Modeling singlet-fission biexciton states as an ab initio spin model: Justifications and applications

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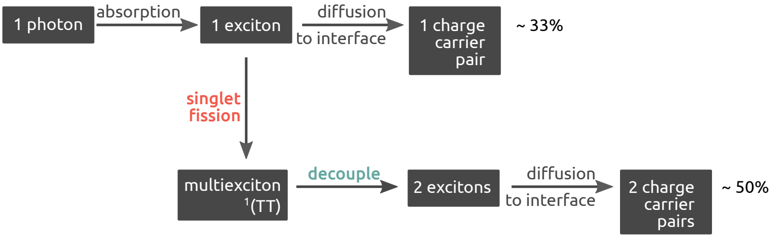
Virginia Tech

Singlet Fission

1 photon $\xrightarrow{\text{absorption}}$ 1 exciton $\xrightarrow[\text{to interface}]{\text{diffusion}}$ 1 charge carrier pair ~ 33%

Singlet Fission



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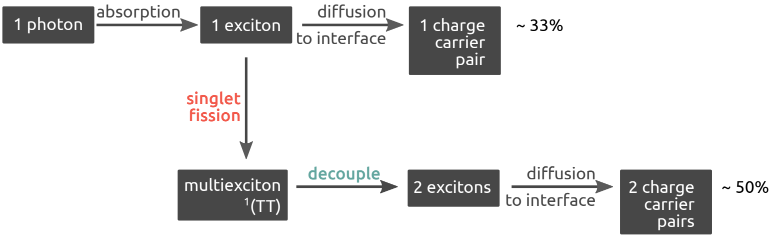

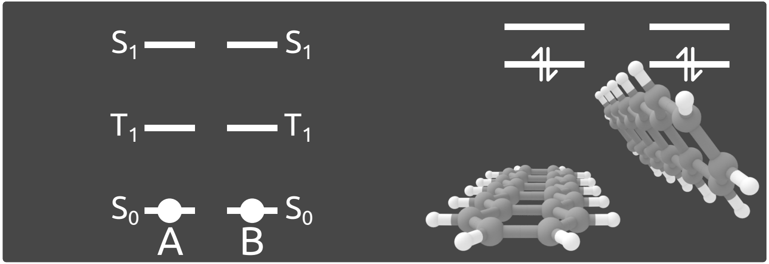

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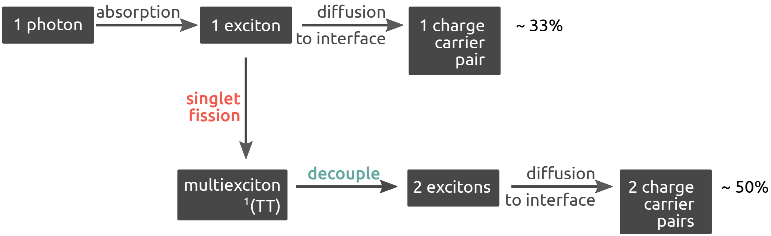

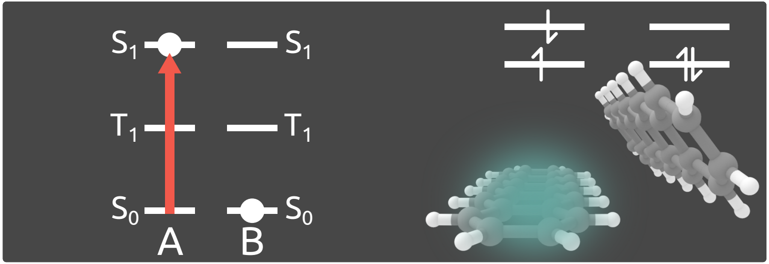

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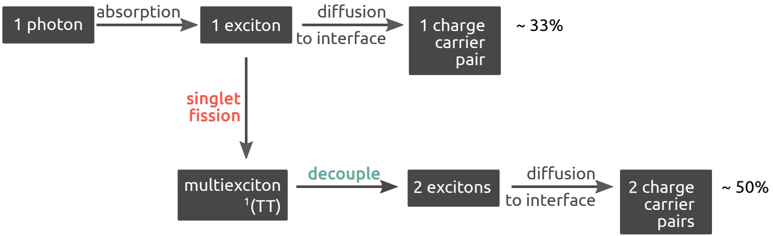

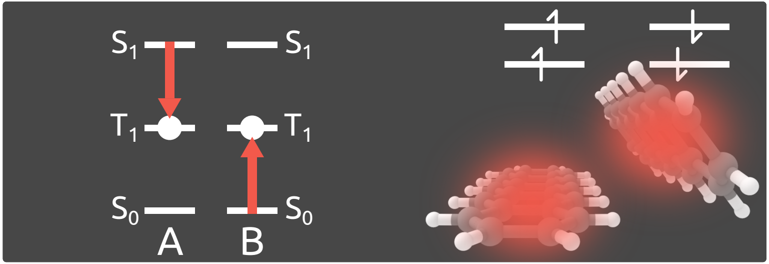

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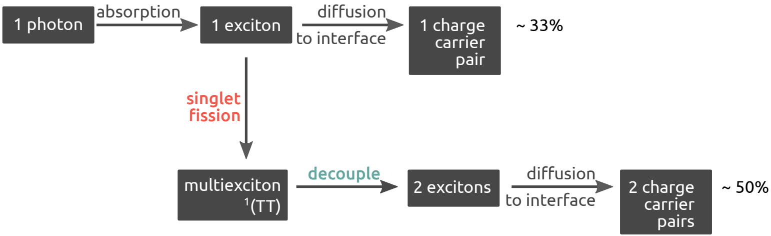

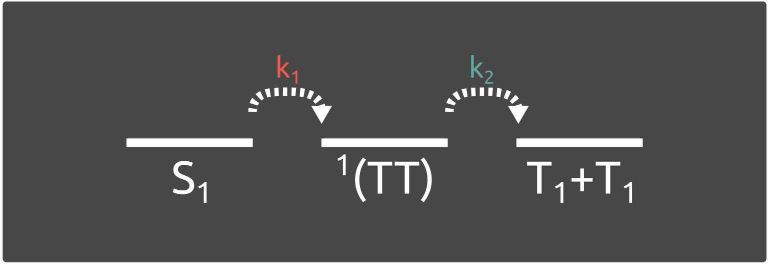

Kolomeisky, Feng, Krylov. JPCC, 118, 5188-5195 (2014)

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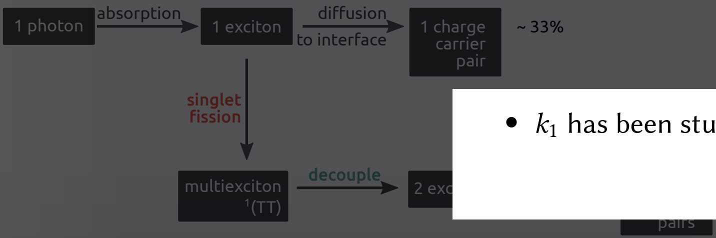
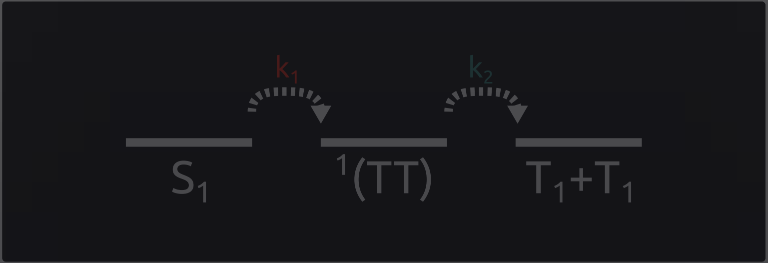


- k_1 has been studied extensively



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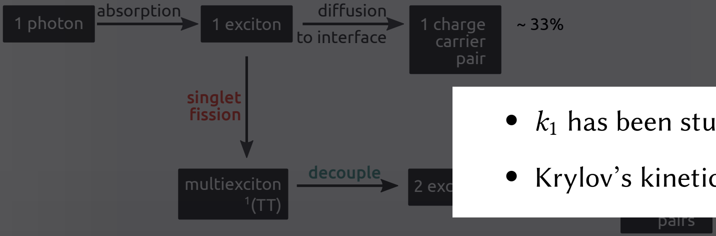
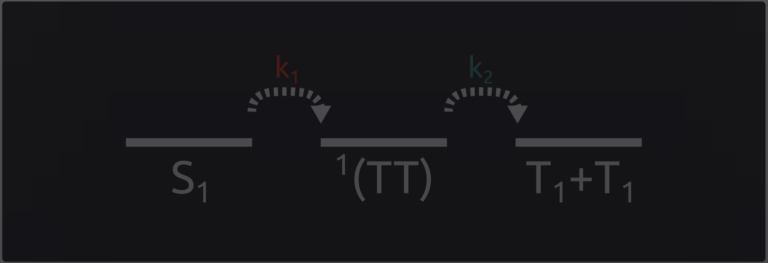


- k_1 has been studied extensively
- Krylov's kinetic model: $k_2 \approx e^{\frac{E_b}{2k_B T}}$



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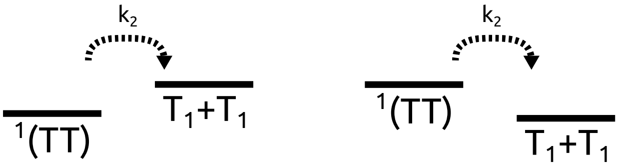

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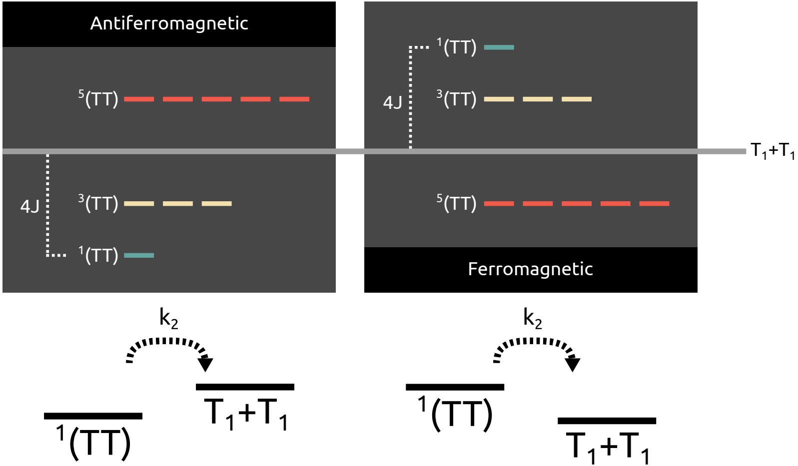

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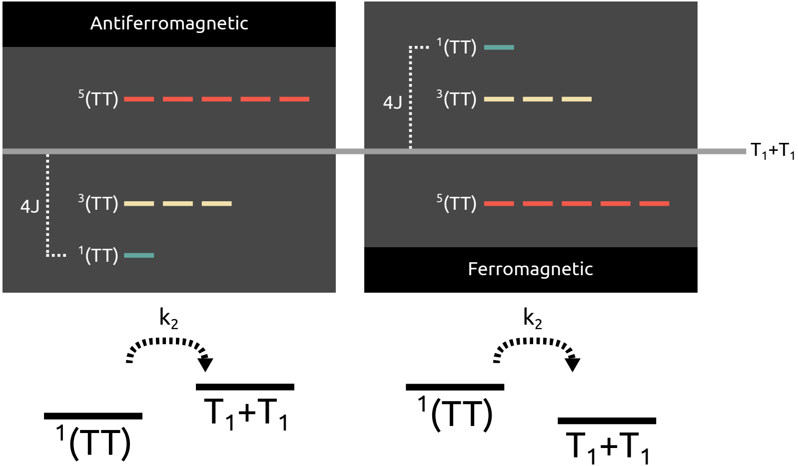

- 2-Spin-flip methods (RAS-2SF) very well suited

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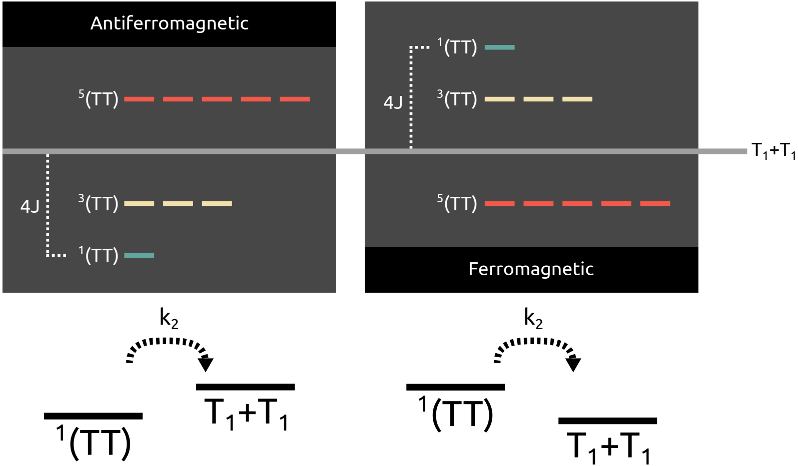

- 2-Spin-flip methods (RAS-2SF) very well suited
- However, the cost grows exponentially with active-space size

Approximation: Spin lattice

- Make approximation: $\hat{H} \approx -2 \sum_{AB} \mathrm{J}_{AB} \hat{S}_A \hat{S}_B$

- Much simpler to solve
- Provides deeper conceptual insight
- We have recently mapped 1SF calculations to a spin-Hamiltonian

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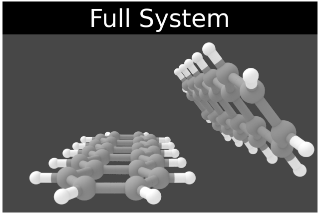

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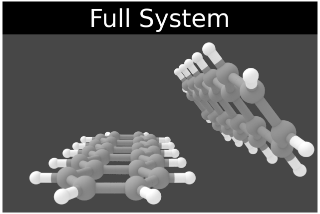

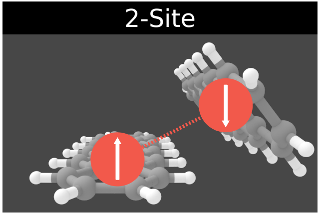

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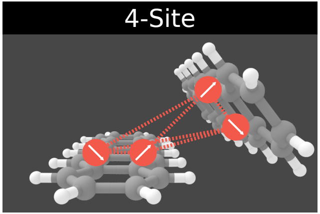

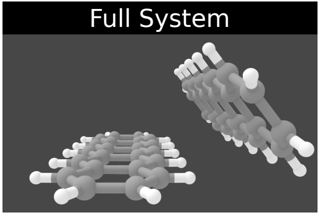

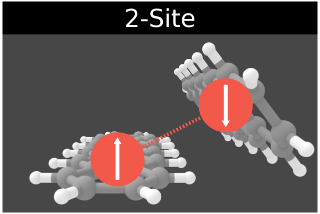

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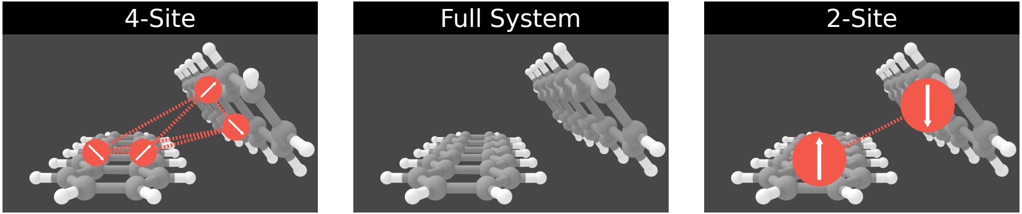

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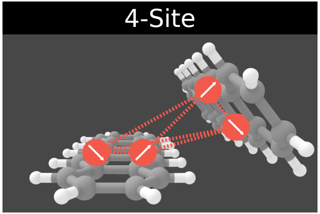

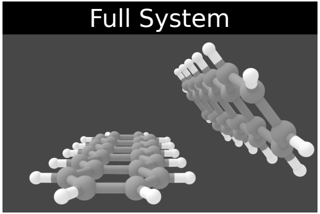

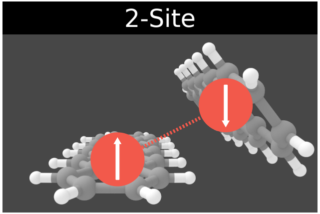

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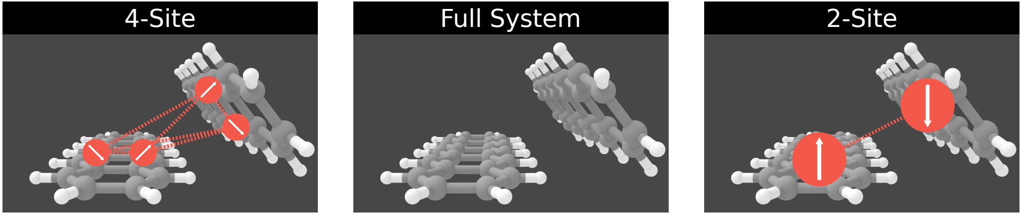

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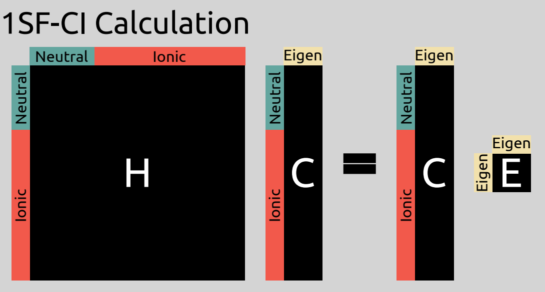
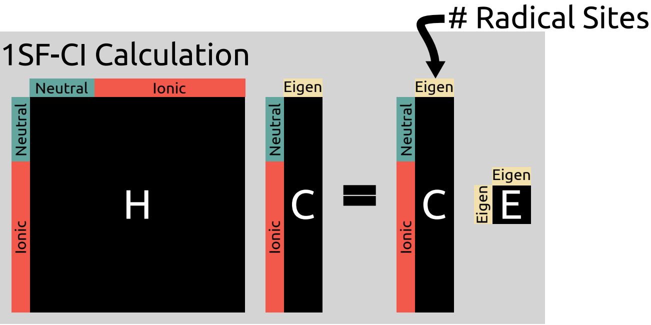
1. Mayhall, JCTC, 12, 4263 (2016)
2. Abraham, Mayhall, JPCL, 8, 5472 (2017)

Extracting the Spin Hamiltonian



Extracting the Spin Hamiltonian



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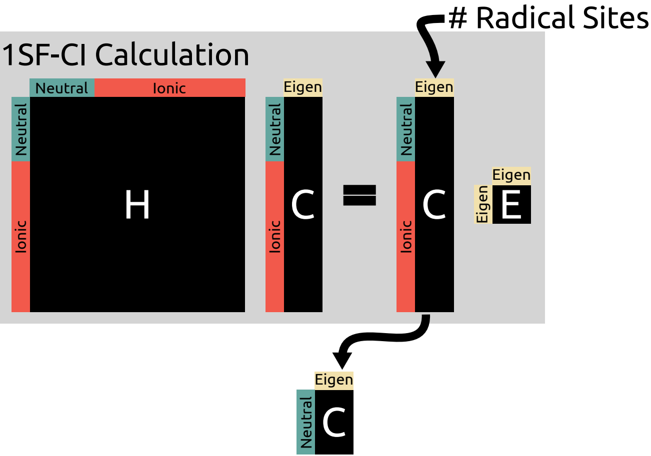

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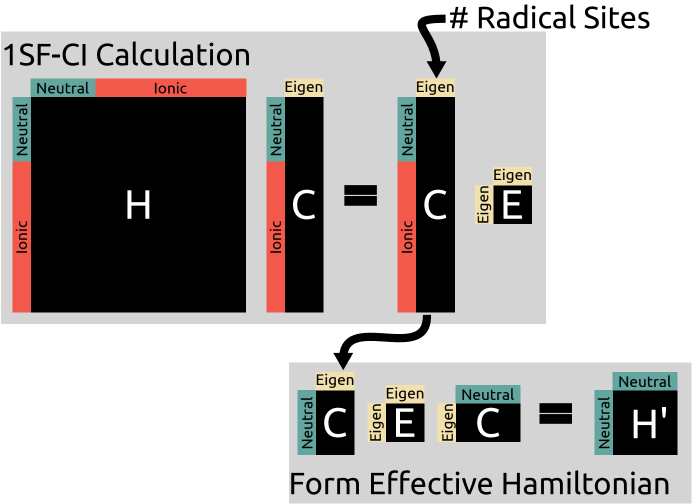

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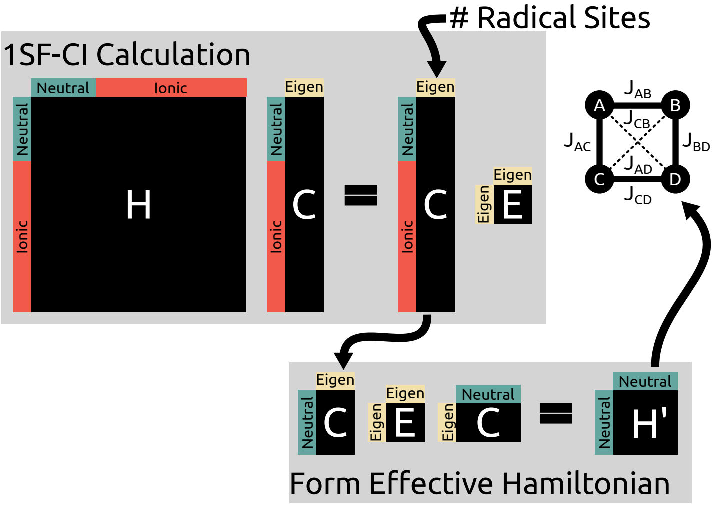
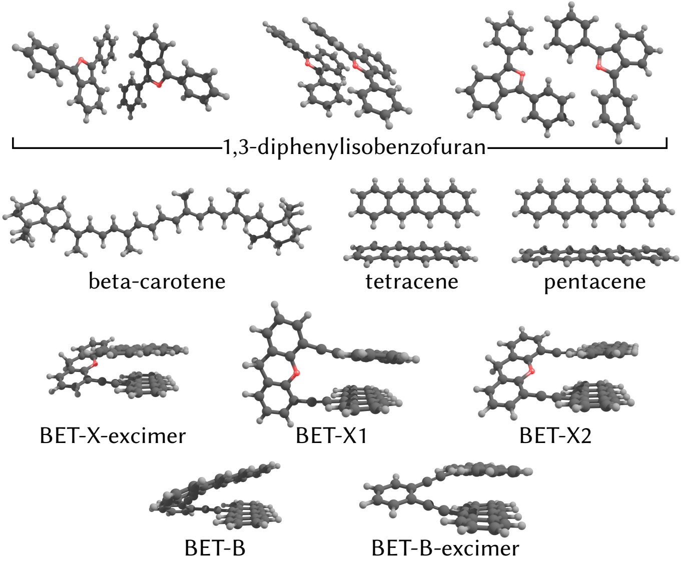


Extracting the Spin Hamiltonian

✓ 1SF calculation → J_{AB} for every pair of radical sites, regardless of total number of sites or electrons

Does this even work?



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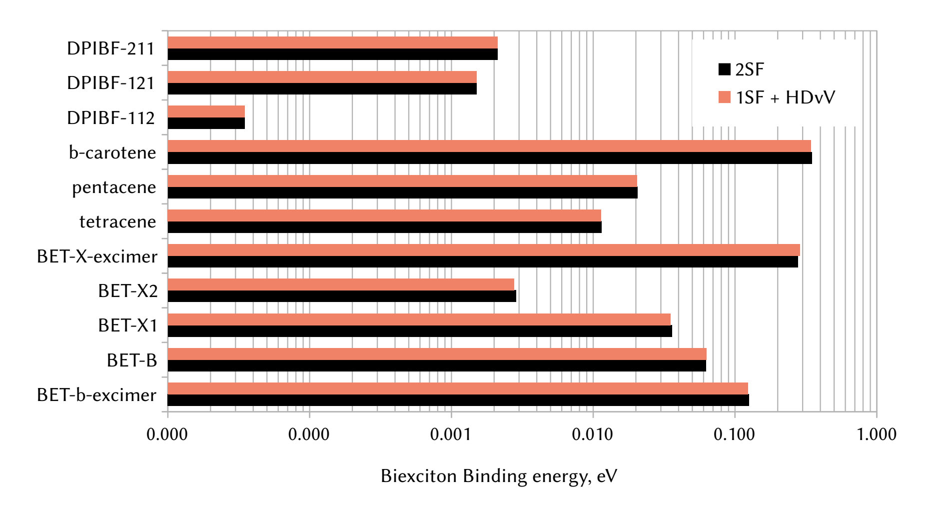

BET-B

BET-B-excimer

Mayhall, JCTC, 12, 4263 (2016)

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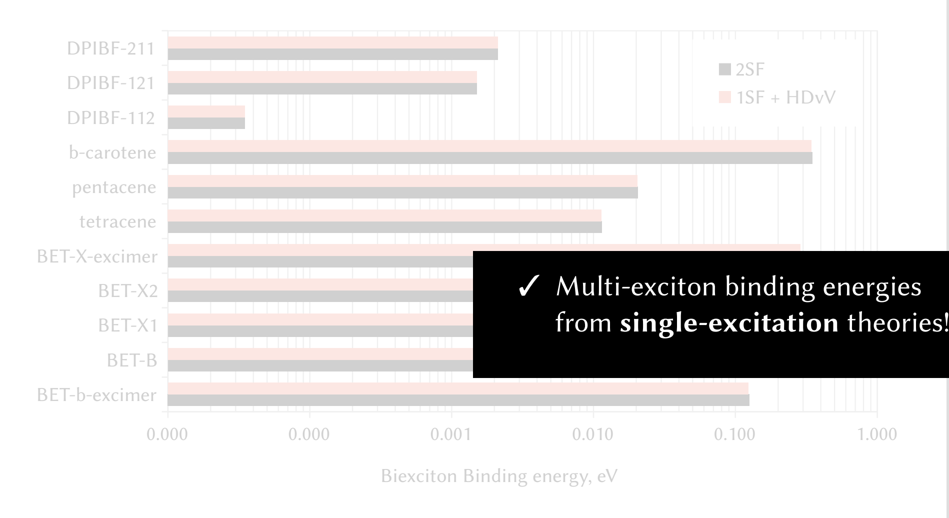
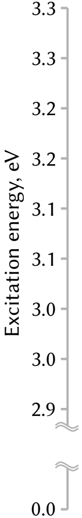
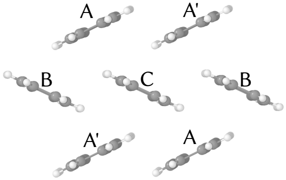


✓ Multi-exciton binding energies from **single-excitation** theories!

Mayhall, JCTC, 12, 4263 (2016)

Multiexcitons in molecular materials





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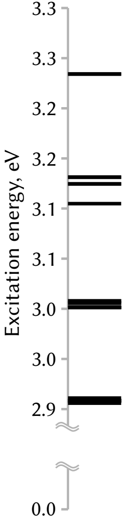
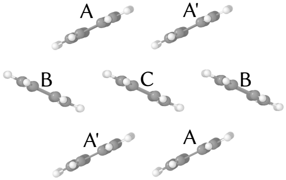
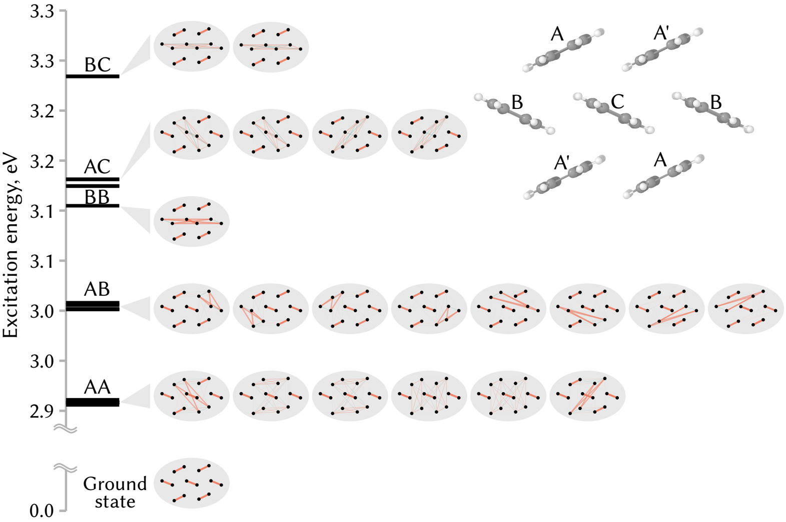




- 21 distinct $^1(TT)$ states
- Surprisingly large energy range!
- Compute correlation functions to characterize multiexciton states

Mayhall, JCTC, 12, 4263 (2016)

Multiexcitons in molecular materials



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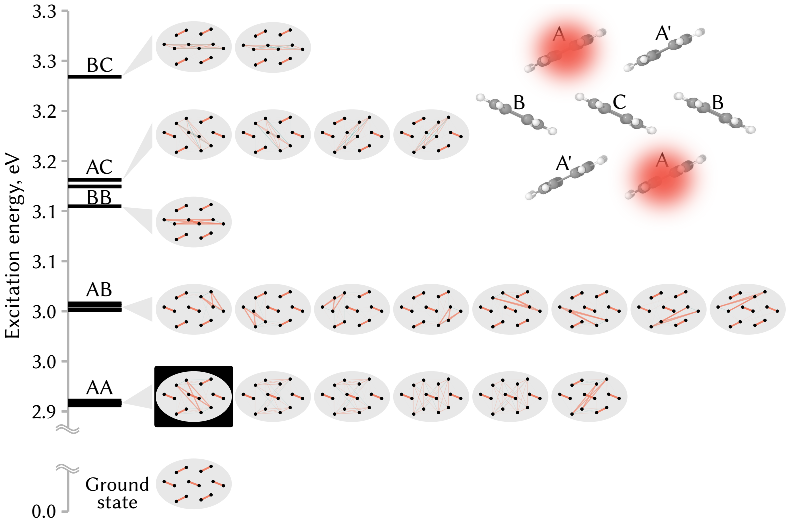

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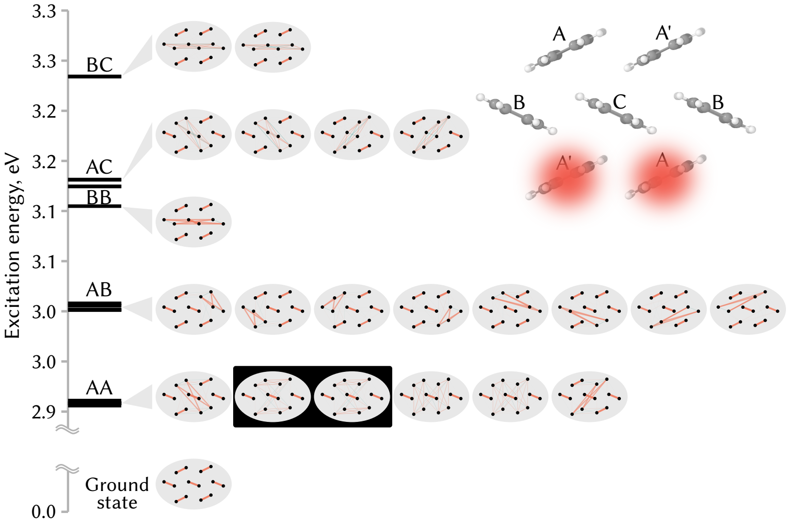

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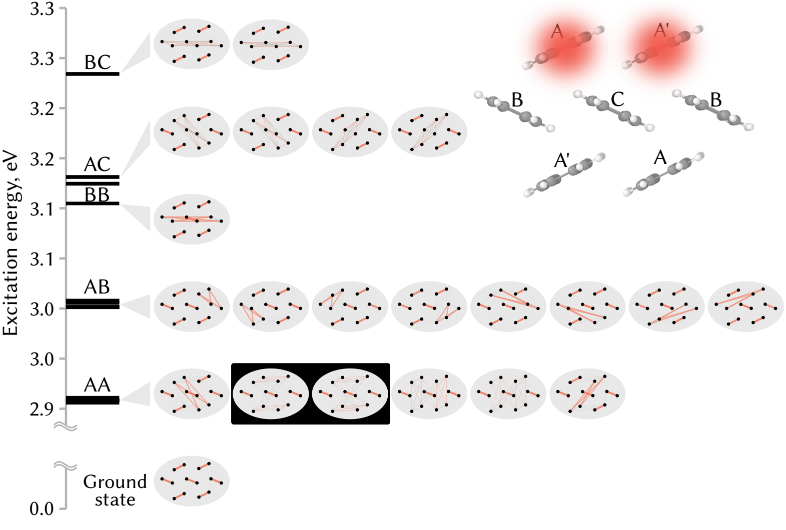

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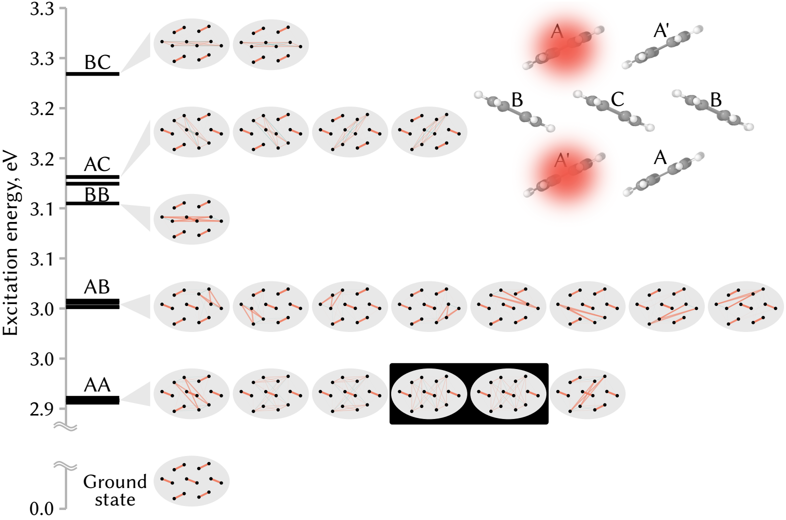

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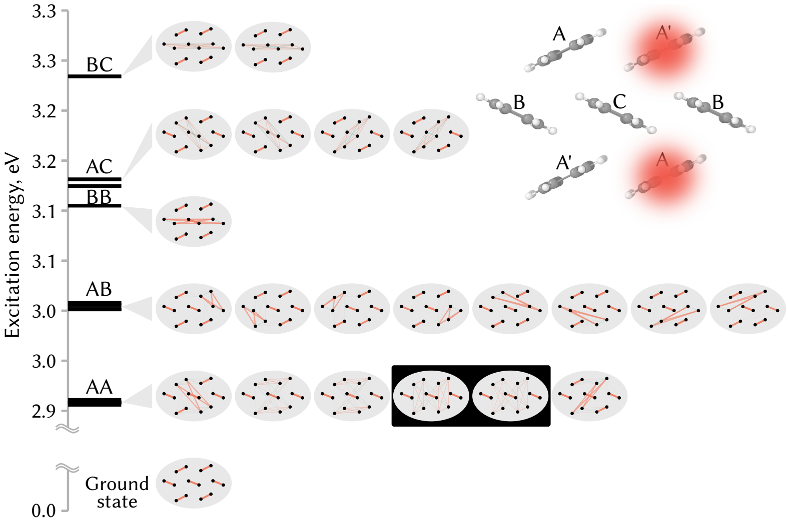

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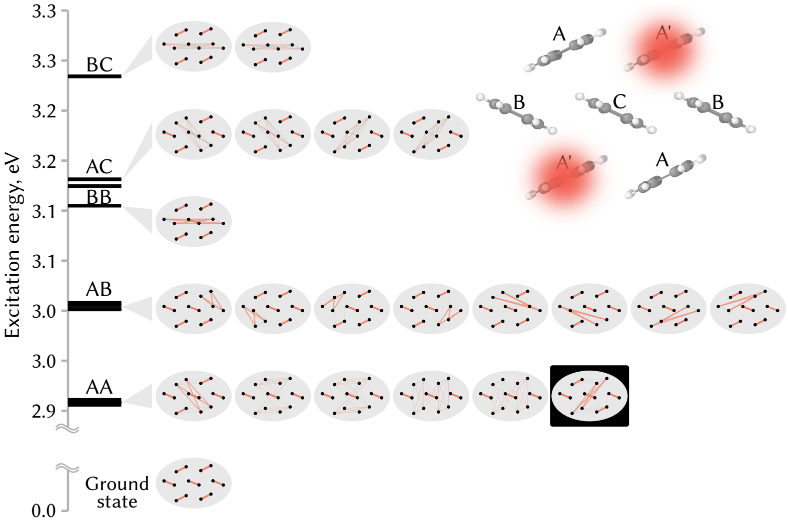

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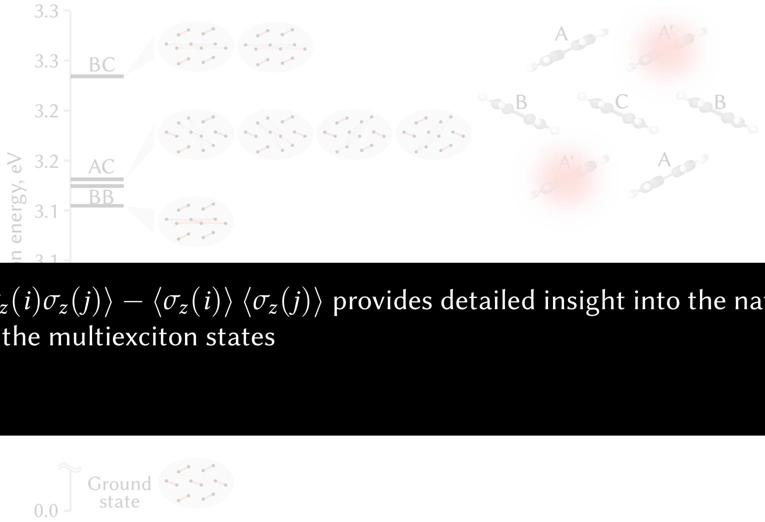

✓ $\langle \sigma_z(i)\sigma_z(j)\rangle - \langle \sigma_z(i)\rangle \langle \sigma_z(j)\rangle$ provides detailed insight into the nature of the multiexciton states

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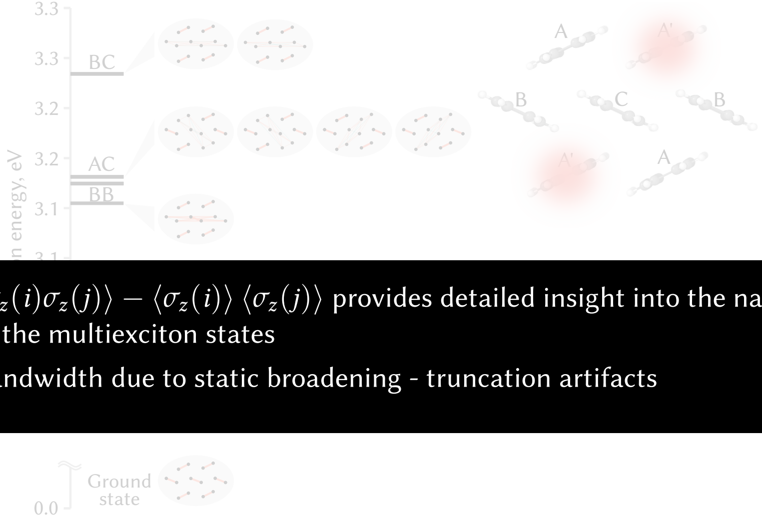
Multiexcitons in molecular materials



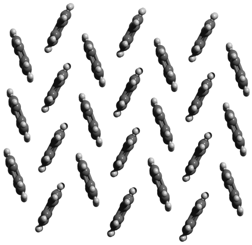
✓ $\langle \sigma_z(i)\sigma_z(j)\rangle - \langle \sigma_z(i)\rangle \langle \sigma_z(j)\rangle$ provides detailed insight into the nature of the multiexciton states

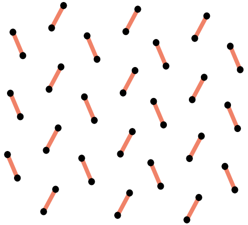
- Bandwidth due to static broadening - truncation artifacts

Mayhall, JCTC, 12, 4263 (2016)

Multiexcitons in molecular materials : Larger clusters

- Use ab initio parameters for systems too large for ab initio





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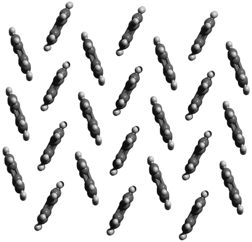
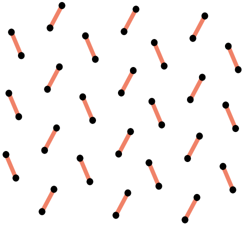
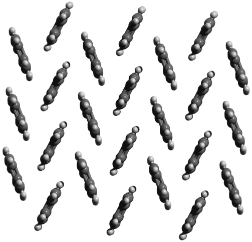
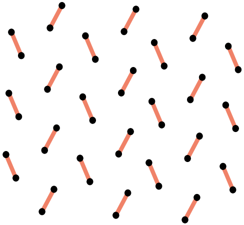




Multiexcitons in molecular materials : Larger clusters

- Use ab initio parameters for systems too large for ab initio
- Spin Lattice *still* exponentially scaling
- Use our recently developed *n*-Body Tucker decomposition
    - Talk tomorrow: COMP 487





Multiexcitons in molecular materials : Biexciton-Perturbation theory

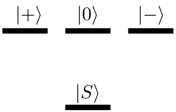
Monomer

$$|+\rangle = |\alpha\alpha\rangle$$

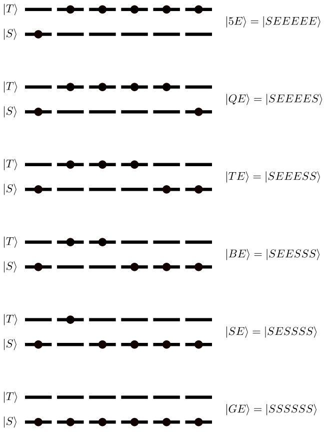
$$|-\rangle = |\beta\beta\rangle$$

$$|0\rangle = \frac{1}{\sqrt{2}}\,|\alpha\beta + \beta\alpha\rangle$$

$$|S\rangle = \frac{1}{\sqrt{2}}\,|\alpha\beta - \beta\alpha\rangle$$



6-mer



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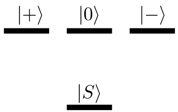

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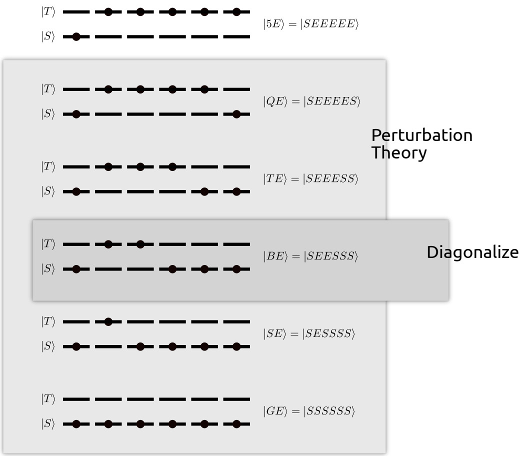

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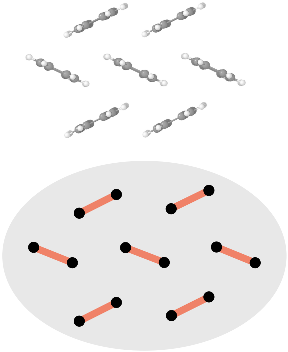
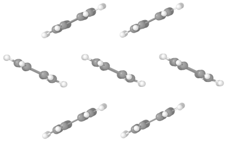
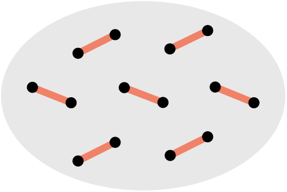
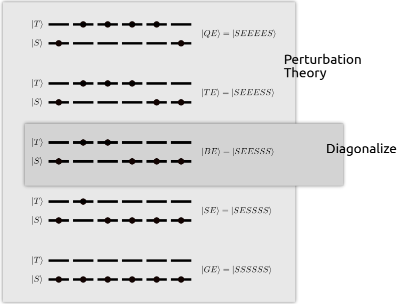


Multiexcitons in molecular materials : Biexciton-Perturbation theory

7-mer







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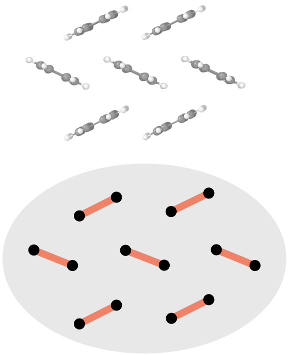

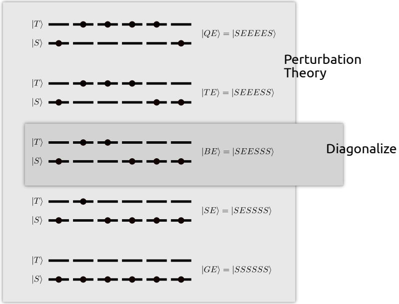

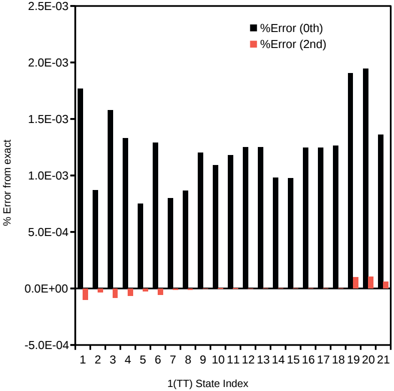

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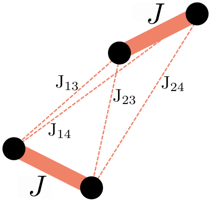

Multiexcitons in molecular materials : Biexciton-Perturbation theory

$$H = \begin{array}{r} \langle SS| \\ \langle S0| \\ \langle 0S| \\ \langle +-| \\ \langle 00| \\ \langle -+| \end{array} \left[\begin{array}{ccc|ccc} 6E & 0 & 0 & -t & t & -t \\ 0 & 2E & t & p & 0 & -p \\ 0 & t & 2E & q & 0 & -q \\ \hline -t & p & q & -r-2E & r & 0 \\ t & 0 & 0 & r & -2E & r \\ -t & -p & -q & 0 & r & -r-2E \end{array}\right]$$

$$E = 0.5 \times J$$
$$r = 0.5 \times (J_{13} + J_{14} + J_{23} + J_{24})$$
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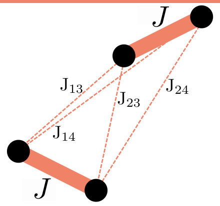

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Block
Diagonalize
Biexcitons

$$H=\begin{array}{r}\langle SS| \\ \langle S0| \\ \langle 0S| \\ {}^{5}(\mathrm{TT}) \\ {}^{1}(\mathrm{TT}) \\ {}^{3}(\mathrm{TT})\end{array}\left[\begin{array}{ccc|ccc} 6E & 0 & 0 & 0 & -\sqrt{3}t & 0 \\ 0 & 2E & t & 0 & 0 & -\sqrt{2}p \\ 0 & t & 2E & 0 & 0 & -\sqrt{2}q \\ \hline 0 & 0 & 0 & r-2E & 0 & 0 \\ -\sqrt{3}t & 0 & 0 & 0 & -2E-2r & 0 \\ 0 & -\sqrt{2}p & -\sqrt{2}q & 0 & 0 & -r-2E \end{array}\right]$$

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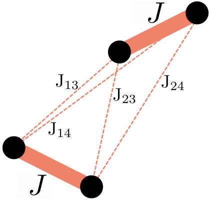

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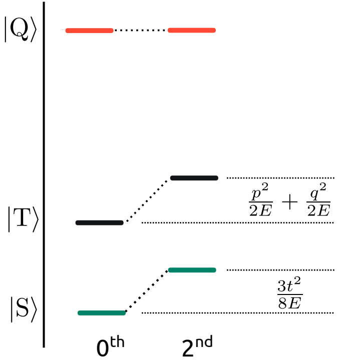
Block Diagonalize Biexcitons

$$H = \begin{array}{r}\langle SS| \\ \langle S0| \\ \langle 0S| \\ {}^{5}(TT) \\ {}^{1}(TT) \\ {}^{3}(TT)\end{array}\left[\begin{array}{ccc|ccc} 6E & 0 & 0 & 0 & -\sqrt{3}t & 0 \\ 0 & 2E & t & 0 & 0 & -\sqrt{2}p \\ 0 & t & 2E & 0 & 0 & -\sqrt{2}q \\ \hline 0 & 0 & 0 & r-2E & 0 & 0 \\ -\sqrt{3}t & 0 & 0 & 0 & -2E-2r & 0 \\ 0 & -\sqrt{2}p & -\sqrt{2}q & 0 & 0 & -r-2E \end{array}\right]$$



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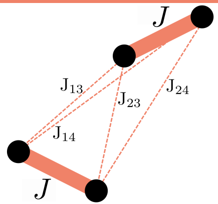


$$H = \begin{array}{c} \langle SS| \\ \langle S0| \\ \langle 0S| \\ \langle +-| \\ \langle 00| \\ \langle -+| \end{array} \left[\begin{array}{ccc|ccc} 6E & 0 & 0 & -t & t & -t \\ 0 & 2E & t & p & 0 & -p \\ 0 & t & 2E & q & 0 & -q \\ \hline -t & p & q & -r-2E & r & 0 \\ t & 0 & 0 & r & -2E & r \\ -t & -p & -q & 0 & r & -r-2E \end{array}\right]$$

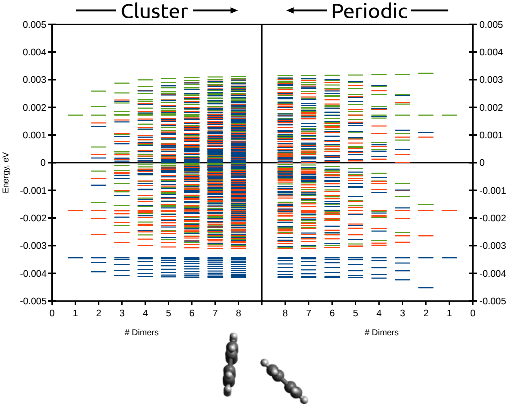
Block Diagonalize Biexcitons

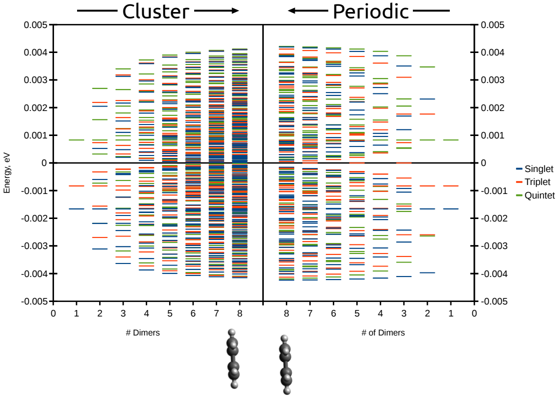
- Zeroth-order identical to simpler 2-site model
- 4-site model gives positional information
- We can understand larger clusters similarly:

$$\mathrm{H} = \begin{array}{c|ccc} & |^1TT(AB)\rangle & |^1TT(AC)\rangle & |^1TT(BC)\rangle \\ \hline \langle ^1TT(AB)| & -2E - 2\mathrm{r}_{AB} & \mathrm{t}_{BC} & \mathrm{t}_{AC} \\ \langle ^1TT(AC)| & \mathrm{t}_{BC} & -2E - 2\mathrm{r}_{AC} & \mathrm{t}_{AB} \\ \langle ^1TT(BC)| & \mathrm{t}_{AC} & \mathrm{t}_{AB} & -2E - 2\mathrm{r}_{BC} \end{array}$$

Multiexcitons in molecular materials : Larger clusters

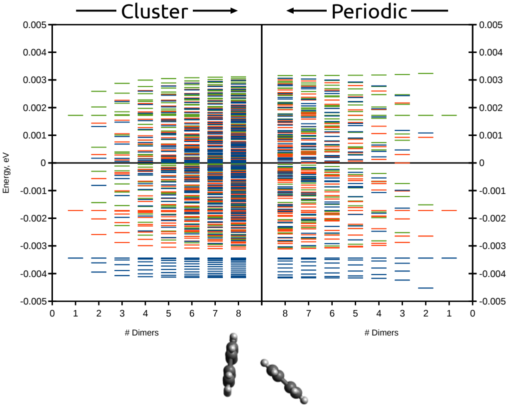
- Herringbone pattern produces a gapped singlet band at the bottom of the spectrum

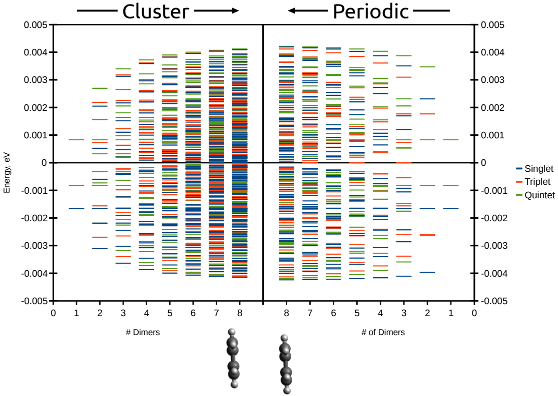




Multiexcitons in molecular materials : Larger clusters

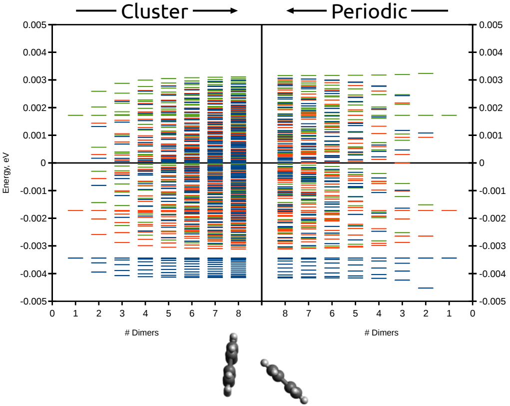
- Herringbone pattern produces a gapped singlet band at the bottom of the spectrum
- Open and Periodic boundary conditions converge

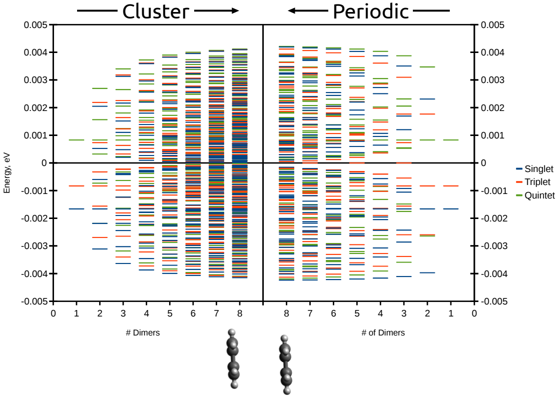




Multiexcitons in molecular materials : Larger clusters

- Herringbone pattern produces a gapped singlet band at the bottom of the spectrum
- Open and Periodic boundary conditions converge
- Parallel alignment has significantly larger coupling/bandwidth





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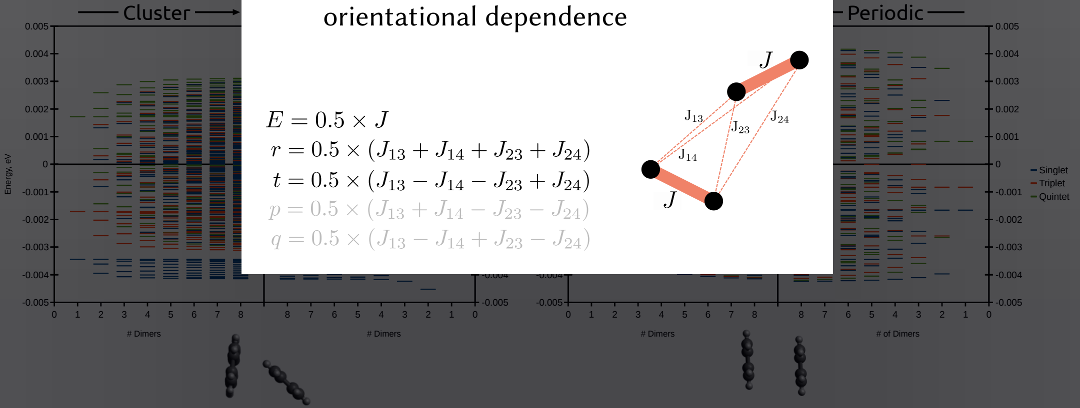

- t is only zeroth-order quantity with orientational dependence

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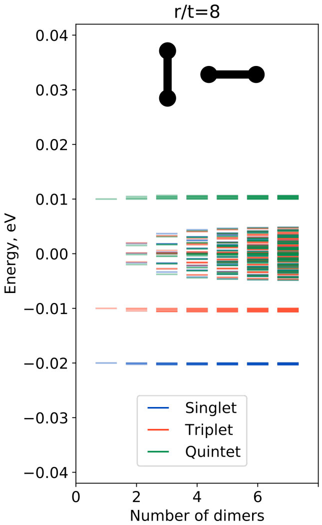
Multiexcitons in molecular materials : Larger clusters

- perpendicular(t=0): parallel(t=max)



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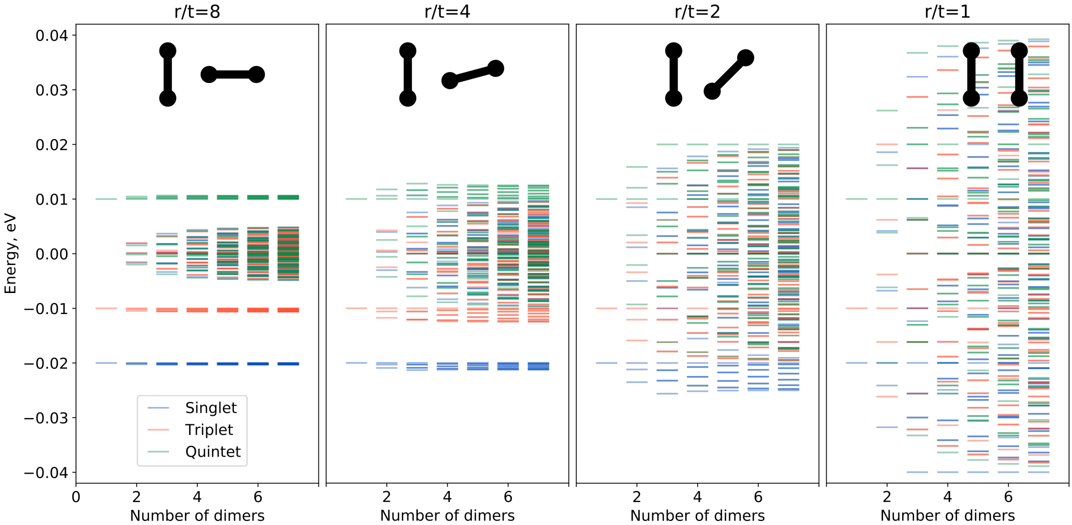
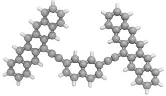


An Ovchinnikov's Rule for excited states

- What about covalently-linked the dimers?
  - More control over dimer-coupling
  - Now both through-*space* and through-*bond* interactions



- Map onto Ising model: $\hat{H} = -\sum_{ij} \mathcal{J}_{ij}\hat{S}_i^z\hat{S}_j^z$
- Ovchinnikov's Rule : $S = \frac{N_\alpha - N_\beta}{2}$

Abraham, Mayhall, JPCL, 8, 5472 (2017)

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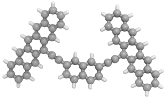

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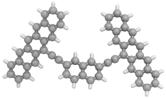

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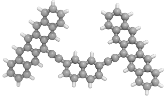

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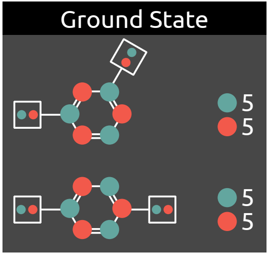

Both **singlets**

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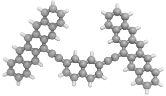

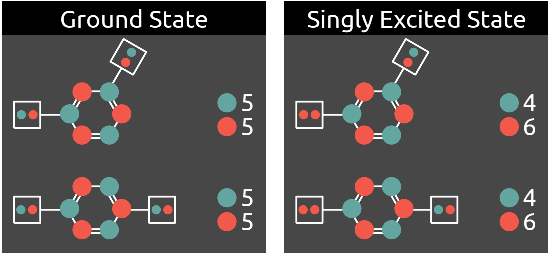

Both **singlets** Both **triplets**

Abraham, Mayhall, JPCL, 8, 5472 (2017)

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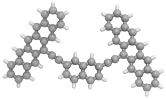

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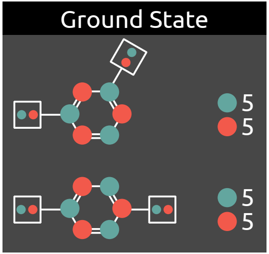

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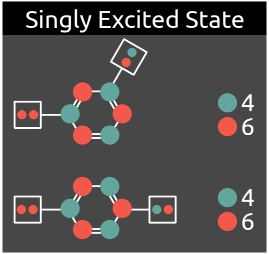

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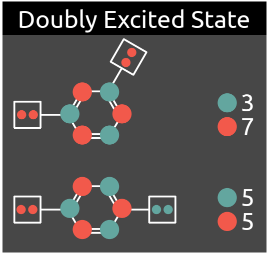

1 **singlet**
1 **quintet**

Abraham, Mayhall, JPCL, 8, 5472 (2017)

An Ovchinnikov's Rule for excited states

- What about covalently-linked the dimers?
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  - Now both through-*space* and through-*bond* interactions

- Map onto Ising model: $\hat{H} = -\sum_{ij} \mathcal{J}_{ij}\hat{S}^z_i\hat{S}^z_j$

- **Hypothesis**: *The through-bond ordering of multiexciton spin-states is predicted by pairity of connection:*
  - *even* $\longrightarrow$ *AF: Bound* $^1(TT)$
  - *odd* $\longrightarrow$ *FM: Unbound* $^5(TT)$

Both **singlets**

Both **triplets**

1 **singlet**
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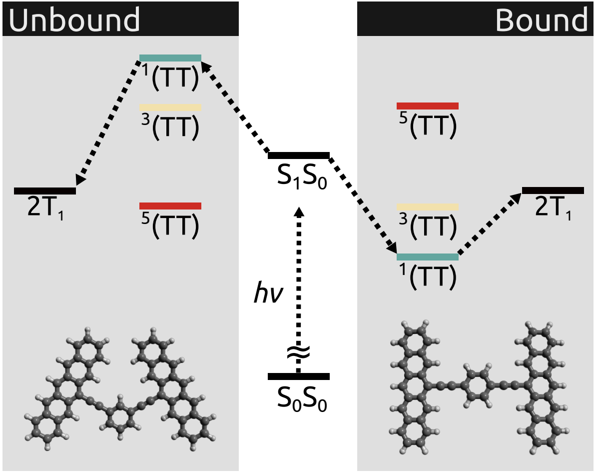
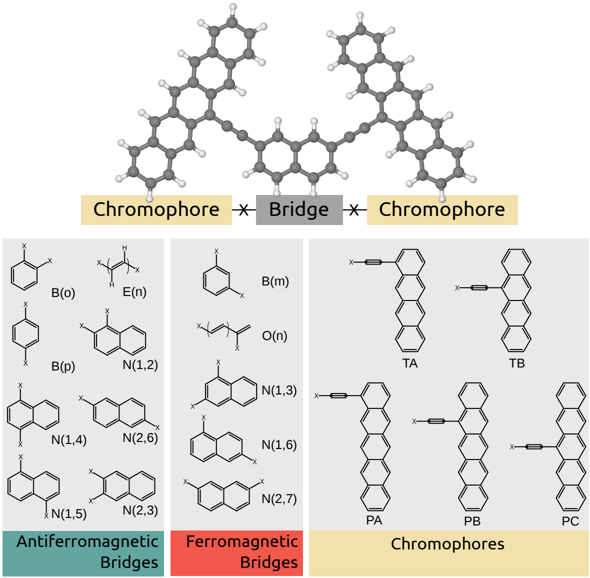
An Ovchinnikov's Rule for excited states



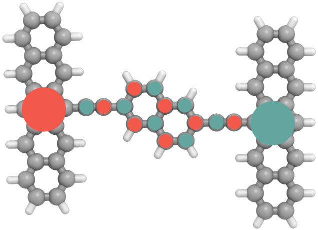
An Ovchinnikov's Rule for excited states

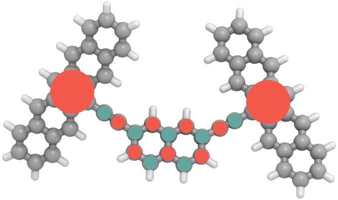
- **Data set**: 125 molecules



An Ovchinnikov's Rule for excited states: Results

meV	TA	TB	PA	PB	PC
	Antiferromagnetic (even) Bridges				
E(0)	6.700	399.164	0.369	47.762	328.825
E(1)	2.755	178.912	0.171	19.366	148.263
E(2)	1.172	77.129	0.073	7.558	63.429
E(3)	0.477	31.452	0.031	3.293	27.107
E(4)	0.207	13.693	0.013	1.539	11.582
E(5)	0.091	5.815	0.006	0.671	4.996
E(6)	0.039	2.397	0.002	0.286	2.105
B(o)	0.526	33.755	0.031	3.038	37.918
B(p)	0.869	51.799	0.053	2.596	42.247
N(1,2)	0.810	53.525	0.051	1.506	61.618
N(1,4)	1.008	39.231	0.062	2.962	25.767
N(1,5)	0.032	1.263	0.002	0.212	1.002
N(1,7)	0.133	8.299	0.007	0.838	6.596
N(2,3)	0.175	14.390	0.010	0.421	21.808
N(2,6)	0.301	18.846	0.012	1.443	15.102
	Ferromagnetic (odd) Bridges				
O(0)	-0.248	-12.768	-0.017	-1.016	-10.211
O(1)	-0.078	-2.937	-0.006	-0.351	-3.944
O(2)	-0.030	-1.408	-0.003	-0.159	-1.263
O(3)	-0.011	-0.467	-0.002	-0.049	-0.142
O(4)	-0.005	-0.179	-0.001	-0.019	-0.194
O(5)	-0.002	-0.090	-0.003	-0.008	-0.061
B(m)	-0.090	-5.784	-0.006	-0.367	-4.597
N(1,3)	-0.071	-3.896	-0.006	-0.362	-4.541
N(1,6)	-0.043	-2.145	-0.004	-0.172	-1.379
N(2,7)	-0.038	-2.530	-0.003	-0.174	-2.212





An Ovchinnikov's Rule for excited states: Results

meV	TA	TB	PA	PB	PC
		Ant[illegible]			
E(0)	6.700	[illegible]			
E(1)	2.755	[illegible]			
E(2)	1.172	[illegible]			
E(3)	0.477	[illegible]			
E(4)	0.207	[illegible]			
E(5)	0.091				
E(6)	0.039				
B(o)	0.526	[illegible]			
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N(1,2)	0.810	[illegible]			
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N(2,3)	0.175	[illegible]			
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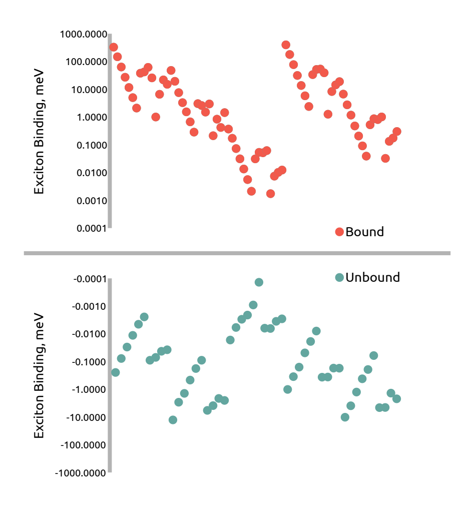
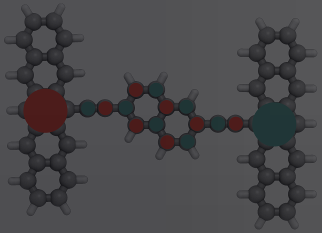
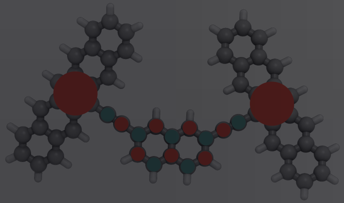
		F[illegible]			
O(0)	-0.248	[illegible]			
O(1)	-0.078	[illegible]			
O(2)	-0.030	[illegible]			
O(3)	-0.011	[illegible]			
O(4)	-0.005	[illegible]			
O(5)	-0.002	[illegible]			
B(m)	-0.090	[illegible]			
N(1,3)	-0.071	[illegible]	[illegible]	[illegible]	[illegible]
N(1,6)	-0.043	-2.145	-0.004	-0.172	-1.379
N(2,7)	-0.038	-2.530	-0.003	-0.174	-2.212

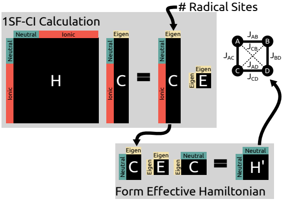






In Summary

1. Bloch Effective Hamiltonian: 1 spin-flip $\longrightarrow$ Heisenberg Hamiltonian



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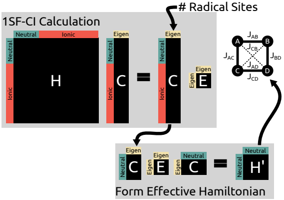

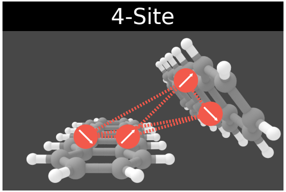

1. Mayhall, JCTC, 12, 4263 (2016)
2. Abraham, Mayhall, JPCL, 8, 5472 (2017)

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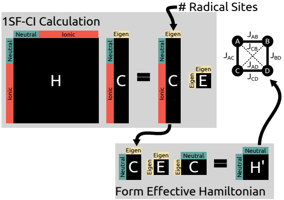

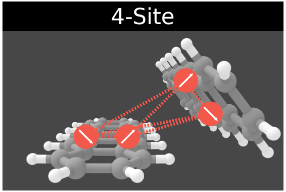

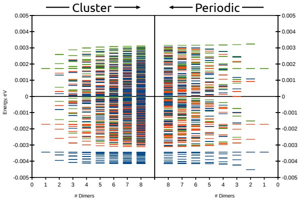

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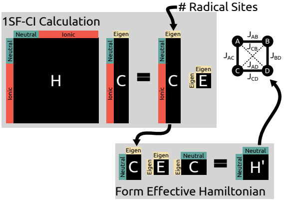

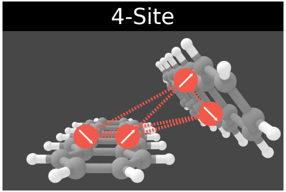

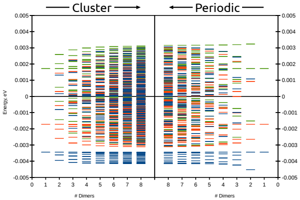

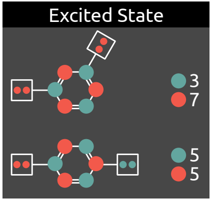

1. Mayhall, JCTC, 12, 4263 (2016)
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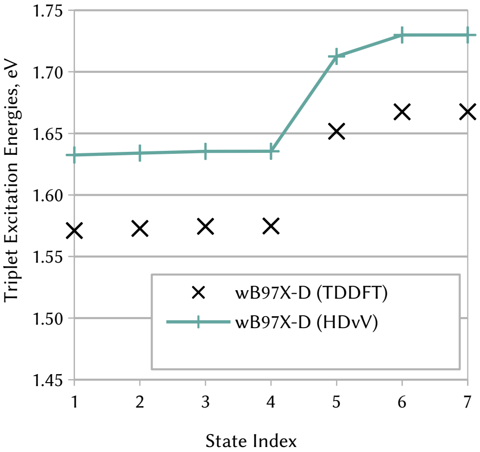
- NSF: 1839136

Multiexcitons in molecular materials

- Compare single exciton triplet states - TDDFT vs. SF-TDDFT+HDvV



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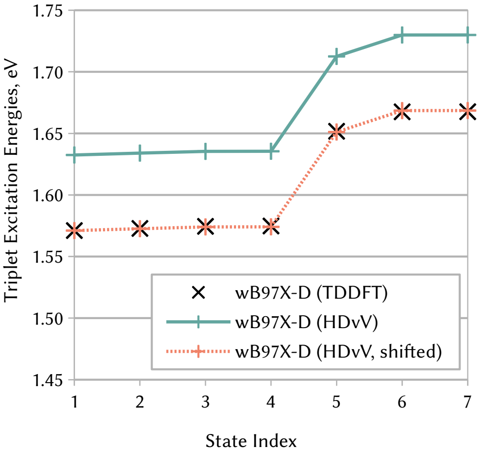

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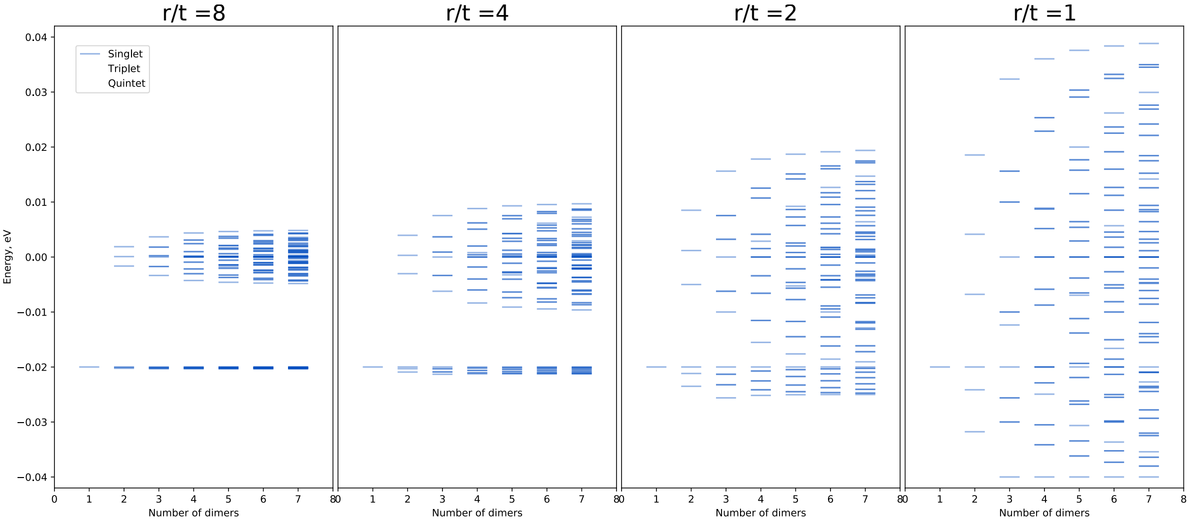
Multiexcitons in molecular materials : Larger clusters

- perpendicular(t=0): parallel(t=max)



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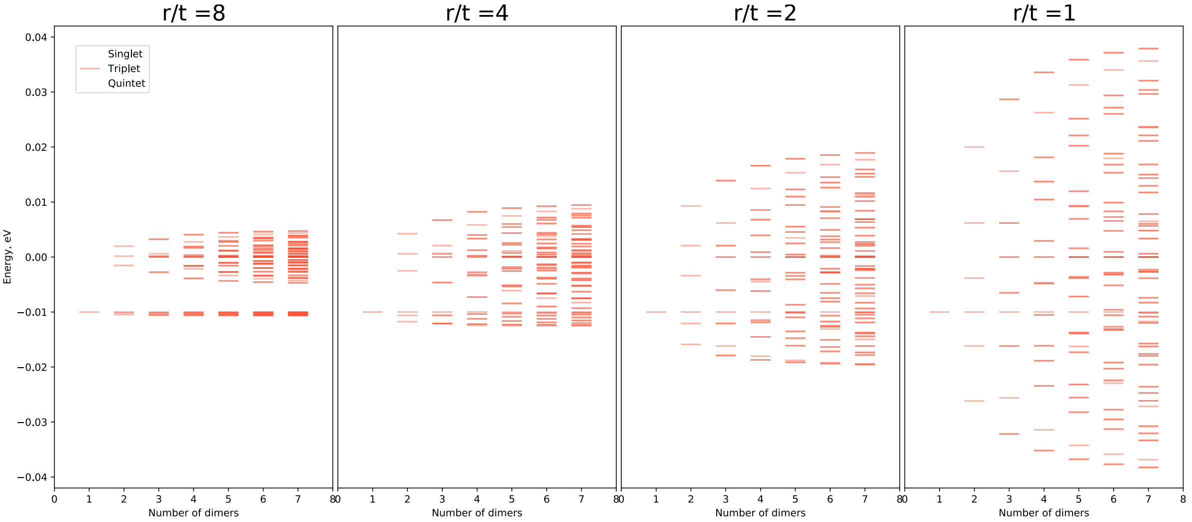

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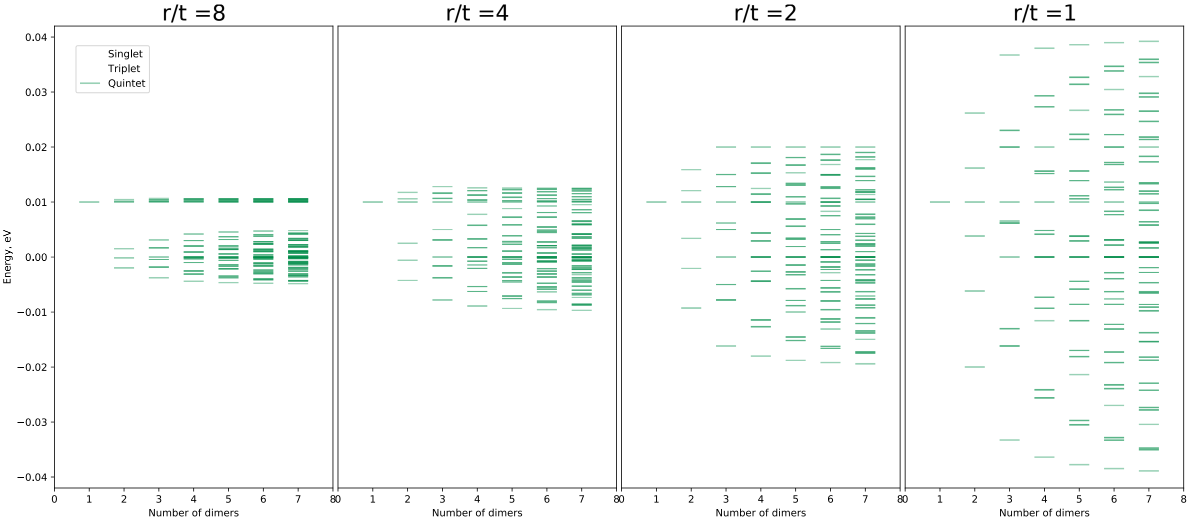
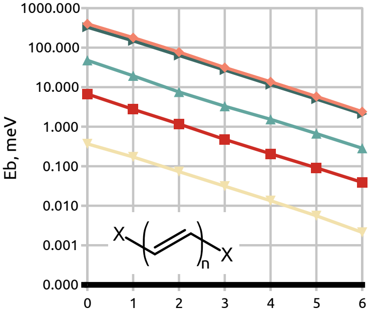
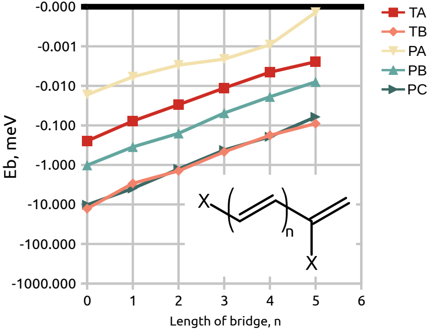


An Ovchinnikov’s Rule for excited states: Distance decay



(a) E(n)



(b) O(n)

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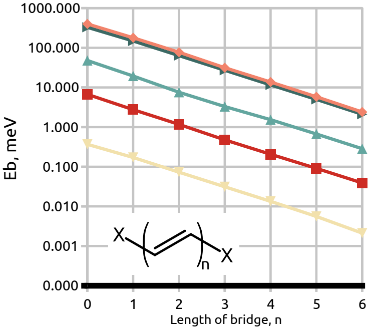

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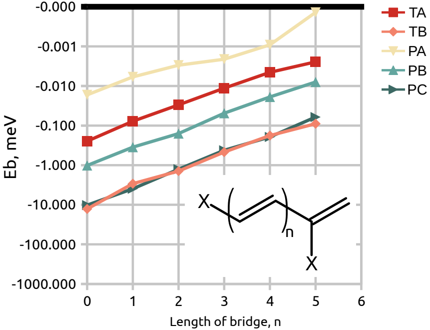
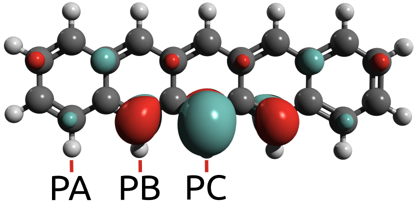
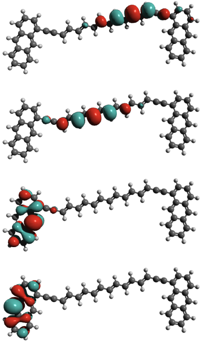


(b) O(n)



An Ovchinnikov's Rule for excited states: Exceptions

Bridges with
low-lying triplet states



Non-alternate
hydrocarbons