

Supporting Information: Accurate and Interpretable Representation of Correlated Electronic Structure via Tensor Product Selected CI

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S1. SINGLET FISSION TETRACENE TETRAMER

TABLE S1. Results for all 31 eigenstates of tetracene tetramer with associated labels based on expectation values of the \hat{S}^2 operator $\langle \hat{S}^2 \rangle$, variational excitation energies (ω_{var}), PT2 energy corrections (ω_{PT2}) for excitation energies in eV, and percentage of charge transfer (% CT) for all 31 eigenstates in the TPSCI wavefunction. With $\epsilon_{\text{cipsi}} = 4e - 4$ resulting in a variational dimension of 128,614.

State	Label	$\langle \hat{S}^2 \rangle$	ω_{var}	ω_{PT2}	% CT
1	S ₀	0.000	0.000	0.000	0.15
2	T ₁	2.000	1.813	0.004	1.49
3	T ₁	2.000	1.834	0.003	0.67
4	T ₁	2.000	1.848	0.003	0.68
5	T ₁	2.000	1.861	0.003	0.44
6	¹ (TT)	0.000	3.635	0.011	4.55
7	¹ (TT)	0.002	3.645	0.010	3.09
8	³ (TT)	2.000	3.647	0.009	2.26
9	⁵ (TT)	5.998	3.651	0.009	1.82
10	¹ (TT)	0.000	3.653	0.010	4.49
11	³ (TT)	2.000	3.654	0.010	3.41
12	¹ (TT)	0.001	3.664	0.009	2.89
13	³ (TT)	2.000	3.665	0.009	3.29
14	³ (TT)	2.000	3.675	0.009	2.33
15	⁵ (TT)	6.000	3.682	0.009	1.52
16	⁵ (TT)	5.996	3.688	0.008	1.10
17	⁵ (TT)	5.591	3.694	0.007	0.84
18	³ (TT)	1.366	3.695	0.007	1.05
19	¹ (TT)	1.100	3.695	0.007	1.06
20	⁵ (TT)	5.944	3.698	0.007	0.76
21	¹ (TT)	0.002	3.707	0.008	1.35
22	³ (TT)	1.999	3.709	0.008	1.25
23	⁵ (TT)	5.999	3.715	0.008	0.68
24	S ₁	0.000	3.809	0.010	12.25
25	S ₁	0.000	3.884	0.007	3.49
26	T ₂	2.000	3.900	0.005	2.42
27	T ₂	2.000	3.916	0.004	1.30
28	S ₁	0.000	3.920	0.008	7.50
29	T ₂	2.000	3.924	0.005	2.33
30	T ₂	2.000	3.928	0.005	2.58
31	S ₁	0.000	3.952	0.007	5.91

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TABLE S2. Bare Hamiltonian to show singlet coupling strengths between $|S_1\rangle$ and $|^1TT\rangle$ in meV.

State	S ₀	S ₁	S ₁	S ₁	S ₁	1,2	1,4	2,3	1,3	2,4	3,4
S ₀	0.00	0.00	0.00	0.00	0.00	-0.84	-0.72	-1.38	-0.88	-0.09	-0.01
S ₁	0.00	0.00	-11.75	-38.45	9.45	-0.22	-0.43	0.00	-0.05	0.00	0.00
S ₁	0.00	-11.75	0.00	-10.15	40.67	-0.68	0.00	-0.94	0.00	-0.03	0.00
S ₁	0.00	-38.45	-10.15	0.00	-8.07	0.00	0.00	-0.59	0.01	0.00	0.00
S ₁	0.00	9.45	40.67	-8.07	0.00	0.00	1.06	0.00	0.00	-0.01	0.00
1,2	-0.84	-0.22	-0.68	0.00	0.00	0.00	-0.05	0.32	1.44	1.12	0.00
1,4	-0.72	-0.43	0.00	0.00	1.06	-0.05	0.00	0.00	0.01	-0.08	0.32
2,3	-1.38	0.00	-0.94	-0.59	0.00	0.32	0.00	0.00	-0.08	0.01	-0.05
1,3	-0.88	-0.05	0.00	0.01	0.00	1.44	0.01	-0.08	0.00	0.00	1.12
2,4	-0.09	0.00	-0.03	0.00	-0.01	1.12	-0.08	0.01	0.00	0.00	1.44
3,4	-0.01	0.00	0.00	0.00	0.00	0.00	0.32	-0.05	1.12	1.44	0.00

TABLE S3. TPSCI Effective Hamiltonian to show the increases singlet coupling strengths between $|S_1\rangle$ and $|^1TT\rangle$ in meV once we include correlations with our external space.

State	S ₀	S ₁	S ₁	S ₁	S ₁	1,2	1,4	2,3	1,3	2,4	3,4
S ₀	0.00	-3.32	-0.32	-3.02	-0.52	-10.45	5.65	4.03	-1.70	-0.06	-0.03
S ₁	-3.32	0.00	27.38	-33.59	-14.64	-6.43	19.46	0.33	0.80	1.31	0.01
S ₁	-0.32	27.38	0.00	9.88	35.63	3.66	2.47	10.16	1.04	0.50	0.00
S ₁	-3.02	-33.59	9.88	0.00	-7.57	0.37	-0.82	14.36	-0.64	-0.08	-0.07
S ₁	-0.52	-14.64	35.63	-7.57	0.00	-0.23	-6.62	0.42	0.10	0.37	0.08
1,2	-10.45	-6.43	3.66	0.37	-0.23	0.00	1.45	3.37	-2.49	-4.48	0.01
1,4	5.65	19.46	2.47	-0.82	-6.62	1.45	0.00	-0.06	-0.05	11.99	1.47
2,3	4.03	0.33	10.16	14.36	0.42	3.37	-0.06	0.00	10.81	-0.06	0.12
1,3	-1.70	0.80	1.04	-0.64	0.10	-2.49	-0.05	10.81	0.00	-0.04	-5.41
2,4	-0.06	1.31	0.50	-0.08	0.37	-4.48	11.99	-0.06	-0.04	0.00	-4.28
3,4	-0.03	0.01	0.00	-0.07	0.08	0.01	1.47	0.12	-5.41	-4.28	0.00

S2. HEXABENZOCORONENE

1. Effect of nbody and δ_{elec} on correlation energy

The main aim of studying hexabenzocoronene is to see how inter-cluster interaction contributes to the correlation energy with the number of clusters (nbody) interacting with each other. We have done a series of TPSCI calculations by constructing the local many-body basis for each sector of Fock space which contained up to $N_I \pm \delta_{elec}$ number of electrons, where we varied δ_{elec} from 1 to 3 for each nbody value (2, 3, 4). For nbody=0, there is no inter-cluster interaction present in the system which is exactly cMF basis. In the nbody=1 case, only excitations inside one cluster are allowed at a time. As discussed in cMF theory section, the interaction between singly excited cluster configurations and ground state cluster configuration should be zero due to the Brillouin condition.

From Fig. (S1), we can see how nbody interactions affect the correlation energy. Most of the correlation energy is recovered from 2-body interactions. If we include 3-body interactions, it can be seen that there is 0.39-0.43 eV contribution from 3-cluster interactions, and 4-body interactions further add only 0.02 eV for $\delta_{elec} = 2$ and nearly 0.002 eV for $\delta_{elec} = 3$ which is smaller than chemical accuracy. From these observations, it can be predicted that the hexabenzocoronene system contains interactions mostly between two benzene rings although the electron density is delocalized all over the systems. However, a significant amount of contributions is achieved through the 3-body interactions. We guess that most of the 3-body interactions are available among two benzene rings present on the outer ring and the central fused benzene ring distributed in a line (para-like) or three vertices of a triangle (ortho-like). This can be confirmed via the computation of 3rd order cumulant of particle number. Whereas 3 benzene rings in the outer ring along with the central benzene contribute negligibly to 4-body correlation energy.

Now, if we focus on δ_{elec} parameter, there is a very small change (less than chemical accuracy) if we shift δ_{elec} value from 1 to 2, and 3. δ_{elec} parameter restricts the Fock sectors (n_α, n_β) based on the allowable electron transitions ($\delta_{elec} = \pm\delta$ electron transfer). From this observation, it can be concluded that configurations created through single electron transition inside each cluster interact mostly with singly excited configurations and ground state configuration from the rest of the systems. Inter-cluster parameter, nbody determines how many inter-cluster interactions are

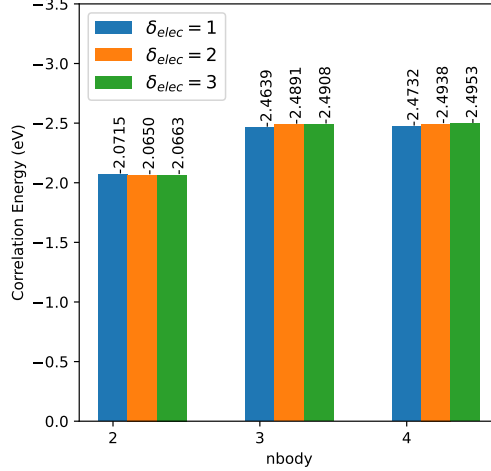


FIG. S1. Effect of nbody and δ_{elec} in recovering correlation energy for hexabenzocoronene. $\epsilon_{cipsi} = 2.5e-4$ and $\epsilon_{foi} = 1e-6$, threshold values are used for TPSCI variational energies in STO-3g basis.

significant for intra-cluster parameter, δ_{elec} . As $\delta_{elec} = 1$ recovers most of the correlation energy for a particular nbody value, the most important physical process that happens in hexabenzocoronene must be electron hopping (charge-transfer) which is further supported by the correlation matrix of particle number operator, \hat{N} and spin projection, \hat{S}^z .

2. Covariance matrix and Average value of \hat{S}^z , \hat{N} , \hat{S}^2 , \hat{Q}

Root = 1, Cov(N_I, N_J):

$$\begin{bmatrix} 0.02550829 & -0.00759149 & -0.00017893 & -0.0004038 & -0.00018108 & -0.00759755 & -0.00955544 \\ -0.00759149 & 0.02551065 & -0.00759694 & -0.00018174 & -0.00040329 & -0.0001787 & -0.0095585 \\ -0.00017893 & -0.00759694 & 0.02548365 & -0.00759733 & -0.00017889 & -0.00040443 & -0.00952713 \\ -0.0004038 & -0.00018174 & -0.00759733 & 0.02550731 & -0.00759024 & -0.00017861 & -0.00955559 \\ -0.00018108 & -0.00040329 & -0.00017889 & -0.00759024 & 0.02551021 & -0.0075972 & -0.0095595 \\ -0.00759755 & -0.0001787 & -0.00040443 & -0.00017861 & -0.0075972 & 0.02548714 & -0.00953065 \\ -0.00955544 & -0.0095585 & -0.00952713 & -0.00955559 & -0.0095595 & -0.00953065 & 0.05728681 \end{bmatrix}$$

Root = 1, Cov(S_I^z, S_J^z):

$$\begin{bmatrix} 0.00925446 & -0.0027587 & -0.00004766 & -0.00013415 & -0.00004725 & -0.00276328 & -0.00350342 \\ -0.0027587 & 0.00925935 & -0.00276279 & -0.00004727 & -0.00013475 & -0.00004721 & -0.00350864 \\ -0.00013415 & -0.00004727 & 0.00925467 & -0.00276338 & -0.00004716 & -0.00013419 & -0.0034995 \\ -0.00004766 & -0.00276279 & -0.00276338 & 0.00925471 & -0.00275859 & -0.00004761 & -0.00350371 \\ -0.00004725 & -0.00013475 & -0.00004716 & -0.00275859 & 0.00926062 & -0.002763 & -0.00350988 \\ -0.00276328 & -0.00004721 & -0.00013419 & -0.00004761 & -0.002763 & 0.00925669 & -0.00350141 \\ -0.00350342 & -0.00350864 & -0.0034995 & -0.00350371 & -0.00350988 & -0.00350141 & 0.02102656 \end{bmatrix}$$

Root = 1, Cov(Q_I, Q_J):

$$\begin{bmatrix} 0.03307346 & 0.01079417 & 0.0001041 & -0.00005672 & 0.00011049 & 0.01080873 & 0.01342415 \\ 0.01079417 & 0.03307551 & 0.01080557 & 0.00011064 & -0.00005735 & 0.00010328 & 0.01342571 \\ 0.0001041 & 0.01080557 & 0.03307124 & 0.01080811 & 0.00010314 & -0.00006024 & 0.01342283 \\ -0.00005672 & 0.00011064 & 0.01080811 & 0.03307314 & 0.01079245 & 0.00010397 & 0.01342431 \\ 0.00011049 & -0.00005735 & 0.00010314 & 0.01079245 & 0.03307654 & 0.01080523 & 0.01342799 \\ 0.01080873 & 0.00010328 & -0.00006024 & 0.00010397 & 0.01080523 & 0.03307683 & 0.01342283 \\ 0.01342415 & 0.01342571 & 0.01342283 & 0.01342431 & 0.01342799 & 0.01342283 & 0.06866612 \end{bmatrix}$$

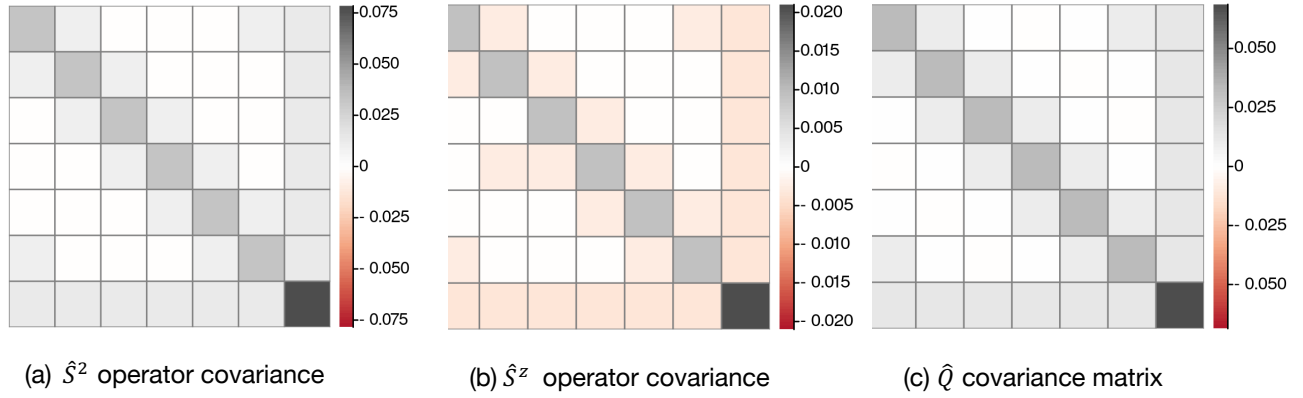


FIG. S2. \hat{S}^2 , spin projection, \hat{S}^z , \hat{Q} covariance matrices for each cluster.

Root = 1, $\text{Cov}(S_i^2, S_j^2)$:

0.03393927	0.01005385	-0.00014237	-0.00009454	-0.00013552	0.01007677	0.01286263
0.01005385	0.03394938	0.01007536	-0.00013532	-0.00009262	-0.00014198	0.01287511
-0.00014237	0.01007536	0.03395539	0.01007542	-0.00014202	-0.00009892	0.0128601
-0.00009454	-0.00013532	0.01007542	0.03394001	0.01005458	-0.00014262	0.012863
-0.00013552	-0.00009262	-0.00014202	0.01005458	0.03395483	0.01007666	0.0128772
0.01007677	-0.00014198	-0.00009892	-0.00014262	0.01007666	0.0339672	0.01287065
0.01286263	0.01287511	0.0128601	0.012863	0.0128772	0.01287065	0.07845006

TABLE S4. Average value of particle number, \hat{N} , spin projection, \hat{S}^z , Q , \hat{S}^2 for each cluster in cc-pVDZ basis.

Cluster	1	2	3	4	5	6	7
$\langle \hat{N} \rangle$	6.00009508	6.00006097	6.00008872	6.00009172	6.00006299	6.00008641	5.9995141
$\langle \hat{S}^z \rangle$	0.00001386	-0.0000144	0.00000359	0.0000157	-0.00001414	0.00000181	-0.00000642
$\langle Q \rangle$	0.03424627	0.03424847	0.03424389	0.03424593	0.03424957	0.03424989	0.07416684
$\langle \hat{S}^2 \rangle$	0.02767142	0.02767881	0.02766855	0.02767127	0.02768138	0.02767573	0.06288520

A. Cr_2 orbitals

A Cr_2 orbitals

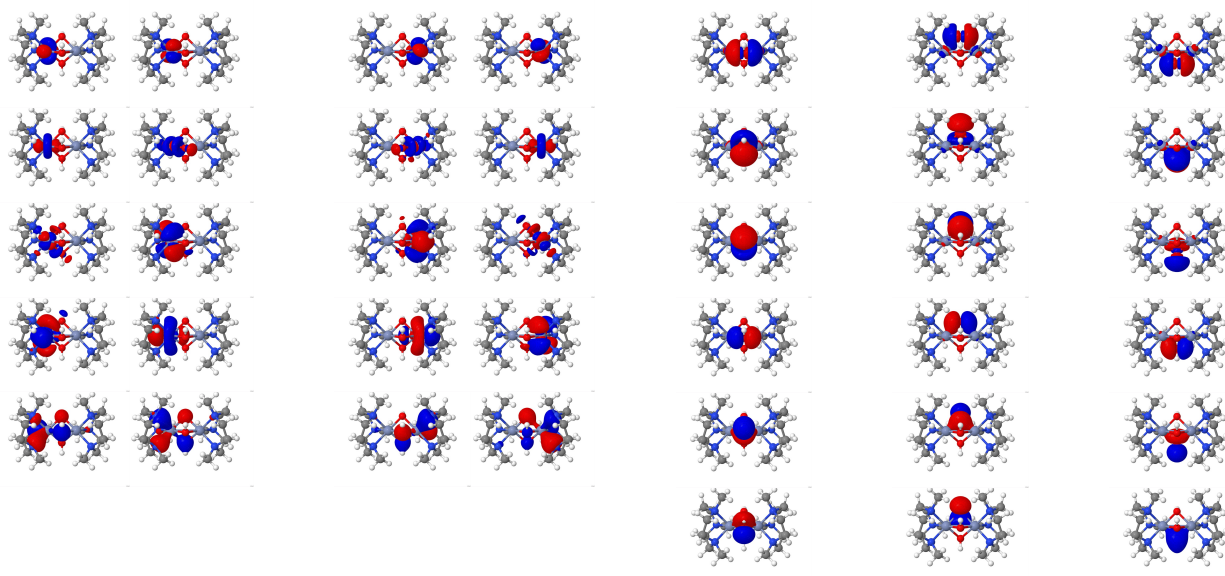


FIG. S3. Molecular orbitals comprising the active site for the dichromium compound. Orbitals are grouped by cluster.