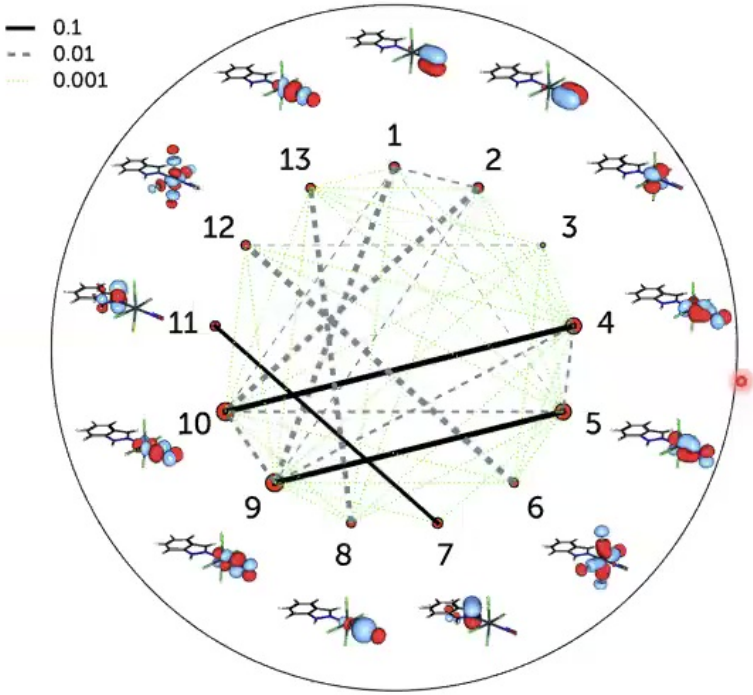


Orbital ordering and entanglement

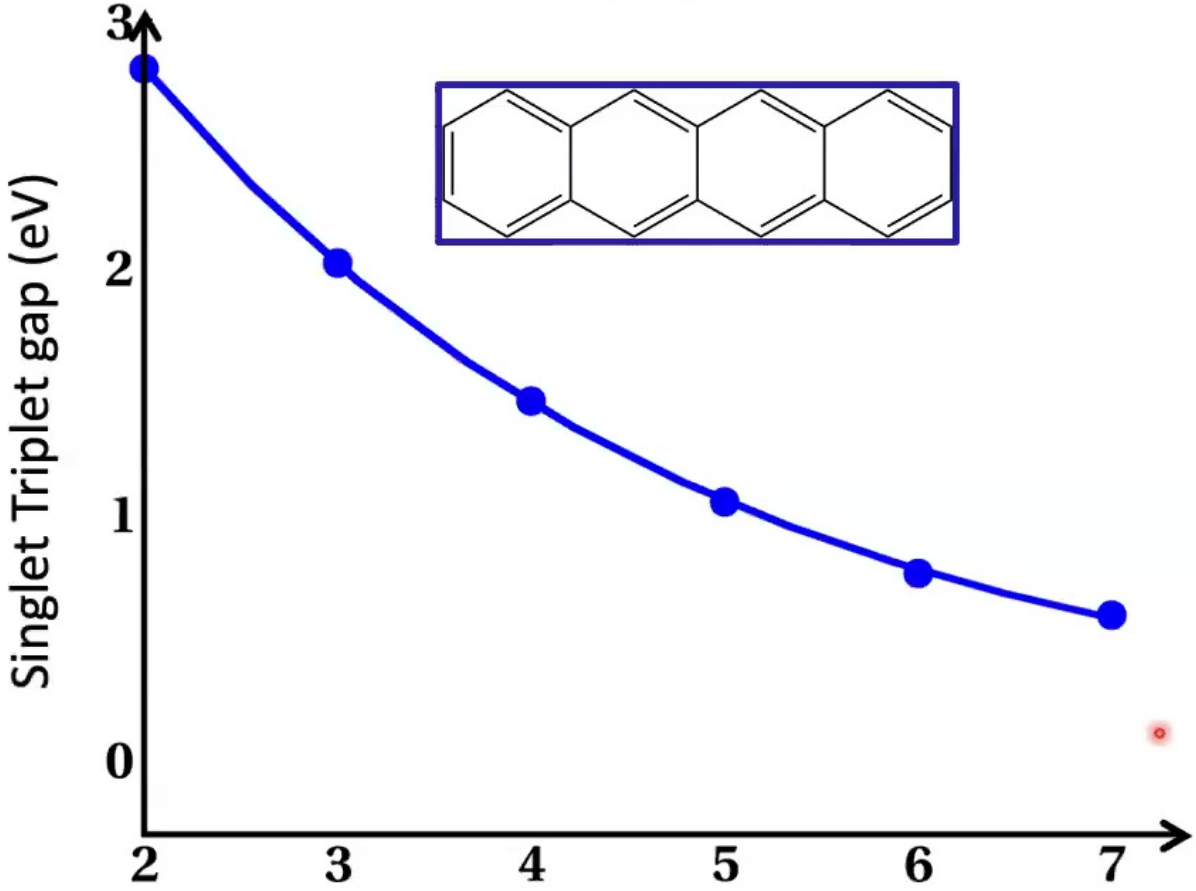


Numerous orbitals in a molecule which are not spatially linearly connected.



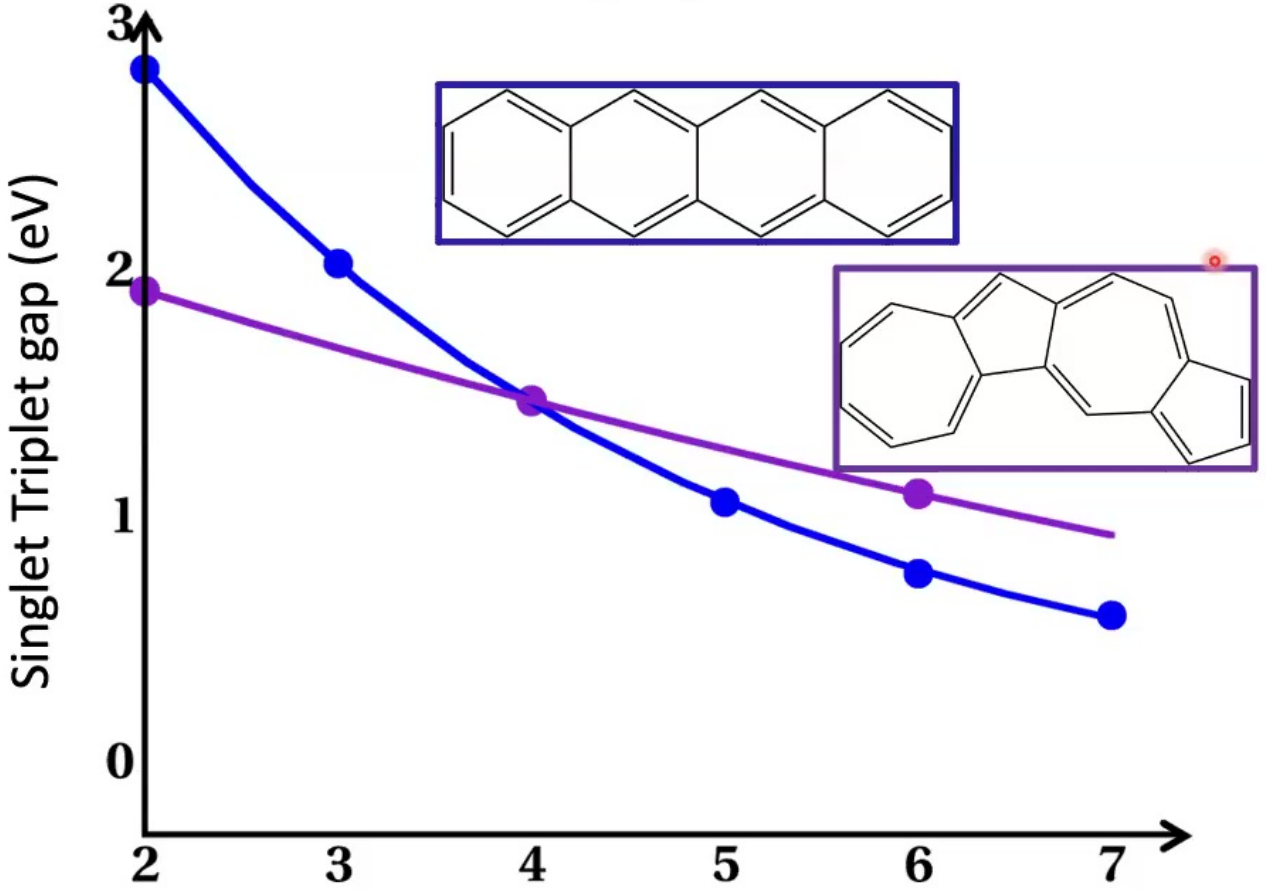
Boguslawski, Tecmer, IJQC (2015)

ST gap



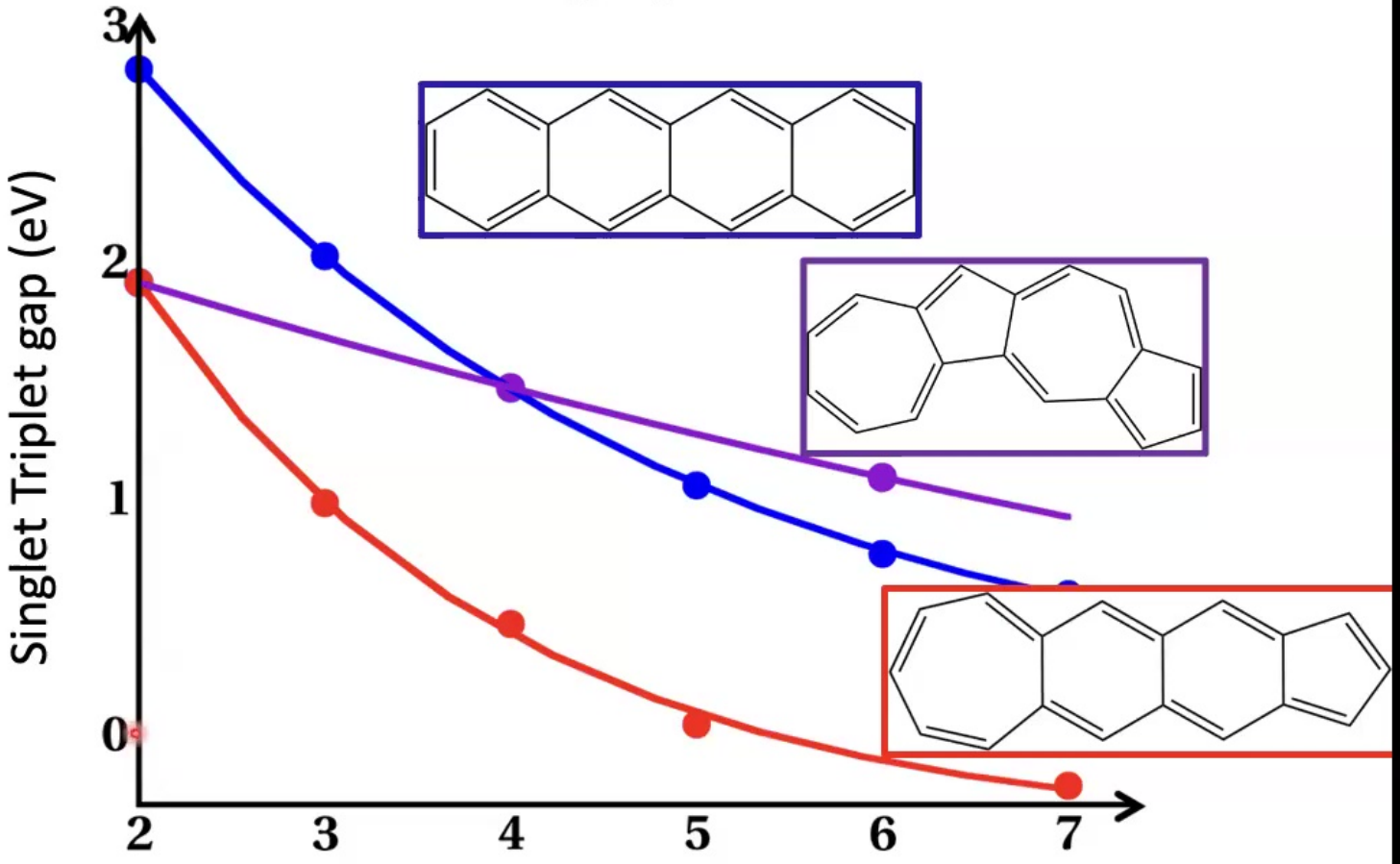
Rano, Ghosh, **DG**, Chemical Science, 2019

ST gap



Rano, Ghosh, **DG**, Chemical Science, 2019

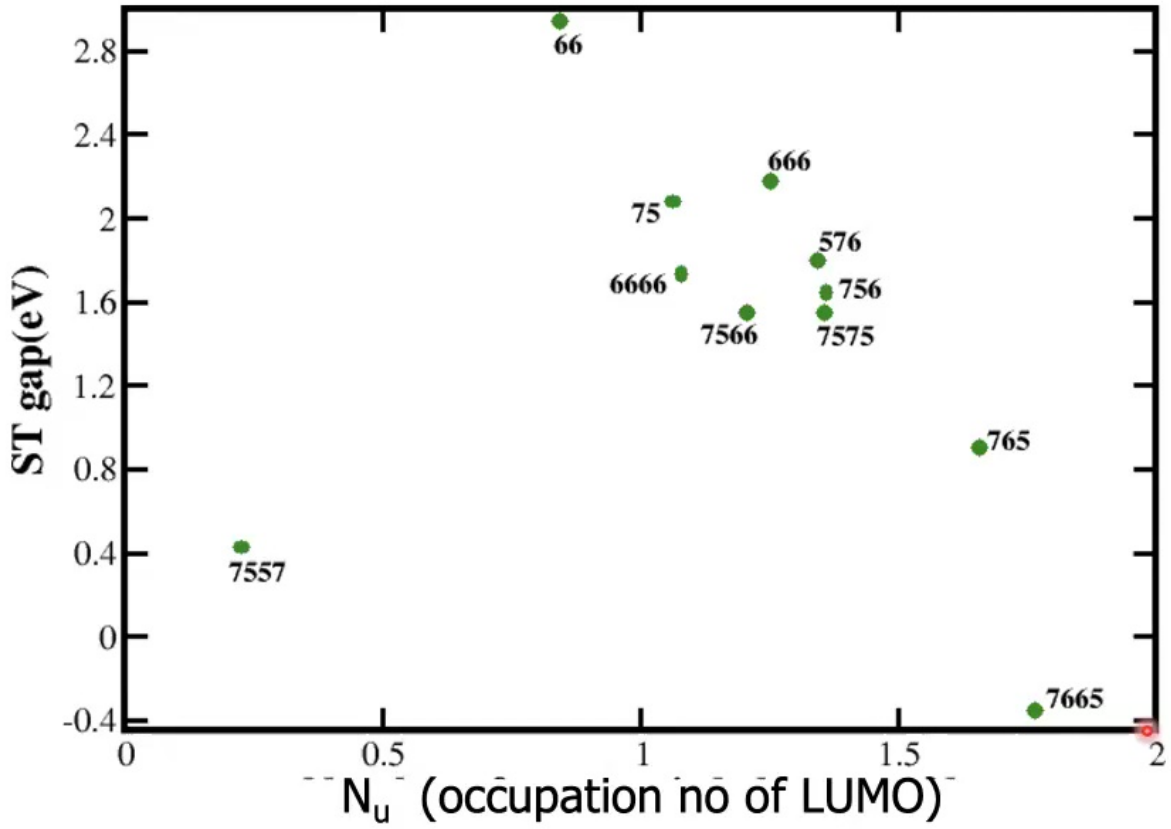
ST gap



Fused acene-azulene has much lower ST gap than polyacenes and **polyazulenes**!!

Rano, Ghosh, **DG**, Chemical Science, 2019

Low ST gap in fused acene-azulene



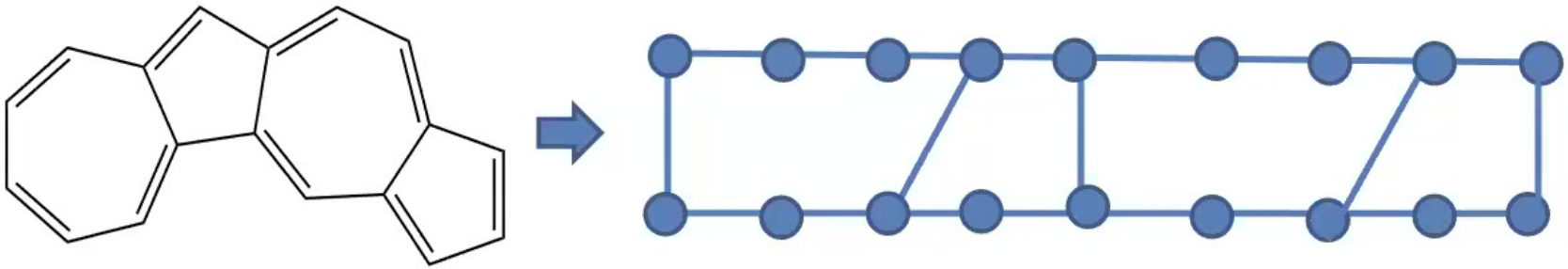
No correlation between diradical nature, HOMO-LUMO gap and ST gap

Spin Frustration

PHYSICAL REVIEW B **95**, 224408 (2017)

Quantum phases of frustrated two-leg spin-$\frac{1}{2}$ ladders with skewed rungs

Geetanjali Giri,[1,*] Dayasindhu Dey,[2,†] Manoranjan Kumar,[2,‡] S. Ramasesha,[1,§] and Zoltán G. Soos[3,‖]
[1]*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*
[2]*S. N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700098, India*
[3]*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*



Effect of spin frustration?

Let us create a model Hamiltonian :

- **Remove all lattice degrees of freedom**, i.e., variation in bond length
- **Remove all details of molecular Hamiltonian** – only nearest neighbor spin interactions

$$\hat{H} = \sum_{i,j} J_{ij} \overrightarrow{S_i} . \overrightarrow{S_j}$$

Effect of spin frustration?

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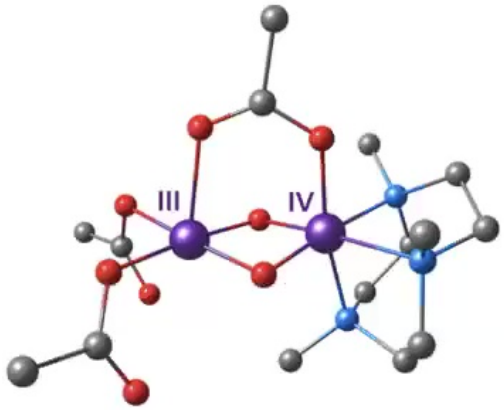
$$\hat{H} = \sum_{i,j} J_{ij} \overrightarrow{S_i} . \overrightarrow{S_j}$$

Single J → All bonds are equivalent.
Nearest neighbors interactions only.
Anti-ferromagnetic coupling – opposite spin in neighbor positions are preferred, i.e., bonding interaction (paired up electrons).

Model Hamiltonian from multireference QC methods

Landes interval rule

$$E(S) - E(S-1) = -2SJ_{AB}$$



Experimental J = -58.5 cm^{-1}

	M = 250	M=1000	M=3000
J (7/2-5/2)	-11.5	-57.5	-57.7
J (5/2-3/2)	-40.9	-58.7	-59.1
J (3/2-1/2)	-163.4	-60.9	-60.1
J	-71.9	-59.0	-59.1

Roemelt et al, JCTC (2018)
Kawakami et al, J Comput Chem (2018)

Partitioning Hamiltonian

$$H\left|\Psi_I\right\rangle = E_I\left|\Psi_I\right\rangle \longrightarrow H_{eff}\left|\tilde{\Psi}_I\right\rangle = E_I\left|\tilde{\Psi}_I\right\rangle$$

Operator can be decomposed into the model (P) and outer (Q) space

$$\tilde{H} = U^{-1}HU$$

Decouple and then project into the model space

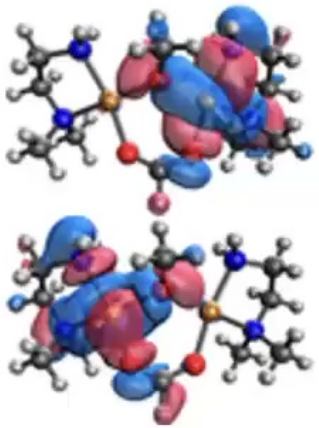
$$H_{eff} = P\tilde{H}P$$

Bloch and van Vleck

Bloch effective Hamiltonian – orders of perturbation (Malrieu and co-workers)

$$2J_{ab} = 2K_{ab} - \frac{4t_{ab}^2}{U}$$

Building a model Hamiltonian for a real molecule

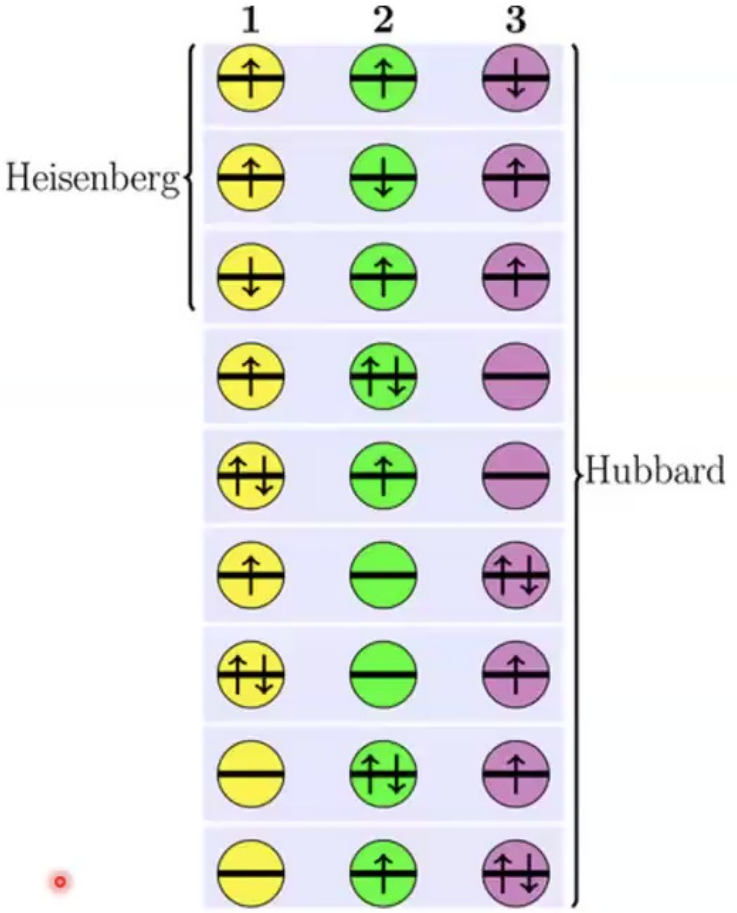


		OS	OS
B	OS	-1.48	35.32
	OS	35.08	1.48

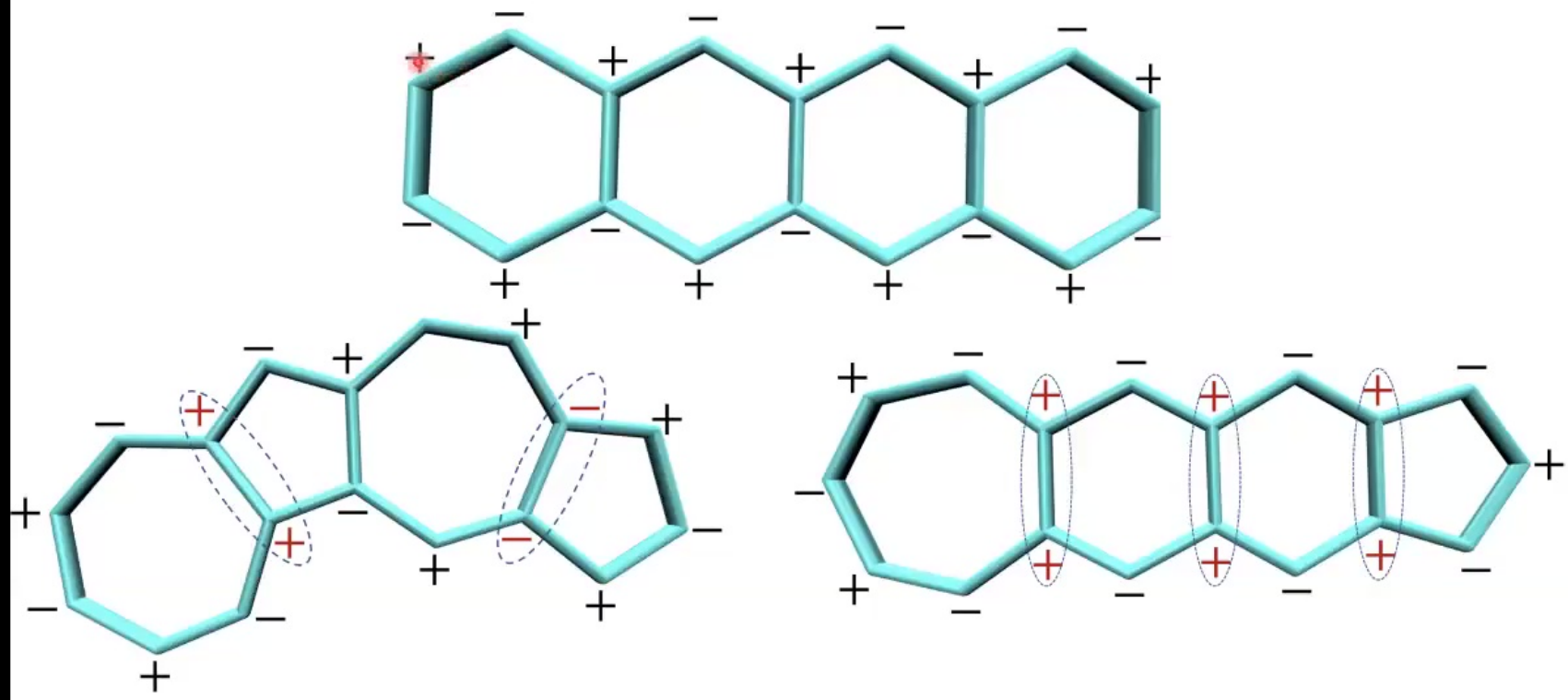
		OS	OS
C	OS	-1.48	35.20
	OS	35.20	1.48

Obtained from strongly correlated wavefunctions over small systems (dimers).

Mayhall, J. Chem. Theory Comput., (2016)
Rano, Ghosh, DG, Chemical Science, (2019)
Pokhilko, Krylov, J. Chem. Phys., (2020)

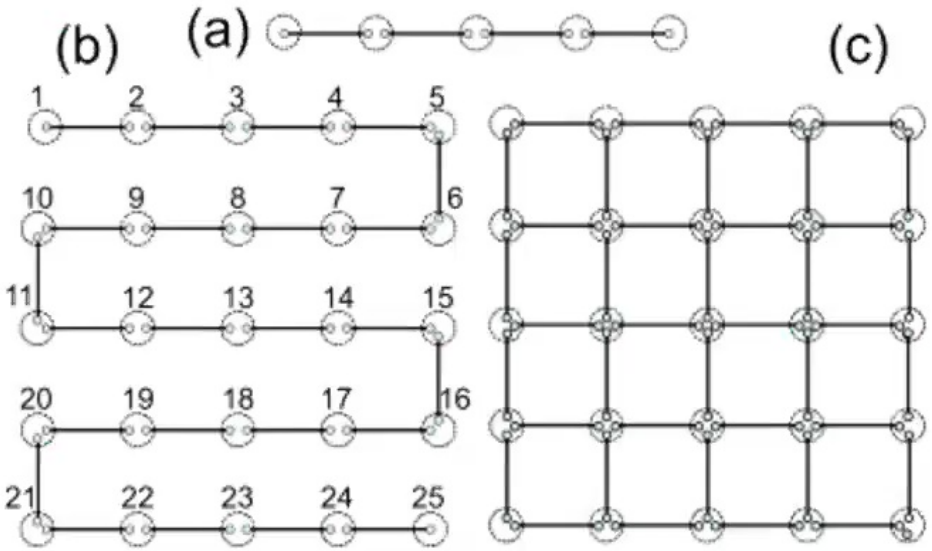


Spin frustrated configurations



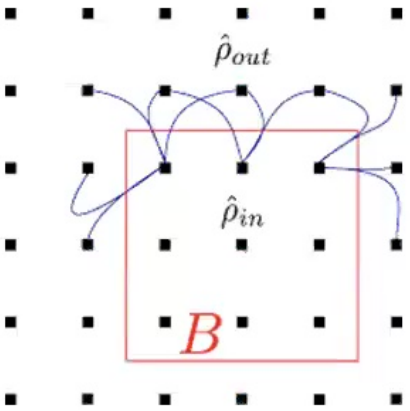
Rano, Ghosh, DG, Chemical Science, (2019)

Problem with extension to 2D systems

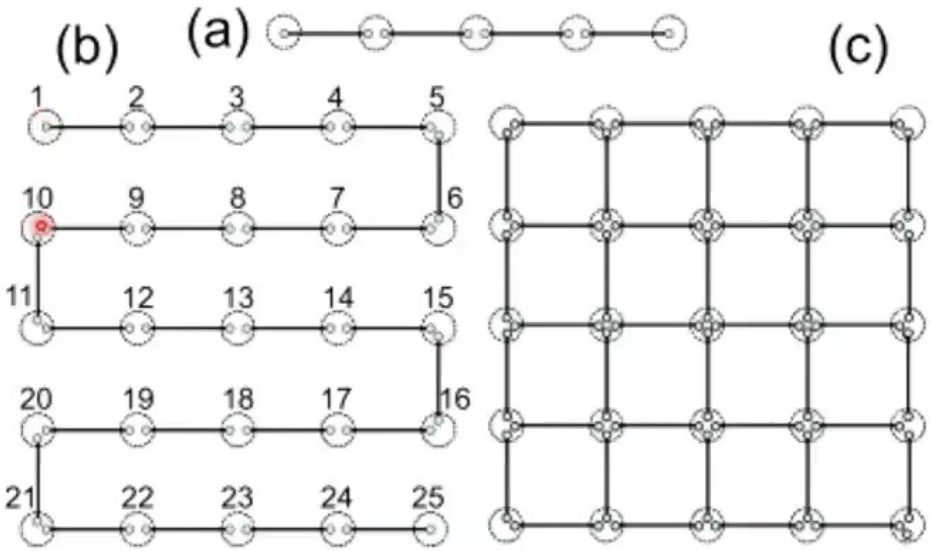


Area Law of Bipartite entanglement –

The **entanglement** entropy grows at most proportionally with the **area of boundary** between the two partitions.



Problem with extension to 2D systems



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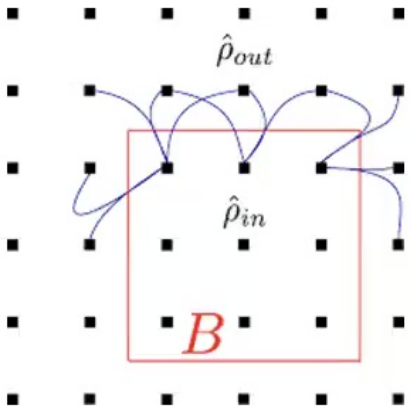
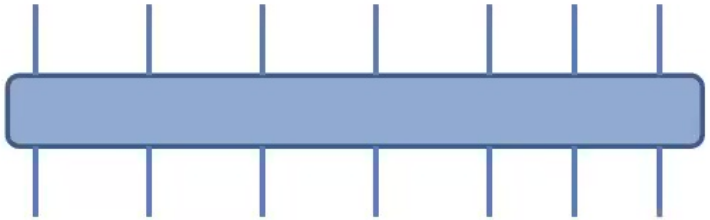
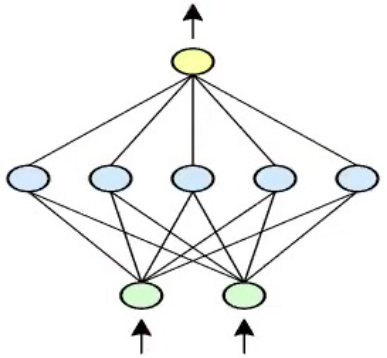


Rephrasing the optimization as a machine learning problem

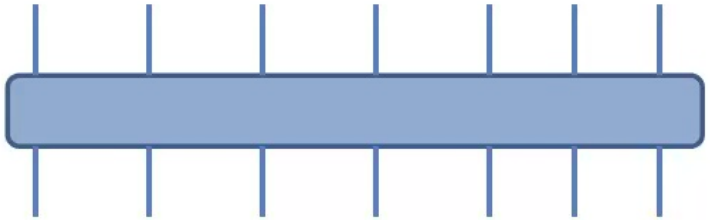


$\Leftrightarrow$



$$f(\vec{x}) = W\phi(\vec{x})$$

Rephrasing the optimization as a machine learning problem



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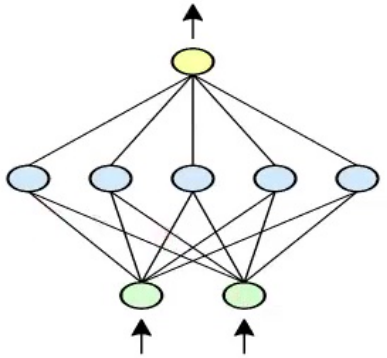
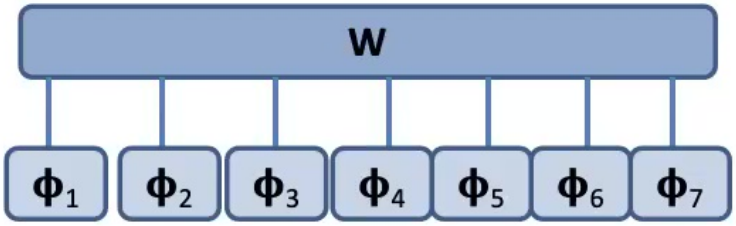


$$y(x) \rightarrow f(x)$$

$$f(\vec{x}) = W\phi(\vec{x})$$

- f(x) is extremely flexible
- f that is close to y for training data
- Simplest form of f(x)

Rephrasing the optimization as a machine learning problem

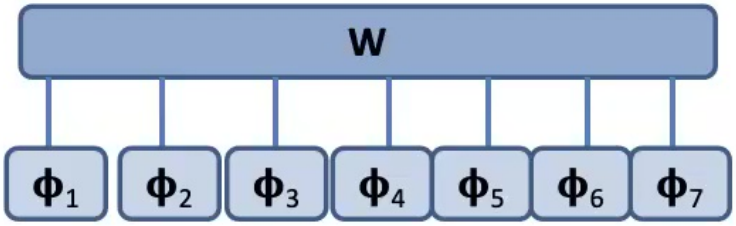


$$f(x) = W.\phi(x)$$

- Instead of minimizing the energy with respect to W, we optimize W to mimic the data.
- What is data? The known weights or CI coefficients.

$$C = | f(x) - y(x) |_W$$

Rephrasing the optimization as a machine learning problem



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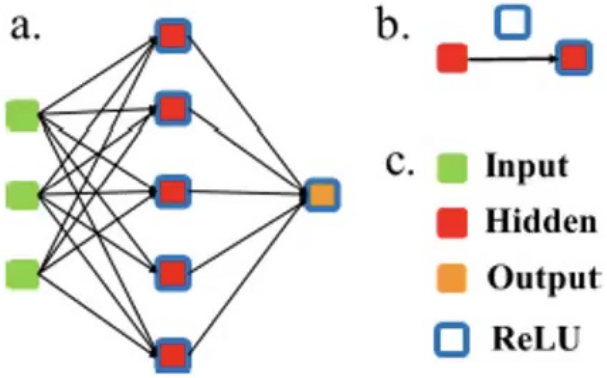
- Instead of minimizing the energy with respect to W, we optimize W to mimic the data.
- What is data? The known weights or CI coefficients.

$$C = | f(x) - y(x) |_W$$

- What is the benefit? We don't have to compute energy!

Network construction



$$u_j^{(1)} = \sum_{i=1}^{N_0} W_{ij}^{(1)} s_i + b_j^{(1)}$$

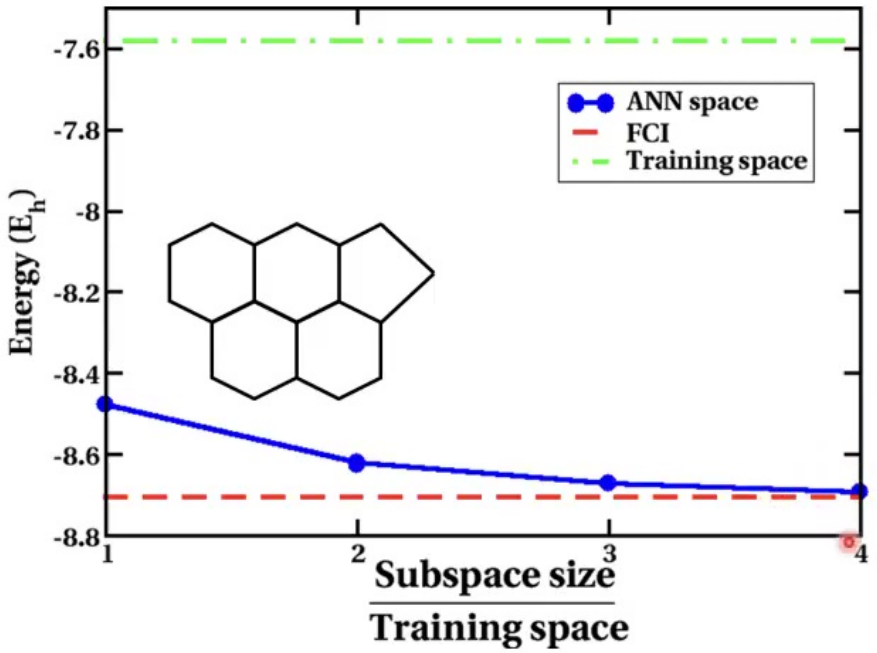
$$u_j^{(n)} = \sum_{i=1}^{N_{n-1}} W_{ij}^{(n)} f\left(u_i^{(n-1)}\right) + b_j^{(n-1)}$$

$\boldsymbol{\Psi}_{\mathrm{j}}$

$$\Psi_{exact} = \sum_j \psi_j \, | j \rangle$$

$$N_{param} = \sum_{n=1}^{L-1} N_n \left(N_{n-1} + 1 \right) + N_{L-1}$$

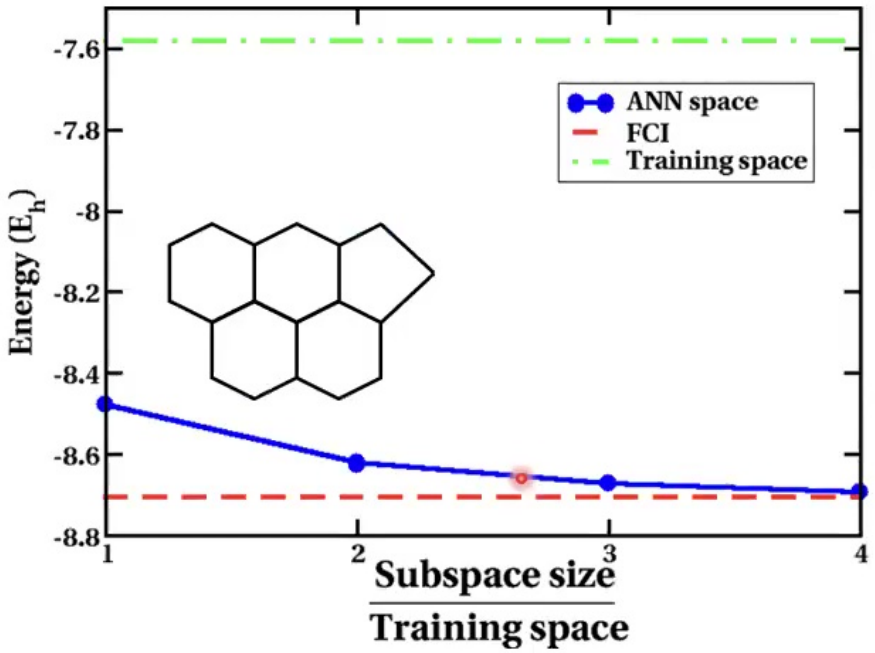
2D PAH energy



Final variational energy of ANN-CI is accurate wrt FCI (exact)

Ghosh, Rano, **DG**, JChemPhys (2021)
Seth, **DG**, J Chem Theory Comput (2023)

2D PAH energy



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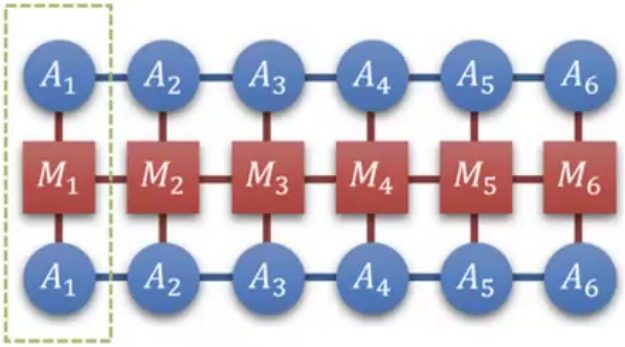
Optimizing MPS (variational vs ML)

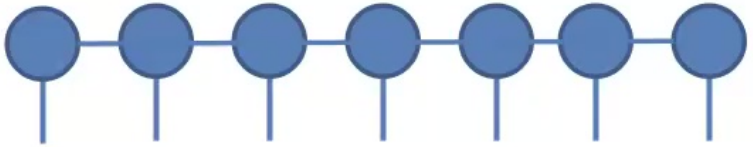


$$\varepsilon[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi \mid \Psi \rangle}$$

Computational scaling :

MPO based – $O(K^4)$

DMRG – $O(K^3)$

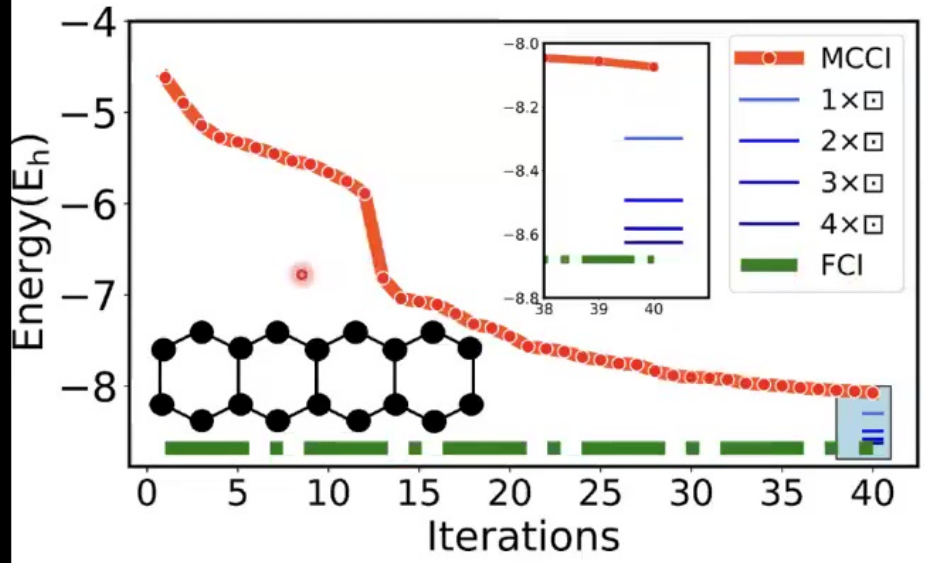


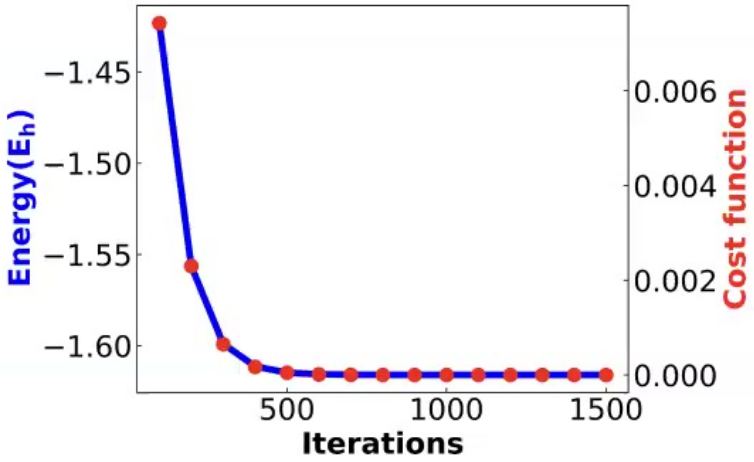
Optimizing each MPS via machine learning:

Scaling – K^*N_T

Stoudenmire, Schwab, arxiv:1605.05775 (2018)
Chan, Keselman, Nakatani, Li, White, JCP (2016)

Optimizing MPS (ML)

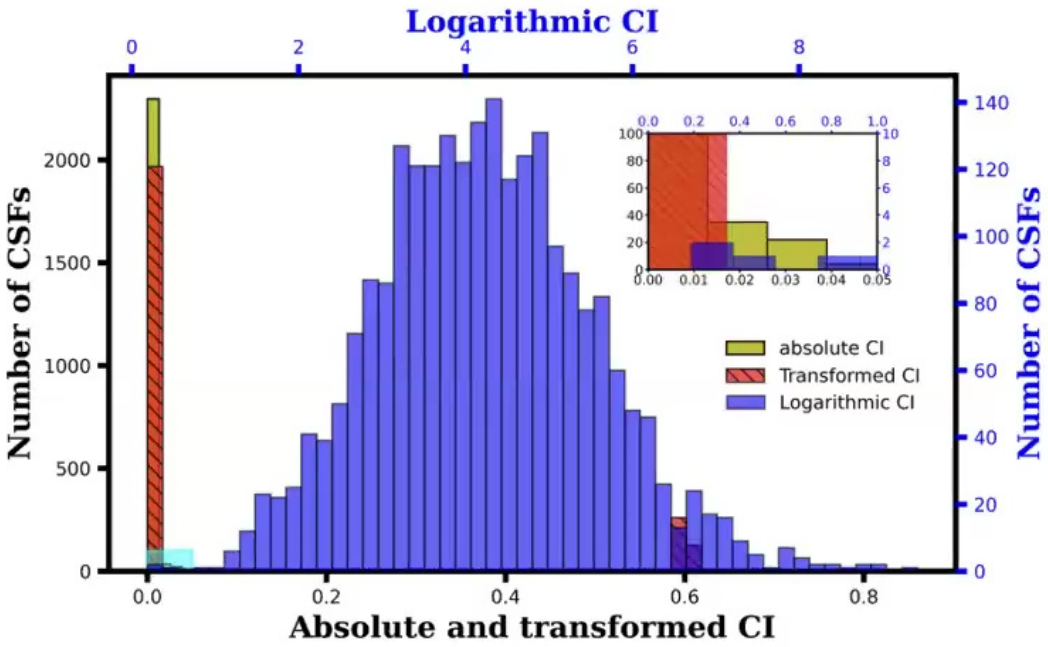




- Accurate estimate of the variational energies
- Energy and cost function are correlated. Cost function optimization can indeed be used as a proxy of energy minimization.

Ghosh, **DG**, J Chem Phys (2023)

Bond breaking problem



$|C_i|$

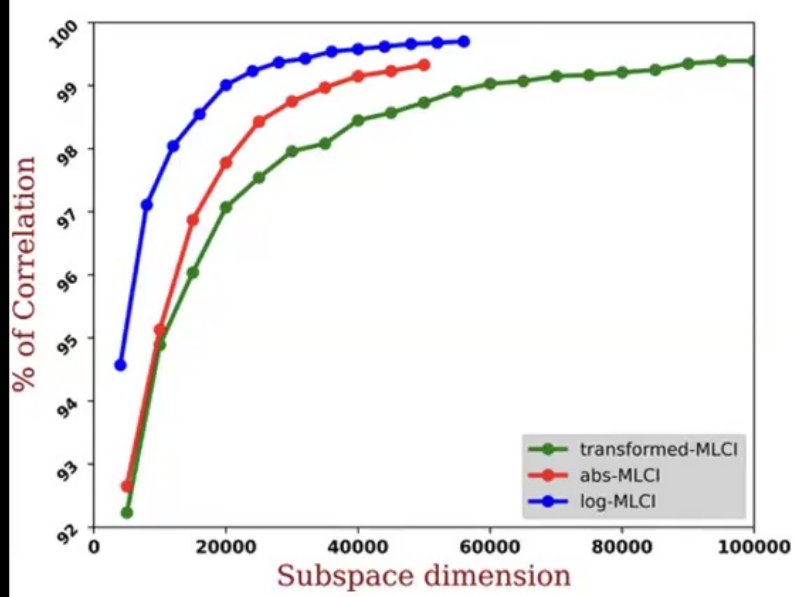
$$\frac{0.4|C_i| + 0.6 - C_{\min}}{1 - C_{\min}}$$

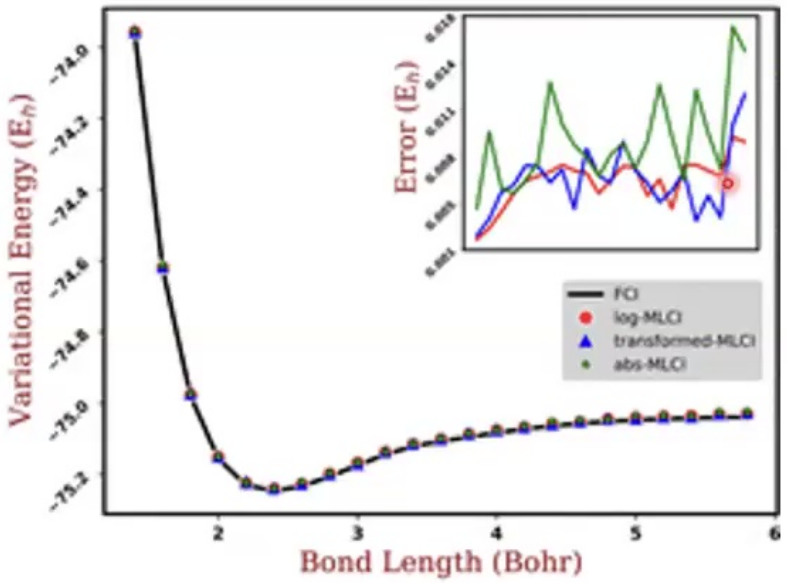
$-\log|C_i|$

- Distribution of CI coefficients is skewed
- Data balancing becomes an issue

Rano, **DG**, J Phys Chem A (2023)

Bond breaking problem

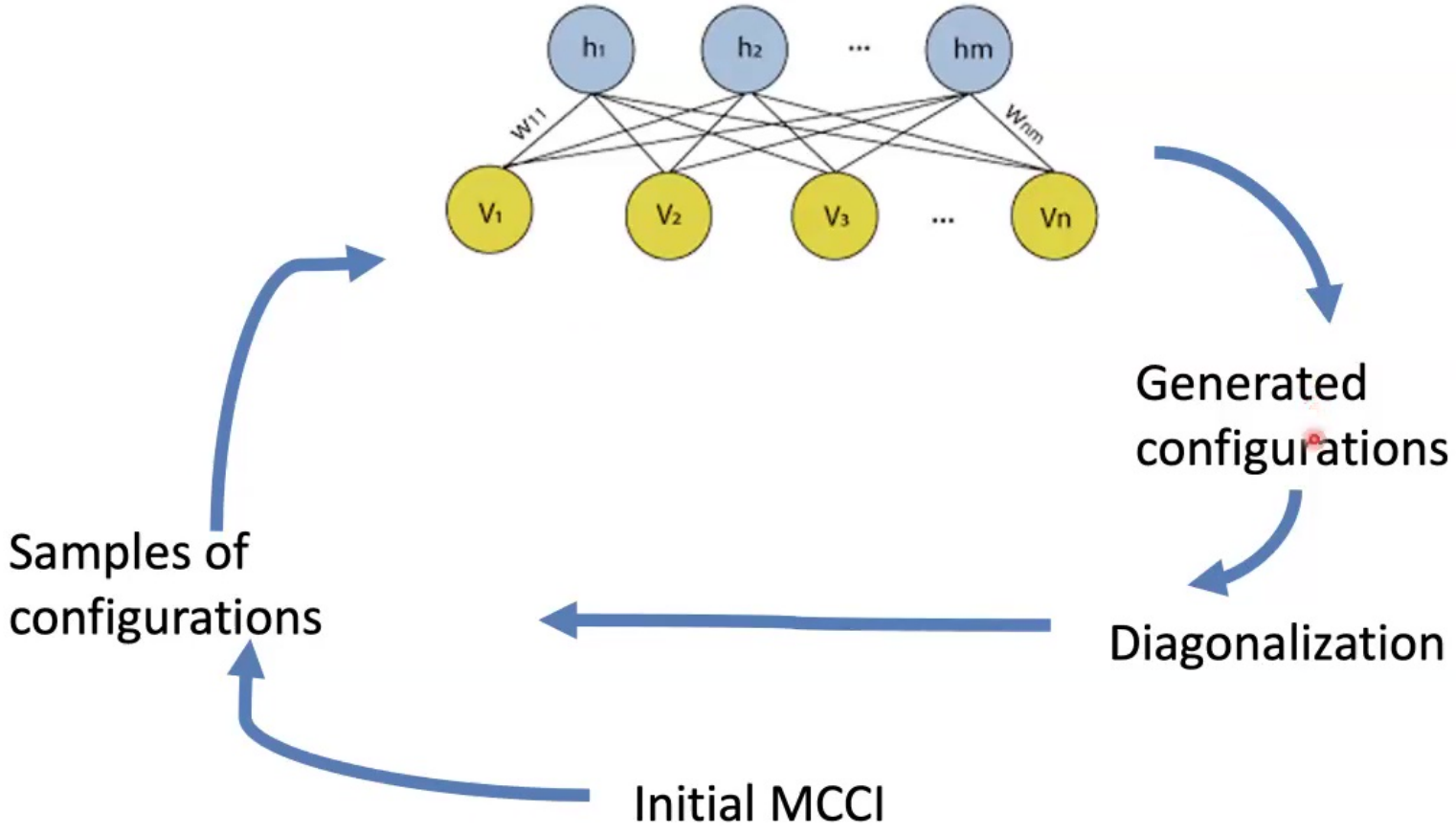




- Logarithm of CI coefficients is most effective

Rano, **DG**, J Phys Chem A (2023)

Generative learning



Conclusion

- Fused acene-azulene shows the largest decrease in ST gap and even possible ST crossover within 5 fused rings.
- This is largely due to spin frustration – which provides a new design principle to propose molecules with low ST gap.
- Extension to 2D systems is possible via artificial neural network.
- MPS optimization using machine learning.
- Generative learning to speed up Monte Carlo
- A very long wish list of methods to test….
- Problems inherent to chemistry has a different structure

Acknowledgement

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Indian Association for the Cultivation of Science

Science and Engineering Research Board

National Supercomputing Mission

Thank You!