Towards quantitative computations of exchange couplings in transition-metal complexes via multireference driven similarity renormalization group

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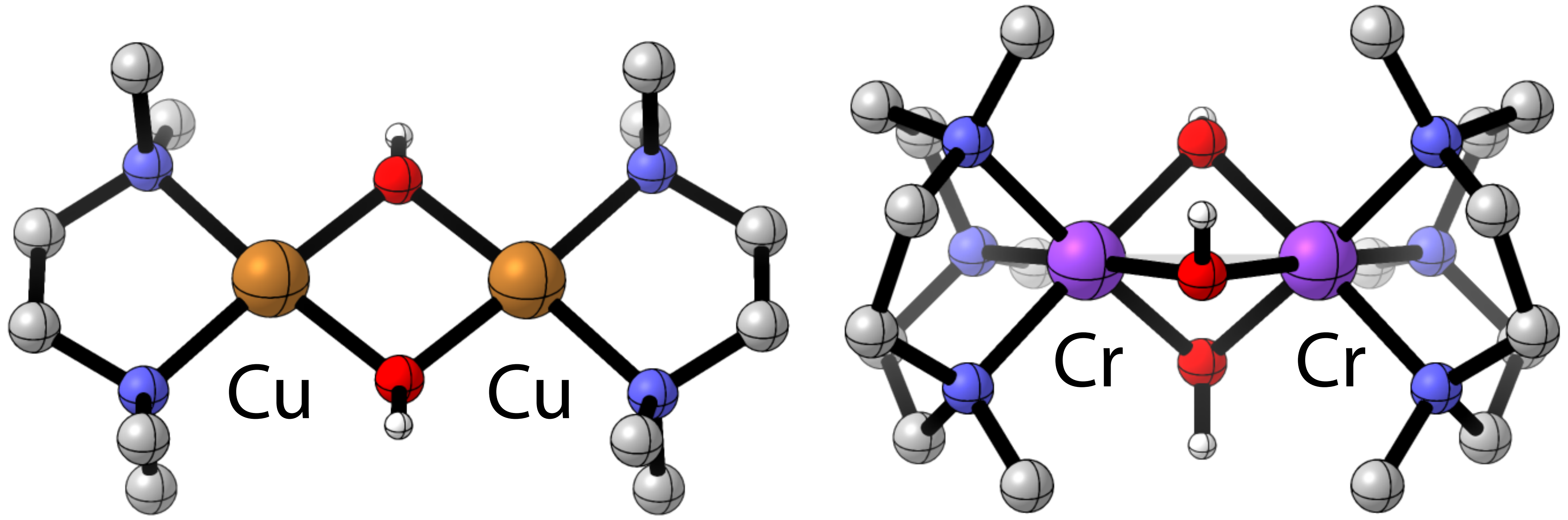
Outline

- Introduction
    - The Heisenberg-Dirac-Van Vleck Hamiltonian
    - Ab Initio Hamiltonian
- Multireference driven similarity renormalization group (DSRG)
- Exchange coupling in bimetallic compounds
    - Analysis of Integrals
    - Characterization of Coupling Pathways
- Conclusions



Forte An open-source suite of quantum chemistry methods for strongly correlated electrons

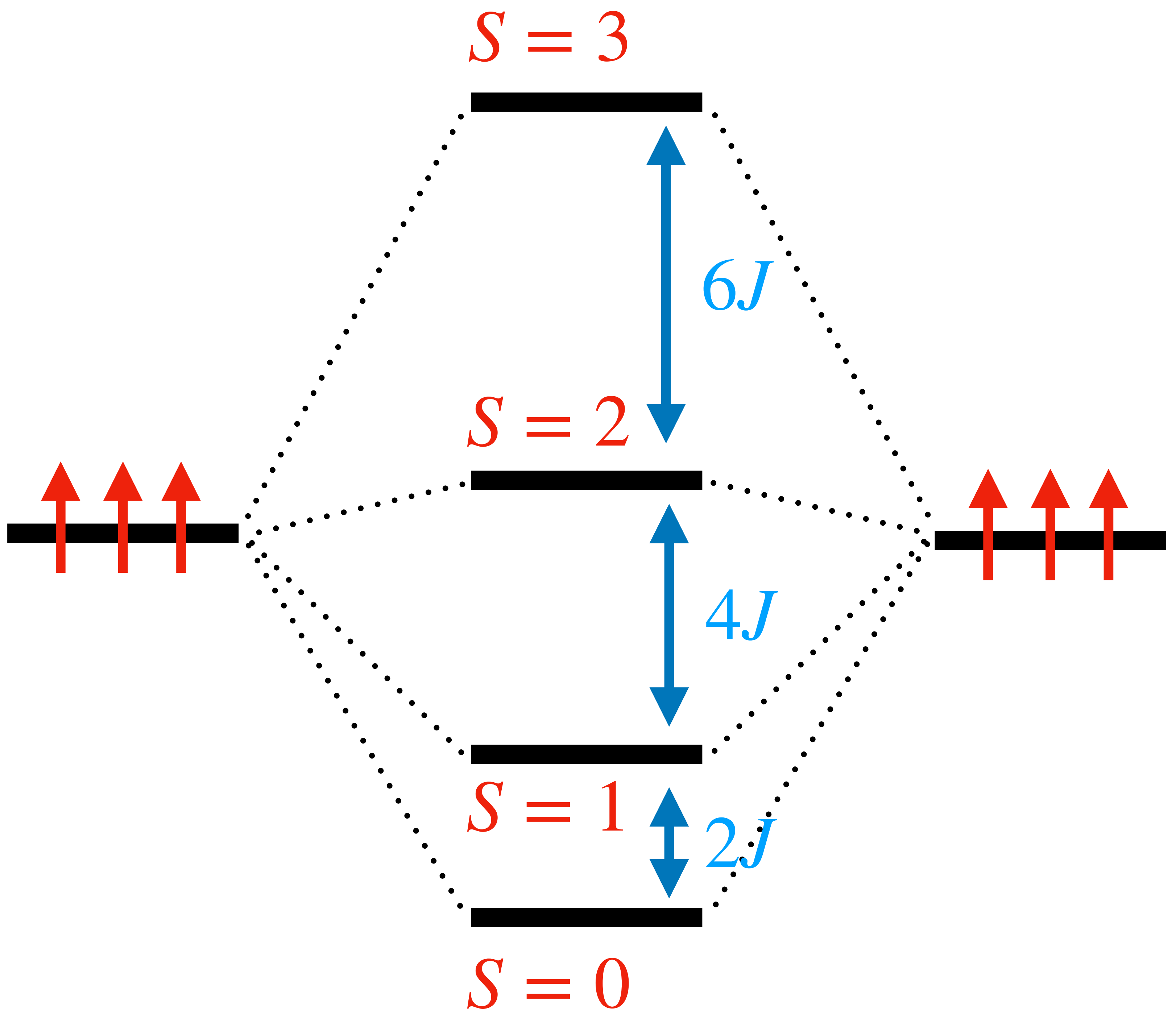
github.com/evangelistalab/forte

Introduction

Heisenberg-Dirac-van Vleck Hamiltonian

$$\hat{H}_{\mathrm{HDVV}} = -2\sum_{i<j} J_{ij}\hat{S}_i \cdot \hat{S}_j$$

- An effective Hamiltonian that acts on a fictitious set of spin states
- Describes a few low-lying multiplets
- J_{ij}: exchange coupling constant, $J_{ij} < 0$: antiferromagnetic coupled
- For a two-spin system:
  - $\hat{H}_{\mathrm{HDVV}} = -2J\hat{S}_1 \cdot \hat{S}_2 = -J(\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2)$
  - $E(J, S, S_1, S_2) = -J[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]$
  - Landé interval: $E(S) - E(S-1) = -2JS$
  - Biquadratic term: $\hat{H}_{\mathrm{HDVV}} = -2J\hat{S}_1 \cdot \hat{S}_2 - j(\hat{S}_1 \cdot \hat{S}_2)^2$



CAS(2,2) Active Space Hamiltonian

- Generic active space Hamiltonian

$$\hat{H}_{\mathrm{a}} = \sum_{uv} f^{\mathrm{c}}_{uv}\hat{E}_{uv} + \frac{1}{2}\sum_{uvxy}(uv|xy)\hat{E}_{uv,xy}$$

- Four configurations in CAS(2,2): $|\phi_1\bar{\phi}_2\rangle, |\phi_2\bar{\phi}_1\rangle, |\phi_1\bar{\phi}_1\rangle, |\phi_2\bar{\phi}_2\rangle$
- CI Matrix

$\hat{H}_{\mathrm{a}}$	$\lvert\phi_1\bar{\phi}_2\rangle$	$\lvert\phi_2\bar{\phi}_1\rangle$	$\lvert\phi_1\bar{\phi}_1\rangle$	$\lvert\phi_2\bar{\phi}_2\rangle$
$\lvert\phi_1\bar{\phi}_2\rangle$	0	K_1	t_1	t_2
$\lvert\phi_2\bar{\phi}_1\rangle$	K_1	0	t_1	t_2
$\lvert\phi_1\bar{\phi}_1\rangle$	t_1	t_1	U_1	K_2
$\lvert\phi_2\bar{\phi}_2\rangle$	t_2	t_2	K_2	U_2

symmetry →

$U_1 = U_2 \equiv U$

$t_1 = t_2 \equiv t$

direct exchange

$$J = \frac{1}{2}[E(S) - E(T)] = K - \frac{2t^2}{U}$$

kinetic exchange

$K_1 = (12|21), K_2 = (12|12), t_1 = f^{\mathrm{c}}_{12} + (11|21), t_2 = f^{\mathrm{c}}_{12} + (12|22), U_1 = f^{\mathrm{c}}_{11} - f^{\mathrm{c}}_{22} + (11|11) - (11|22), U_2 = f^{\mathrm{c}}_{22} - f^{\mathrm{c}}_{11} + (22|22) - (22|11)$

CAS(2,2) Active Space Hamiltonian: Examples

Table 1. Magnetic Couplings (in cm^{-1}) Calculated with Different CI Wave Functions (Figure 10) Using a Minimal CAS as Reference[a]

	CASCI	CAS+S	DDCI2	DDCI	exp.
La_2CuO_4[b]	−255	−706	−744	−1077	[−1030, −1096][h]
$Sr_2CuO_2Cl_2$[b]	−160	−464	−482	−952	−1008[i]
$[Cu(OH)]_2$-AF[c]	−35	−159	−184	−500	−507[j]
$[Cu(OH)]_2F$[d]	33	73	63	157	172[k]
$[Cu(L1)(C_2O_4)]_2$[e]	−7.3	−21.9	−23.2	−78.3	−75[l]
$[Ni(C_2O_4)]_2$-A[f]	−1.0	−8.5	0−8.9	−16.0	−28.8[m]
$[Ni(C_2O_4)]_2$-B[g]	−2.8	−7.1	−7.7	−11.4	−22.8[m]

[a]The MOs of the highest spin state are used to express the Slater determinants of the CI expansion. [b]From embedded cluster calculations (see section 4.6). [c]$[Cu(OH)]_2$-AF = $[Cu(tmeen)(OH)]_2Br_2$, with tmeen = *N,N,N′,N′*-tetramethylethylenediamine. [d]$[Cu(OH)]_2F$ = $[Cu(bipy)(OH)]_2(NO_3)_2$, with bipy = 2,2′-bipyridine. [e]L1 = 1,1,4,7,7-pentaethyldiethylenetriamine. [f]$[Ni(C_2O_4)]_2$-A = $[Ni(L2L3)(C_2O_4)]$, with L2 = diethylenetriamine, L3 = H_2O. [g]$[Ni(C_2O_4)]_2$-B = $[Ni(L4)(C_2O_4)]$, with L4 = (C_2O_4).

CHEMICAL REVIEWS
Review
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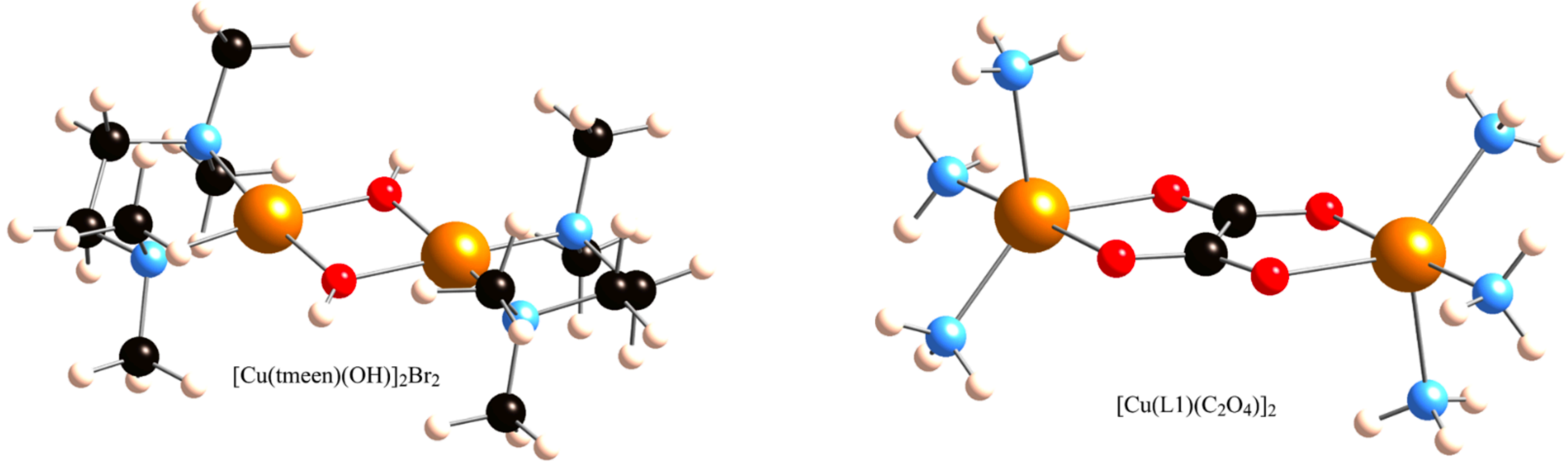
Magnetic Interactions in Molecules and Highly Correlated Materials: Physical Content, Analytical Derivation, and Rigorous Extraction of Magnetic Hamiltonians

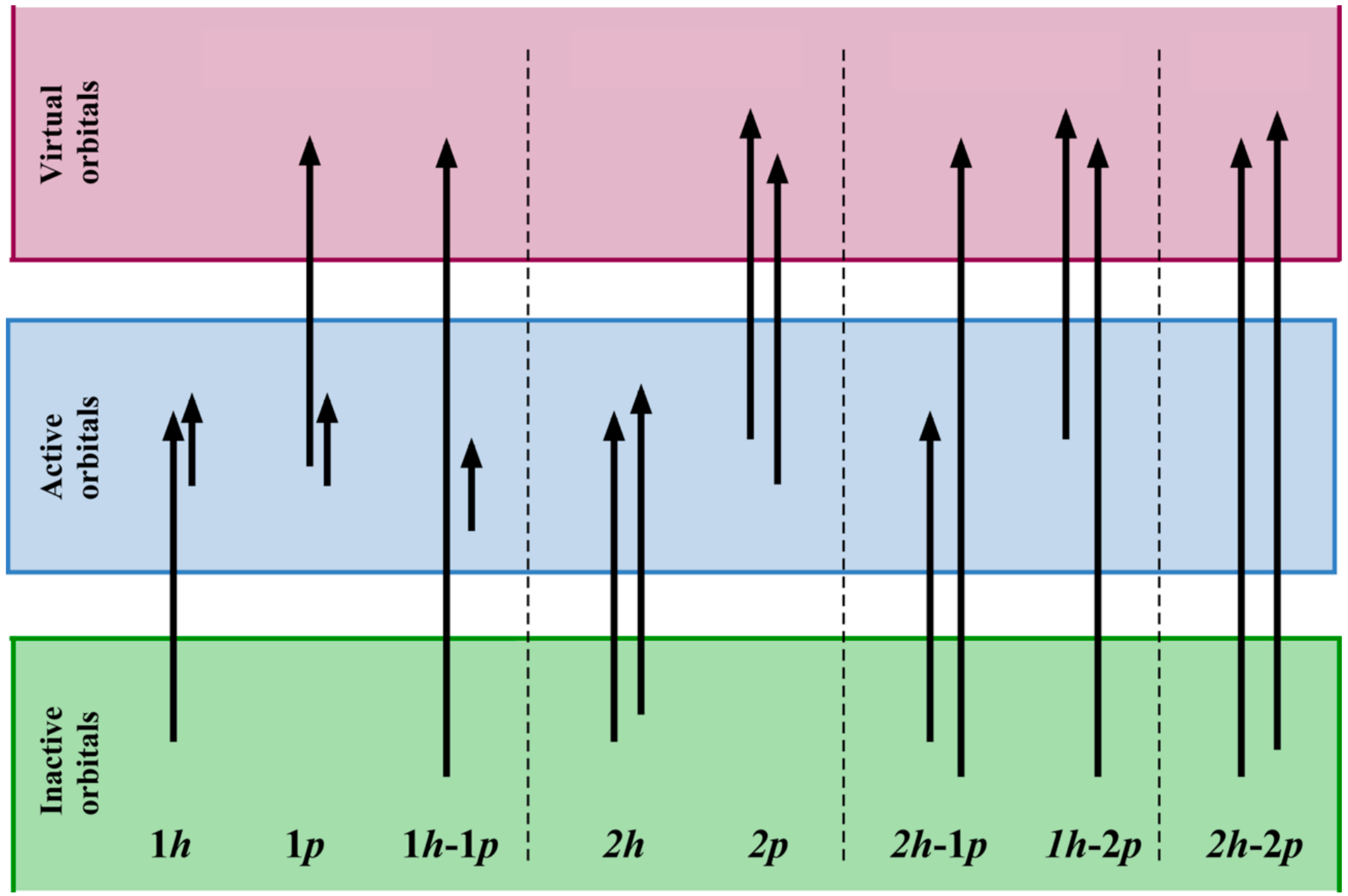
Jean Paul Malrieu,[†] Rosa Caballol,[‡] Carmen J. Calzado,[§] Coen de Graaf,[‡,∥] and Nathalie Guihéry*[,†]



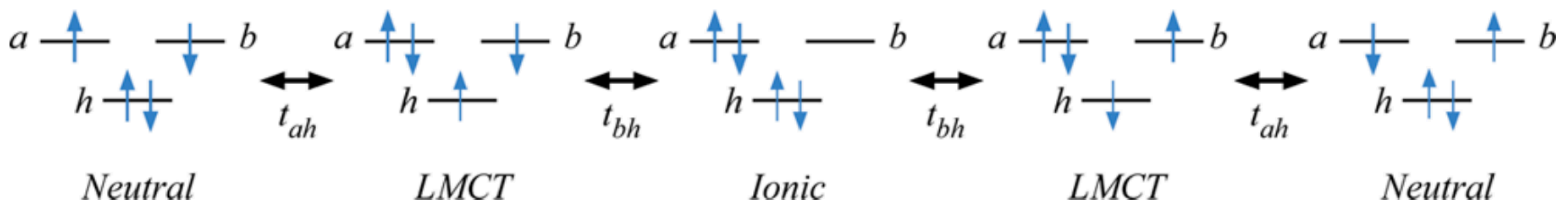
- 😀 correct sign
- 🙁 ~25% of the experimentally derived values

1. Malrieu, Caballol, Calzado, de Graaf, Guihéry, *Chem. Rev.* **114**, 429–492 (2012).

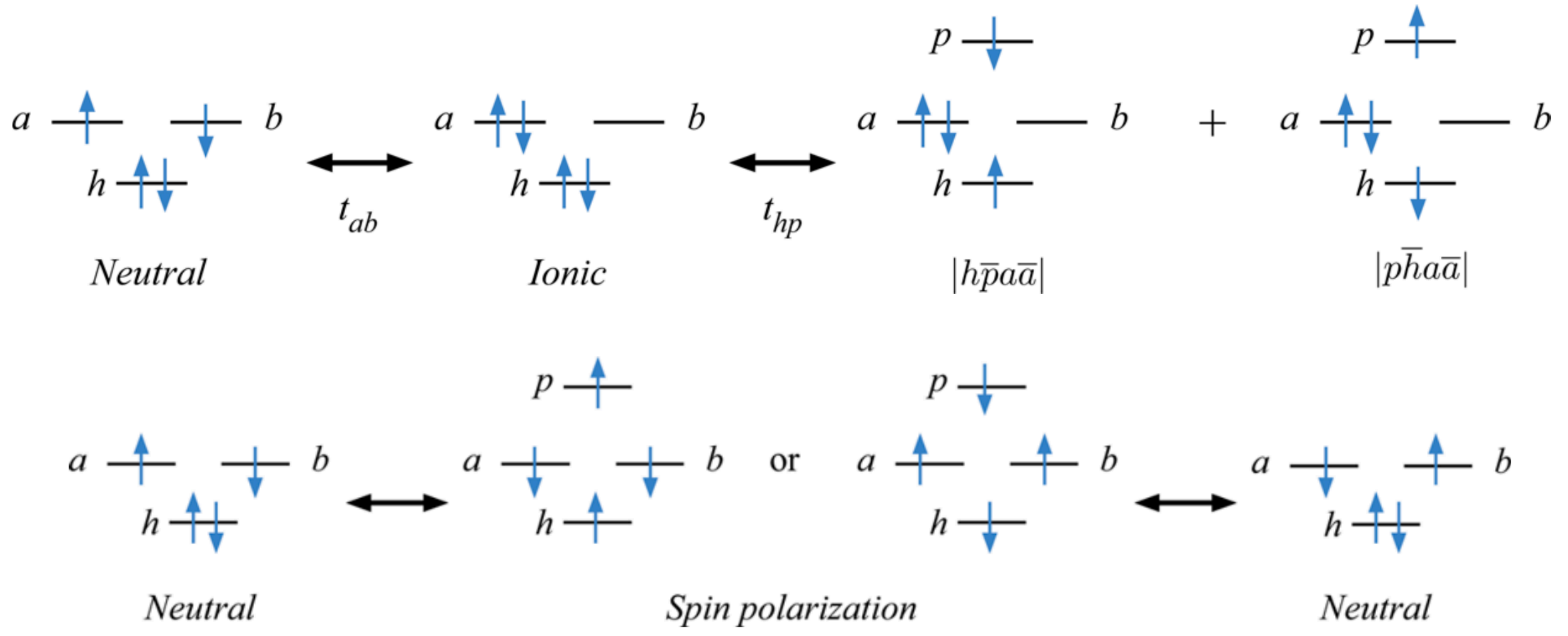
Beyond Minimal Active Space: External Configurations



ligand-mediated superexchange



1h-1p: dynamic charge/spin polarization



1. Malrieu, Caballol, Calzado, de Graaf, Guihéry, *Chem. Rev.* **114**, 429–492 (2012).

Difference-Decicated Configuration Interaction

- From QDPT2, 2h-2p does not contribute to energy differences:

$$\langle \Phi_I | \hat{H}^{\mathrm{eff}} | \Phi_J \rangle = \langle \Phi_I | \hat{H} | \Phi_J \rangle - \sum_r \frac{\langle \Phi_I | \hat{V} | \Phi_r \rangle \langle \Phi_r | \hat{V} | \Phi_J \rangle}{E_r - E_J}$$

- DDCI: MRCI with singles and doubles excluding 2h-2p
- Systematic improvable: CAS+S to DDCI2 to DDCI
- High computational cost
  - Large ligands / basis set
  - Many magnetic centers
  - Many unpaired electrons per magnetic center[2]

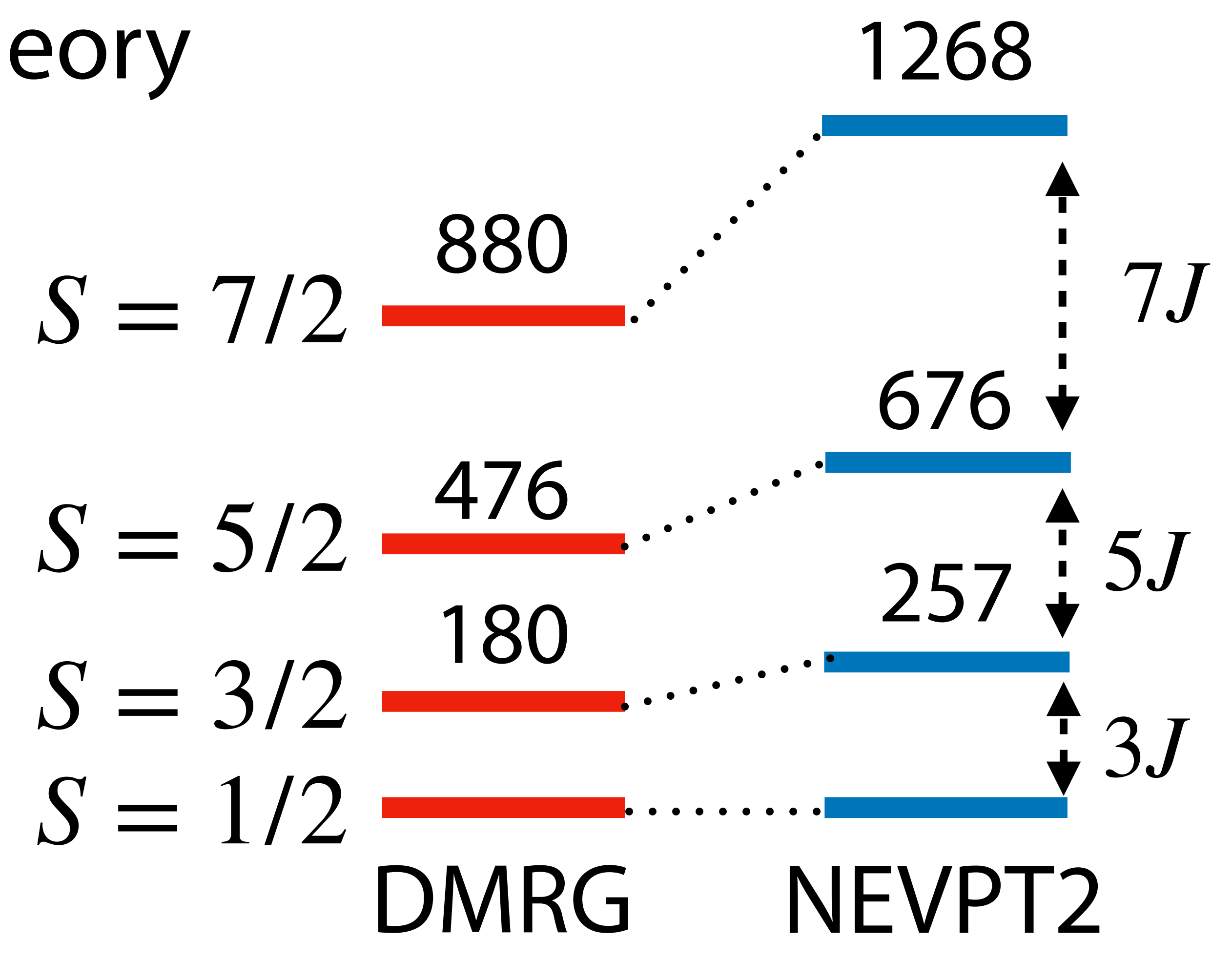
Table 3. Impact of the Different Excitations of the DDCI Space on the Magnetic Coupling Constants (in cm^{-1})[a]

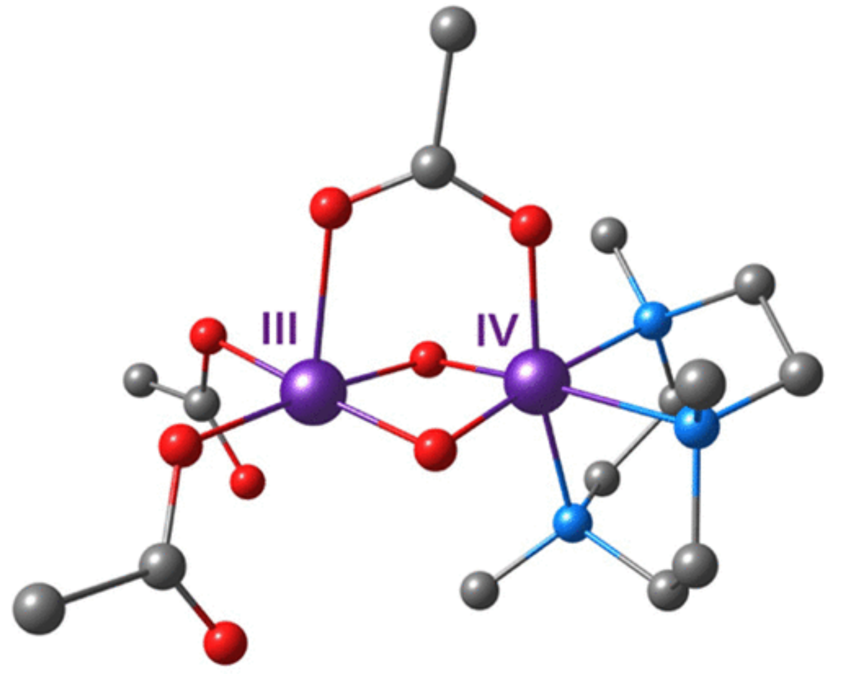
	La_2CuO_4[b]	$Sr_2CuO_2Cl_2$[b]	$[(Cu(tmeen)OH)_2]^{2+}$[c]	$[(Cu(bipy)OH)_2]^{2+}$[d]
CAS	−255	−160	−35	33
CAS+1*h*	−276	−169	−37	33
CAS+1*p*	−285	−180	−49	34
CAS+(1*h*-1*p*)	−523	−336	−102	61
CAS+(2*h*-1*p*)	−274	−167	−38	40
CAS+(1*h*-2*p*)	−189	−123	−10	36
CAS+S	−706	−464	−159	73
DDCI2	−744	−482	−184	63
DDCI2+(2*h*-1*p*)	−1462	−1256	−750	195
DDCI2+(1*h*-2*p*)	−569	−386	−117	57
DDCI	−1077	−952	−500	157
exp.	[−1030, −1096][e]	−1008[f]	−509[g]	172[h]

1. Malrieu, Caballol, Calzado, de Graaf, Guihéry, *Chem. Rev.* **114**, 429–492 (2012).
2. Calzado, Angeli, Caballol, Malrieu, *Theo. Chem. Acc.* **126**, 185–196 (2010).

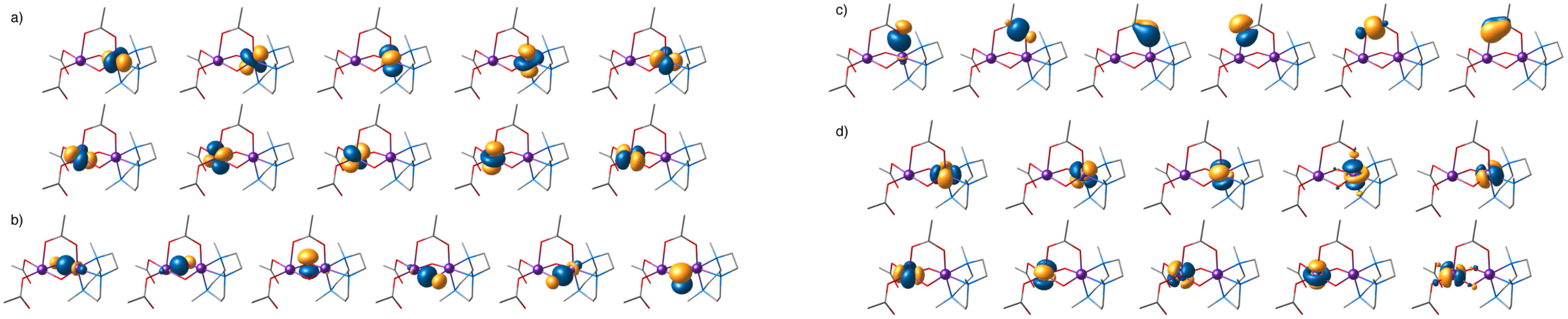
Extended Active Spaces: DMRG+NEVPT2

- Extended active space + second-order perturbation theory
- Shown to be accurate on Mn(III)-Mn(IV) dimer[1]
  - (19e,16o) active space (from Mn 3d and O 2p)
  - SA-DMRG-SCF: -59.0 cm^{-1}, NEVPT2: -84.7 cm^{-1}
- Need to perform separate NEVPT2 computations
- How to choose the active space systematically?





exp: $J = -90$ cm^{-1}



1. Roemelt, Krewald, Pantazis, *J. Chem. Theory Comput.* **14**, 166–179 (2018).

Extended Active Spaces: DMRG+DSRG-PT2

Perturbative analysis

$$\hat{A} \approx \hat{A}^{(1)} + \hat{A}^{(2)} + \cdots$$

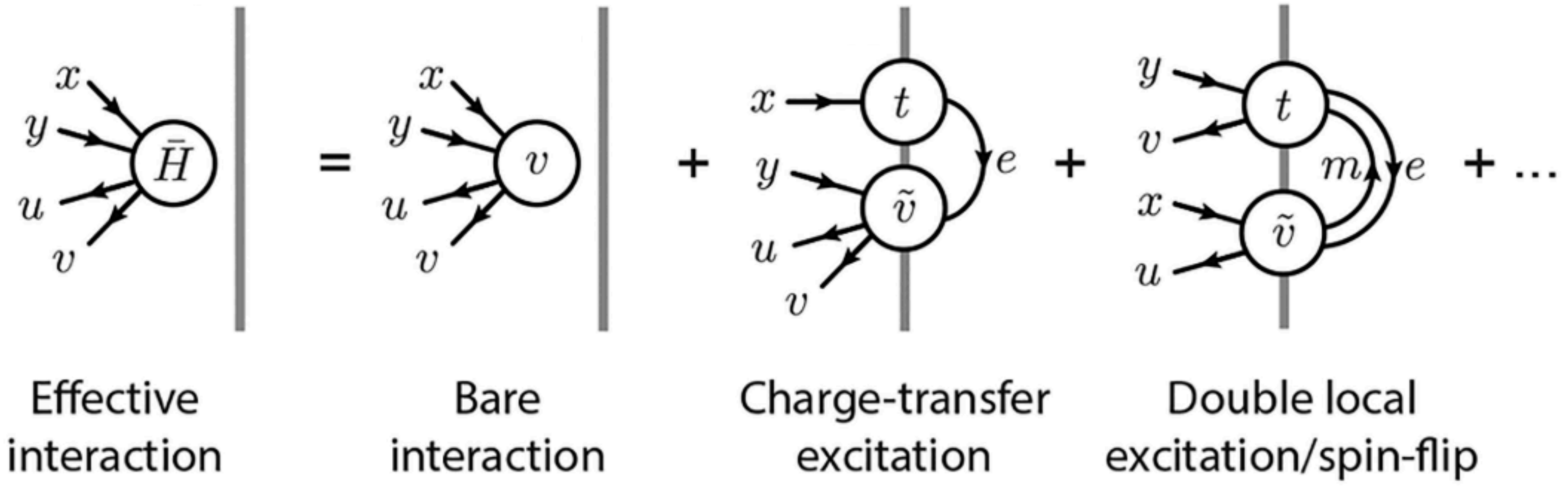
$$\hat{H}^{(0)} = E_0 + \sum_p \varepsilon_p \{\hat{a}_p^\dagger \hat{a}_p\}$$

$$\longrightarrow \quad t_{ab}^{ij,(1)}(s) = \frac{\langle ij \| ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}[1 - e^{-s(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)^2}]$$

parameter *s* regularizes cluster amplitudes

Second-order Hamiltonian[1]

$$\bar{H}^{[2]} = \hat{H} + [\hat{H}, \hat{A}^{(1)}] + \frac{1}{2}[[\hat{H}^{(0)}, \hat{A}^{(1)}], \hat{A}^{(1)}] \approx \bar{H}_0 + \sum_{pq} \bar{f}_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs} \overline{(pq\,|\,rs)} \hat{E}_{pq,rs}$$



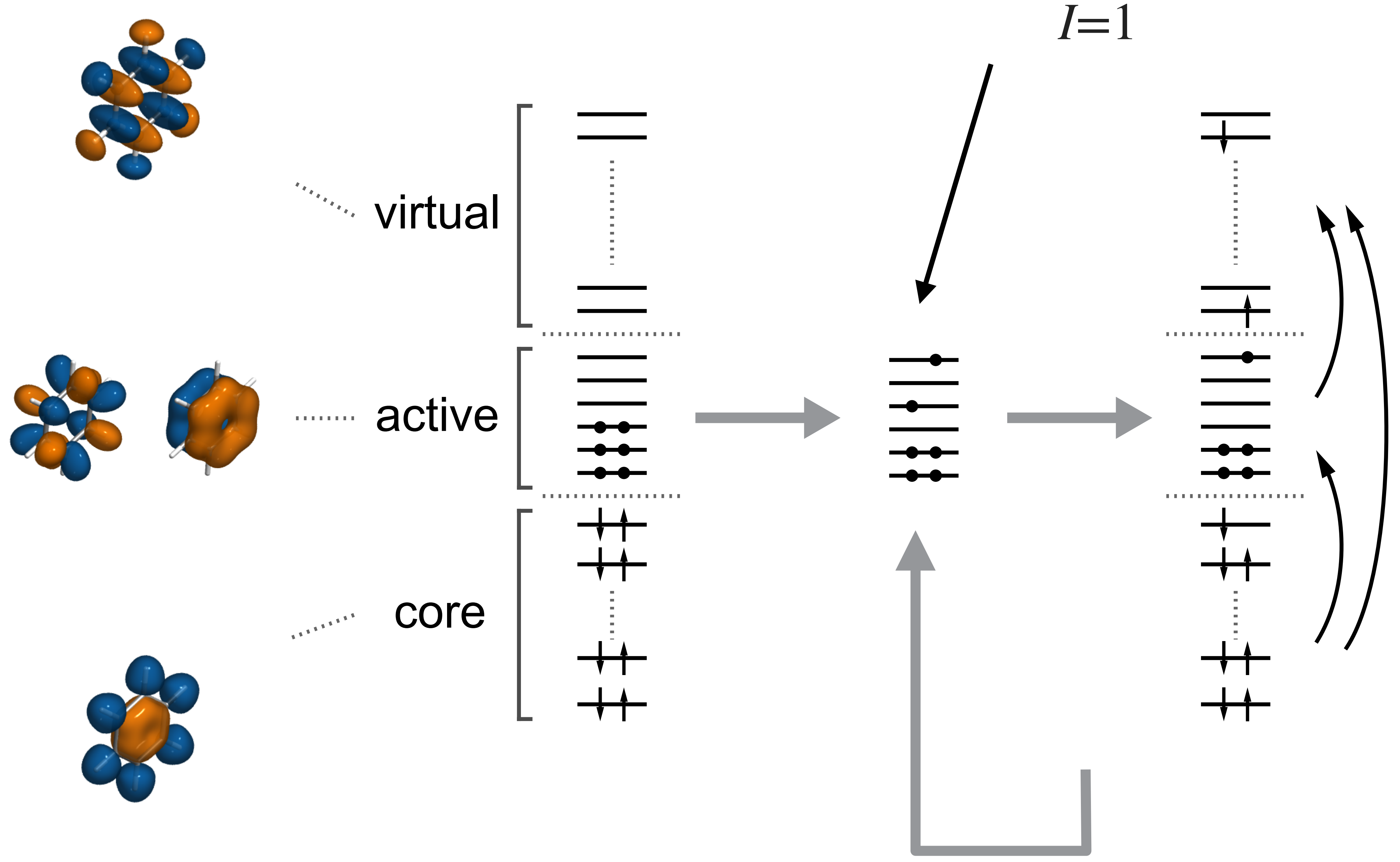
Solve the active-space Hamiltonian using these effective interactions!

1. He, Li, Evangelista, *J. Chem. Theory Comput.* **18**, 1527–1541 (2022).

Multireference driven similarity renormalization group

Genuine Multireference Methods

$$|\Psi_0\rangle = \sum_{I=1}^{\mathcal{M}} |\Phi_I\rangle c_I$$



1. Static correlation

a multi-configurational reference

2. Dynamical correlation

excitations outside active space

$$|\Psi\rangle = \hat{\Omega}|\Psi_0\rangle$$

3. Reference relaxation

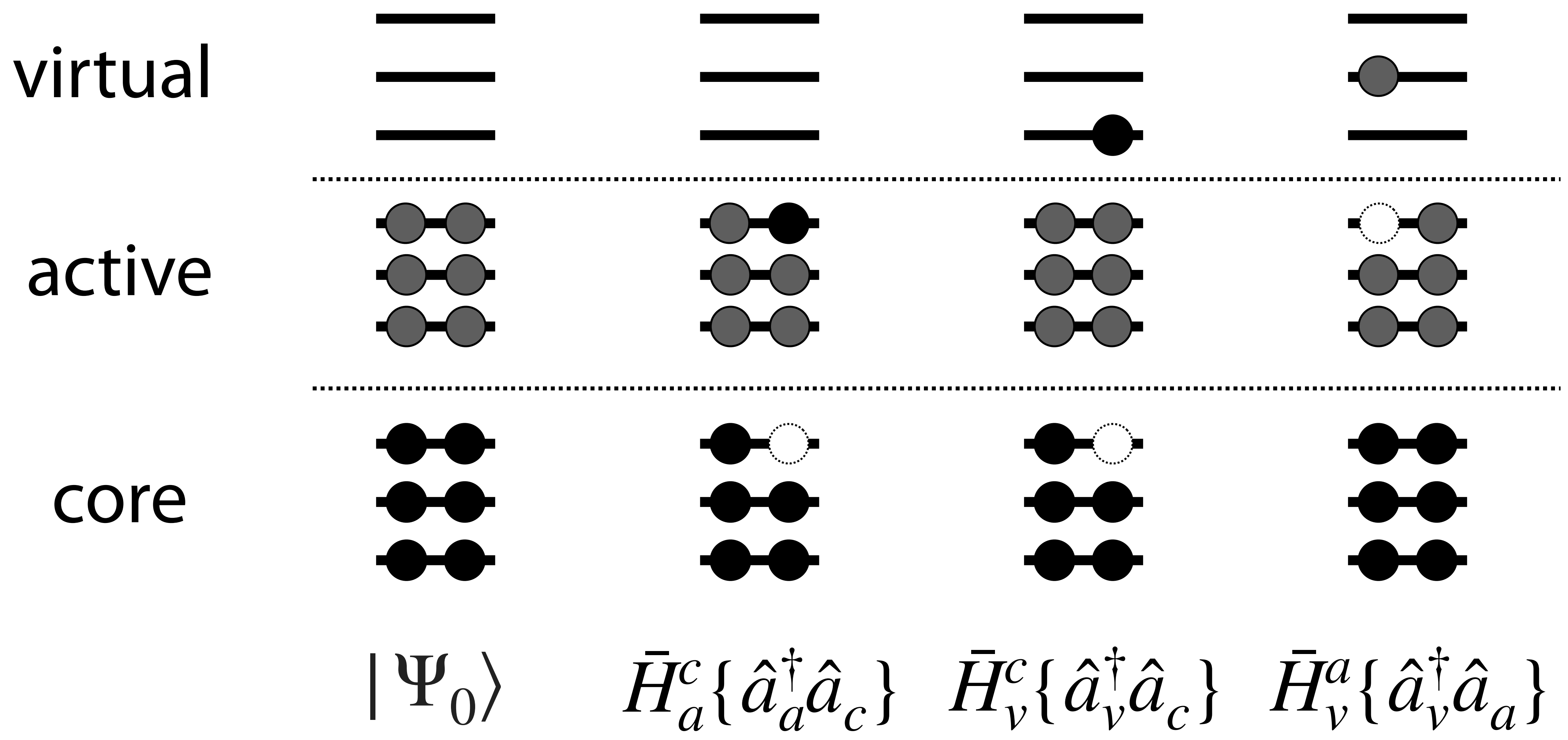
couple static / dynamical correlation

Multireference Driven Similarity Renormalization Group

Treat dynamical correlation via ***unitary*** transformation of the Hamiltonian[1–5]

$$\hat{H} \rightarrow \bar{H} = e^{-\hat{A}} \hat{H} e^{\hat{A}} = \bar{H}_0 + \sum_{pq} \bar{H}_p^q \{\hat{a}_q^p\} + \frac{1}{4} \sum_{pqrs} \bar{H}_{pq}^{rs} \{\hat{a}_{rs}^{pq}\} + \frac{1}{36} \sum_{pqrstu} \bar{H}_{stu}^{pqr} \{\hat{a}_{pqr}^{stu}\} + \cdots$$

Diagonalize $\bar{H}$ in ***Fock space***: zero some of $\bar{H}_{rs\cdots}^{pq\cdots}$ that couples the reference and its excited configurations



Many-Body Conditions[6–8]

$$\bar{H}_1^{\mathrm{N}} = \bar{H}_a^c \{\hat{a}_a^\dagger \hat{a}_c\} + \bar{H}_v^c \{\hat{a}_v^\dagger \hat{a}_c\} + \bar{H}_v^a \{\hat{a}_v^\dagger \hat{a}_a\} + \mathrm{H.c.} = 0$$

✓ unknowns = equations

✕ numerical unstable

1. Kutzelnigg, Koch, *J. Chem. Phys.* **79**, 4315 (1983).
2. Hoffmann, Simons, *J. Chem. Phys.* **88**, 993 (1988).
3. Yanai, Chan, *J. Chem. Phys.* **124**, 194106 (2006).
4. Chen, Hoffmann, *J. Chem. Phys.* **137**, 014108 (2012).
5. Liu, Asthana, Cheng, Mukherjee, *J. Chem. Phys.* **148**, 244110 (2018).
6. Kutzelnigg, *J. Chem. Phys.* **77**, 3081 (1982).
7. Datta, Kong, Nooijen, *J. Chem. Phys.* **134**, 214116 (2011).
8. Datta, Nooijen, *J. Chem. Phys.* **137**, 204107 (2012).

Multireference Driven Similarity Renormalization Group

Avoid numerical issues by using driven similarity renormalization group[1]

Introduce the ***flow parameter s*** $\bar{H} = e^{-\hat{A}}\hat{H}e^{\hat{A}} \quad \rightarrow \quad \bar{H}_{\mathrm{DSRG}}(s) = e^{-\hat{A}(s)}\hat{H}e^{\hat{A}(s)}$

Define how $\bar{H}^{\mathrm{N}}$ evolves with respect to *s* $\bar{H}^{\mathrm{N}} = 0 \quad \rightarrow \quad [\bar{H}_{\mathrm{DSRG}}(s)]^{\mathrm{N}} = \hat{R}(s)$

Derived from 1st-order PT $\hat{R}(s) = [\bar{H}^{ij\cdots}_{ab\cdots}(s) + \Delta^{ij\cdots}_{ab\cdots} t^{ij\cdots}_{ab\cdots}(s)]e^{-s(\Delta^{ij\cdots}_{ab\cdots})^2}\{\hat{a}^\dagger_a\hat{a}^\dagger_b\cdots\hat{a}_j\hat{a}_i\}$

1st-order amplitudes

$$t^{ij,(1)}_{ab}(s) = \frac{\langle ij \| ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}[1 - e^{-s(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)^2}]$$

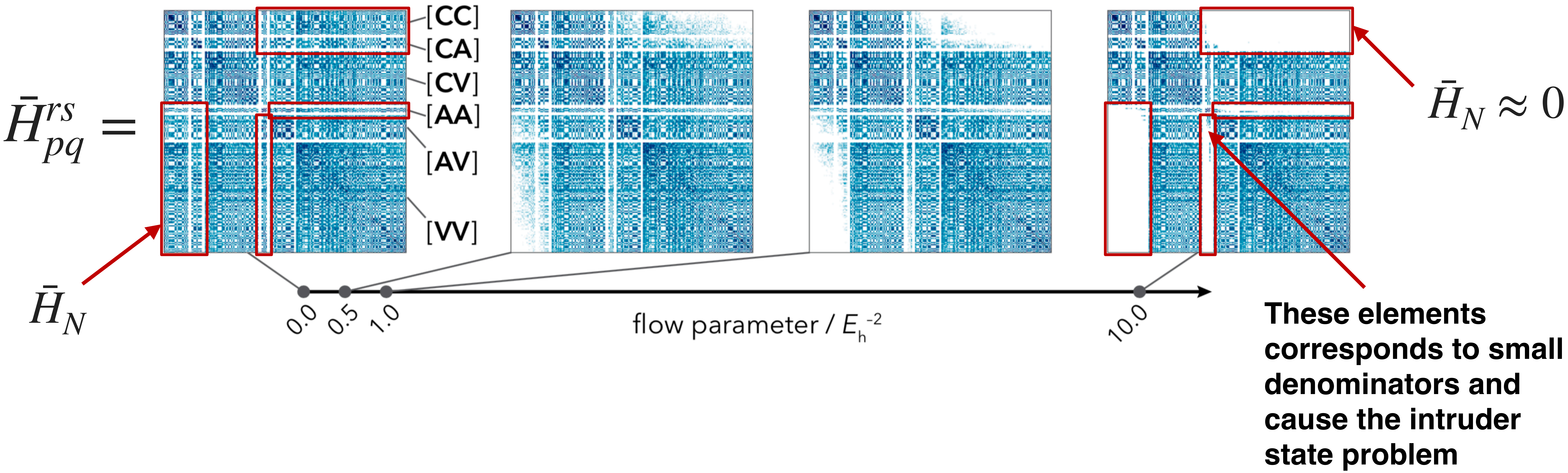
regularized for small denominators

1. Evangelista, *J. Chem. Phys.* **141**, 054109 (2014).

Multireference Driven Similarity Renormalization Group

The source operator $[\hat{R}(s)]$ drives the Hamiltonian to a band diagonal form

$$\bar{H}^{rs}_{pq} =$$



C. Li and F. A. Evangelista, *Annu. Rev. Phys. Chem.* (2019).

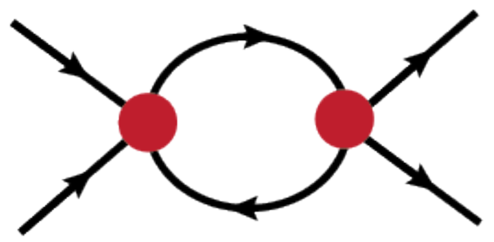
How source operator is "derived"?

Comparing to the in-medium SRG Hamiltonian[1]

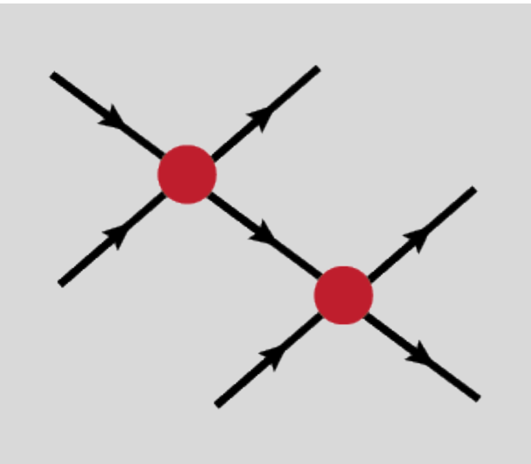
In IM-SRG: $\hat{H} \quad \rightarrow \quad \bar{H}_{\text{SRG}}(s) = \hat{U}^{\dagger}(s)\hat{H}\hat{U}(s) = \bar{H}_0(s) + \bar{f}^p_q(s)\{\hat{a}^q_p\} + \frac{1}{4}\bar{v}^{rs}_{pq}(s)\{\hat{a}^{pq}_{rs}\} + \cdots$

SRG flow equation $\frac{\mathrm{d}}{\mathrm{d}s}\bar{H}(s) = [\hat{\eta}(s), \bar{H}(s)]$ with a generator $\hat{\eta}(s) = [\bar{H}^{\mathrm{D}}(s), \bar{H}^{\mathrm{N}}(s)]$

In IM-SRG(2): $\frac{\mathrm{d}}{\mathrm{d}s}\bar{H}(s) = [\hat{\eta}(s), \bar{H}(s)]_{1,2} \longrightarrow$



+ … +



+…

eliminate higher-body interactions

From perturbative analysis, the source operator of DSRG is chosen such that

$$\bar{E}^{[2]}_0(s) = \bar{H}^{[2]}_0(s) = \frac{1}{4}|v^{ij}_{ab}|^2 \frac{[1 - e^{-2s(\Delta^{ij}_{ab})^2}]}{\Delta^{ij}_{ab}}$$

1. Evangelista, *J. Chem. Phys.* **141**, 054109 (2014).

MR-DSRG Truncated Schemes

$$\bar{H} = e^{-\hat{A}}\hat{H}e^{\hat{A}} = \hat{H} + [\hat{H},\hat{A}] + \frac{1}{2}[[\hat{H},\hat{A}],\hat{A}] + \cdots$$

nonterminating series

Practical methods within the MRDSRG framework

DSRG with singles and doubles $\hat{A} \approx \hat{A}_1 + \hat{A}_2$ **MR-LDSRG(2)**

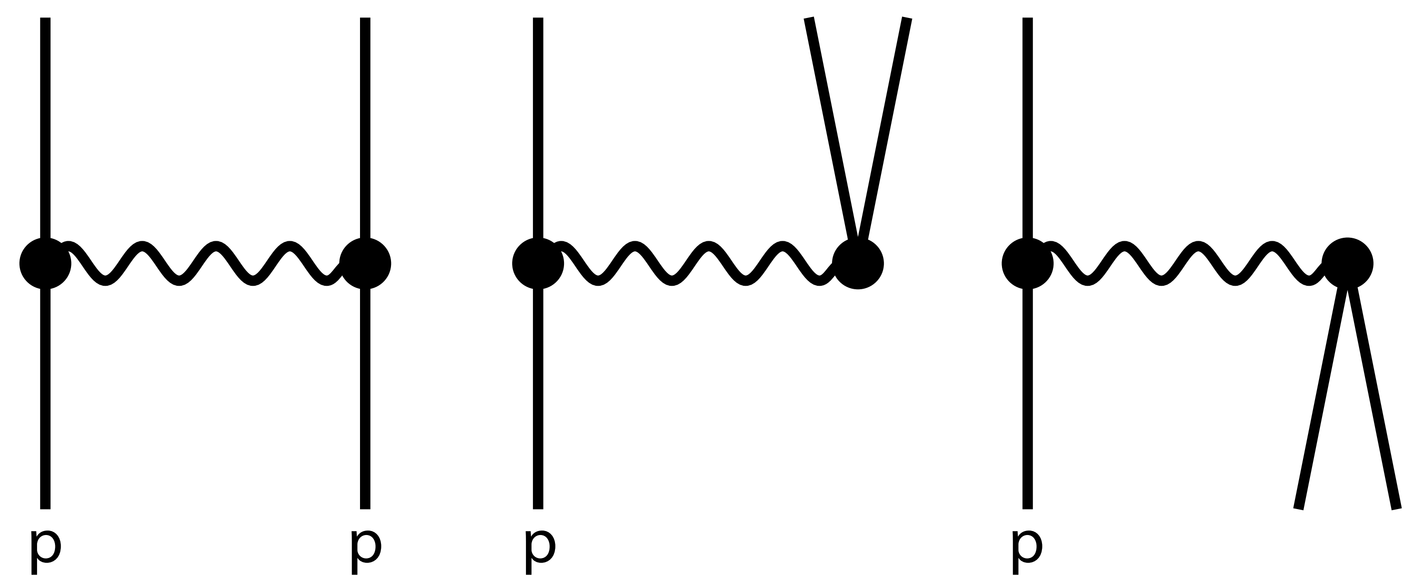
Linear commutator approximation[1] $\bar{H} \approx \hat{H} + [\hat{H},\hat{A}]_{0,1,2} + \frac{1}{2}[[\hat{H},\hat{A}]_{1,2},\hat{A}]_{0,1,2} + \cdots$

only require 1-, 2-, and 3-RDMs of the reference

A memory friendly version of MR-LDSRG(2): sq-MR-LDSRG(2) + NIVO[2]

$$\tilde{H} = e^{-\hat{A}_1}\hat{H}e^{\hat{A}_1}$$

$$\bar{H} \approx \tilde{H} + [\tilde{H},\hat{A}_2]_{0,1,2'} + \frac{1}{2}[[\tilde{H},\hat{A}_2]_{1,2'},\hat{A}_2]_{0,1,2'} + \cdots$$



1. Yanai, Chan, *J. Chem. Phys.* **124**, 194106 (2006).

2. T. Zhang, C. Li, and F. A. Evangelista, *J. Chem. Theory Comput.* (2019).

MR-DSRG Truncated Schemes

$$\bar{H} = e^{-\hat{A}}\hat{H}e^{\hat{A}} = \hat{H} + [\hat{H}, \hat{A}] + \frac{1}{2}[[\hat{H}, \hat{A}], \hat{A}] + \cdots$$

nonterminating series

Practical methods within the MRDSRG framework

MR-LDSRG(2)

DSRG with singles and doubles $\hat{A} \approx \hat{A}_1 + \hat{A}_2$

Linear commutator approximation[1] $\bar{H} \approx \hat{H} + [\hat{H}, \hat{A}]_{0,1,2} + \frac{1}{2}[[\hat{H}, \hat{A}]_{1,2}, \hat{A}]_{0,1,2} + \cdots$

only require 1-, 2-, and 3-RDMs of the reference

Perturbation theories based on MR-LDSRG(2)

$$\hat{A} \approx \hat{A}^{(1)} + \hat{A}^{(2)} + \cdots$$

$$\hat{H}^{(0)} = E_0 + \sum_{p} \varepsilon_p \{\hat{a}_p^\dagger \hat{a}_p\}$$

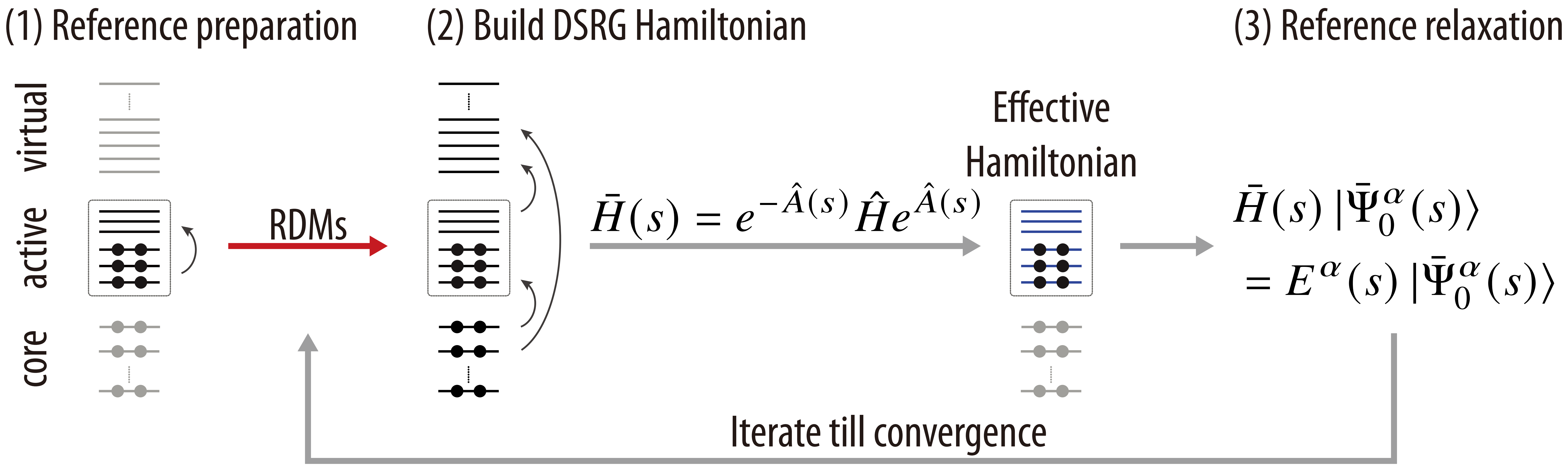
$\longrightarrow$

$$t_{ab}^{ij,(1)}(s) = \frac{\langle ij \| ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}[1 - e^{-s(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)^2}]$$

one-shot methods with regularized amplitudes

1. Yanai, Chan, *J. Chem. Phys.* **124**, 194106 (2006).

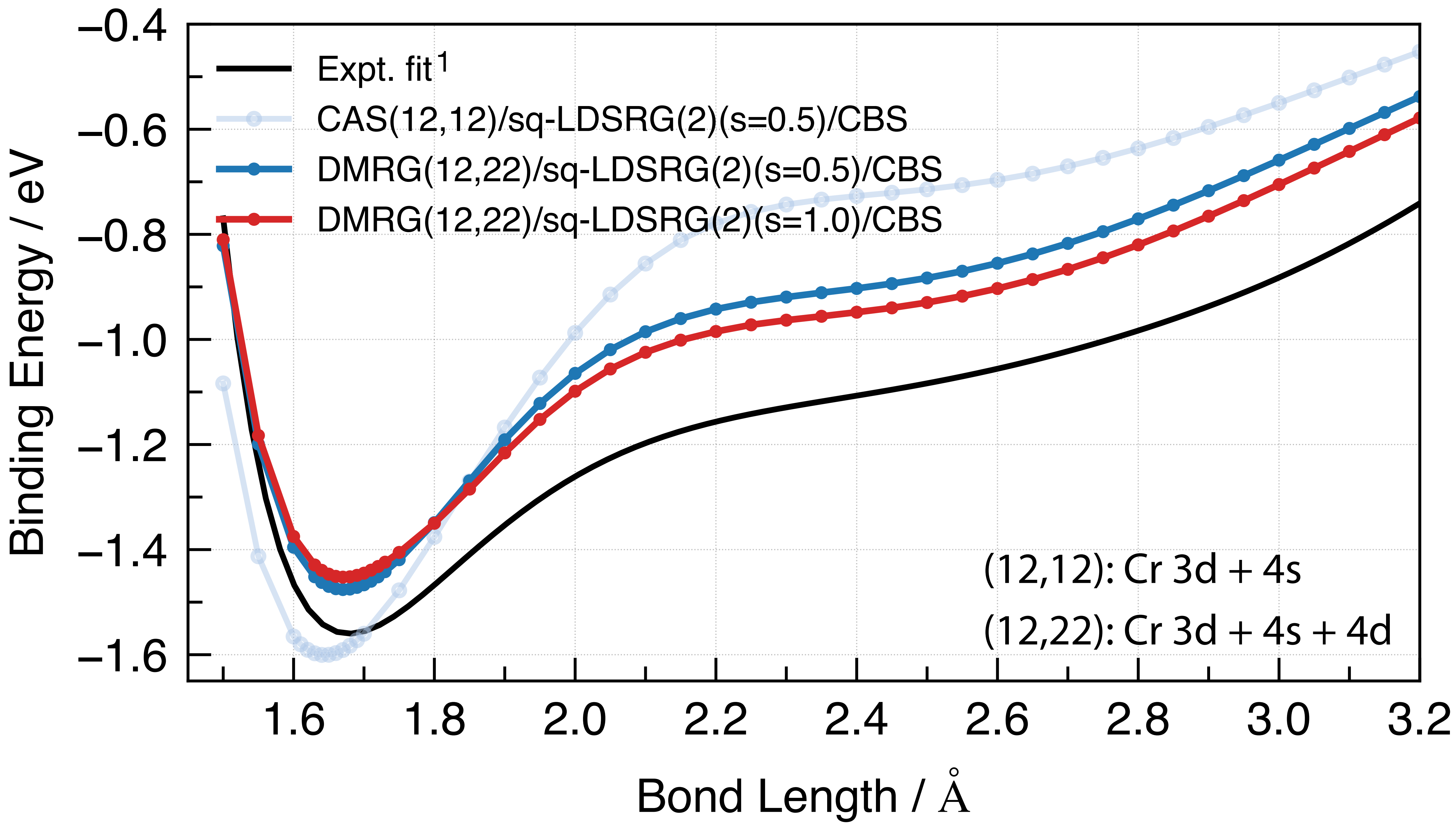
The MR-DSRG Procedure



- **RDMs** carry all information of the reference state:
  - CASCI, RASCI, SCI, DMRG, …
  - state specific / state averaged RDMs
- Include reference relaxations (one-shot for DSRG-PT)
- A "downfolding" scheme: $N \rightarrow N_{\mathrm{act}}$

compute J values using effective interactions!

Potential Energy Curve of Cr_2

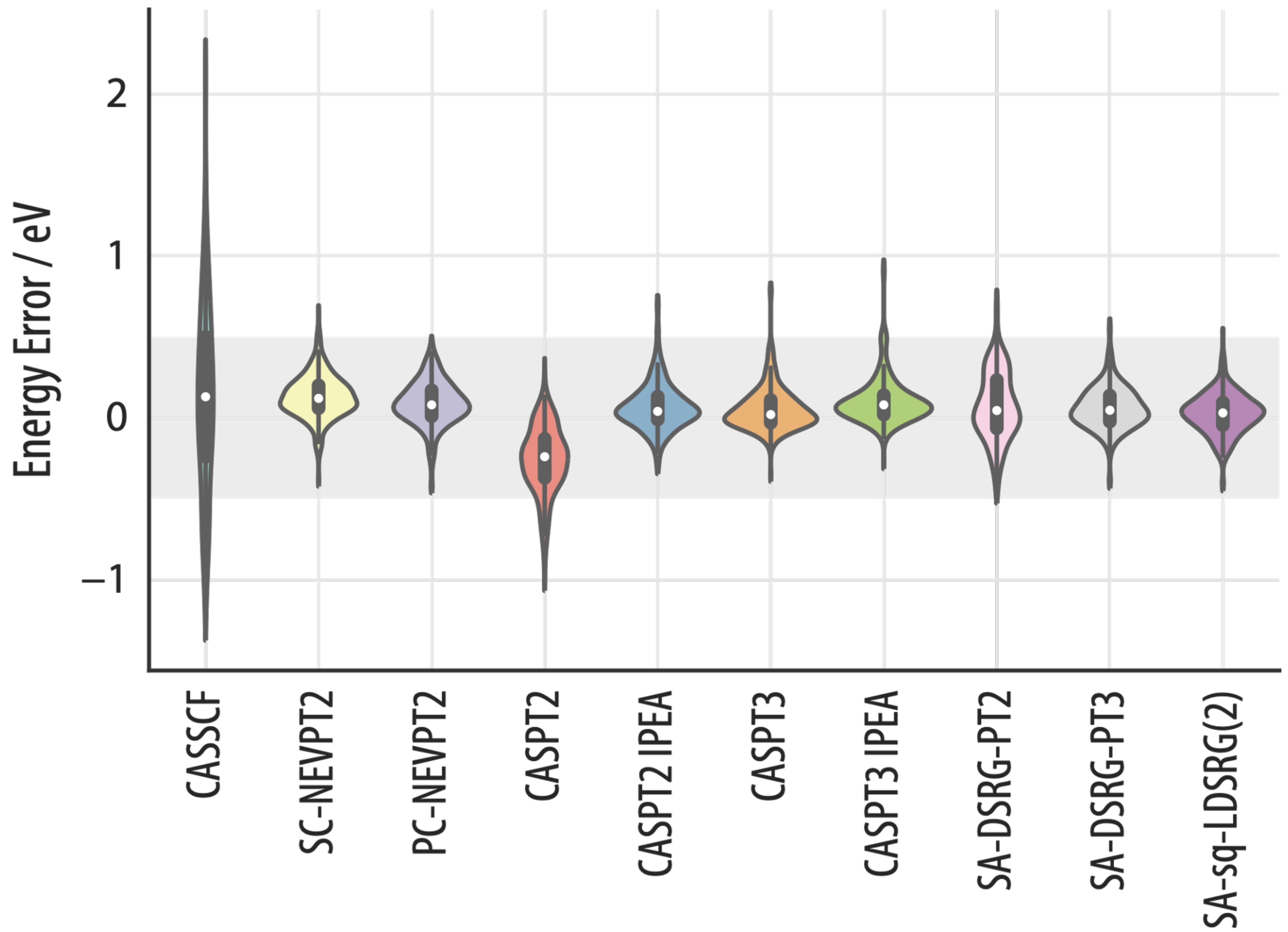


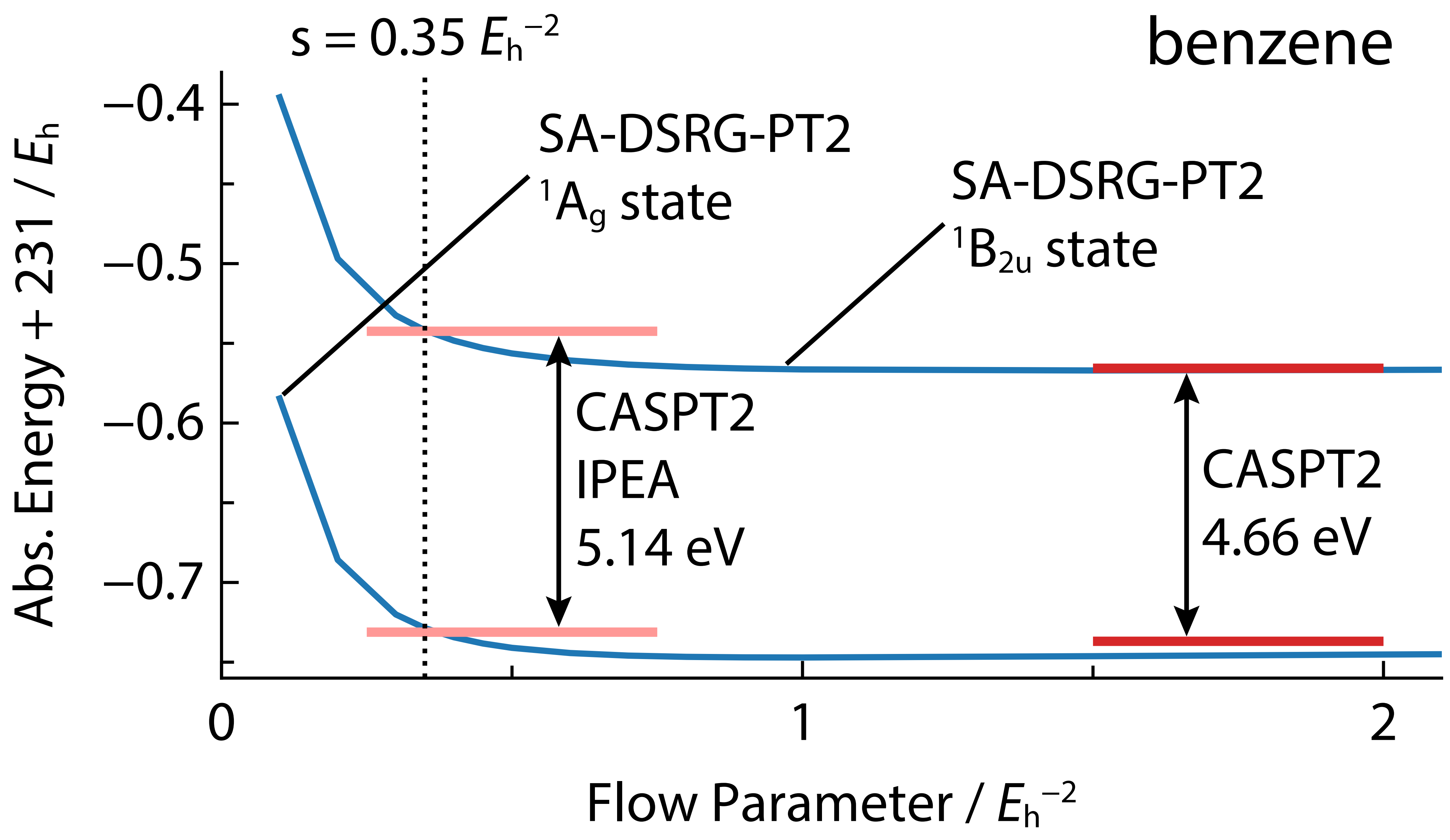
	r_e / Å	ω_e / cm^{-1}	$\Delta G_{1/2}$ / cm^{-1}	D_e / eV
sq-LDSRG(2)[4]	1.672	479	447	1.45
Exp.[2,3]	1.68	480.6 ± 0.5	455 ± 10	1.472 ± 0.052

1. Larsson, Zhai, Umrigar, Chan, *J. Am. Chem. Soc.* **144**, 15932 (2022).
2. Casey, Leopold, *J. Phys. Chem.* **97**, 816 (1993).
3. Hilpert, Ruthardt, *Ber. Bunsenges. Phys. Chem.* **91**, 724 (1987).
4. C. Li, X. Wang, H. Zhai, W.-H. Fang, *J. Chem. Theory Comput.* (2025).

Vertical Excitation Energies (SA-RDMs)

Compare against theoretical best estimates in QUEST database[1]

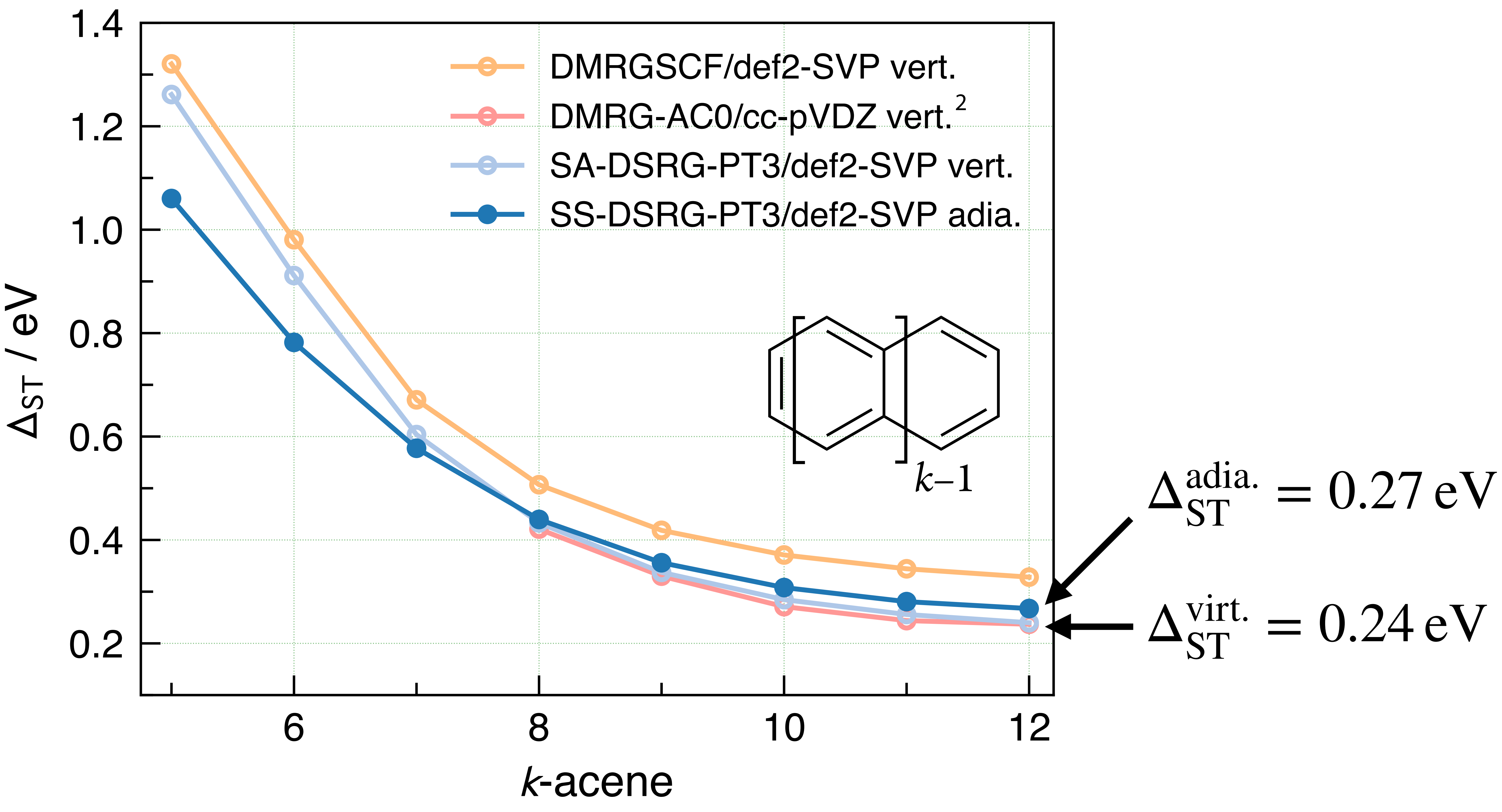




Accuracy: CASPT2 < SA-DSRG-PT2 < NEVPT2 ~ CASPT2 IPEA ~ CASPT3 ~ SA-DSRG-PT3 ~ SA-sq-LDSRG(2)

1. Sarkar, Loos, Boggio-Pasqua, Jacquenmin, *J. Chem. Theory Comput.* **18**, 2418 (2022).
2. M. Wang, W.-H. Fang, C. Li, *J. Chem. Theory Comput.* (2023).

Singlet-Triplet Gaps of Oligoacenes



full valence π active space (4*k*+2,4*k*+2)

UB3LYP/6-31G(d,p) geometries[1]

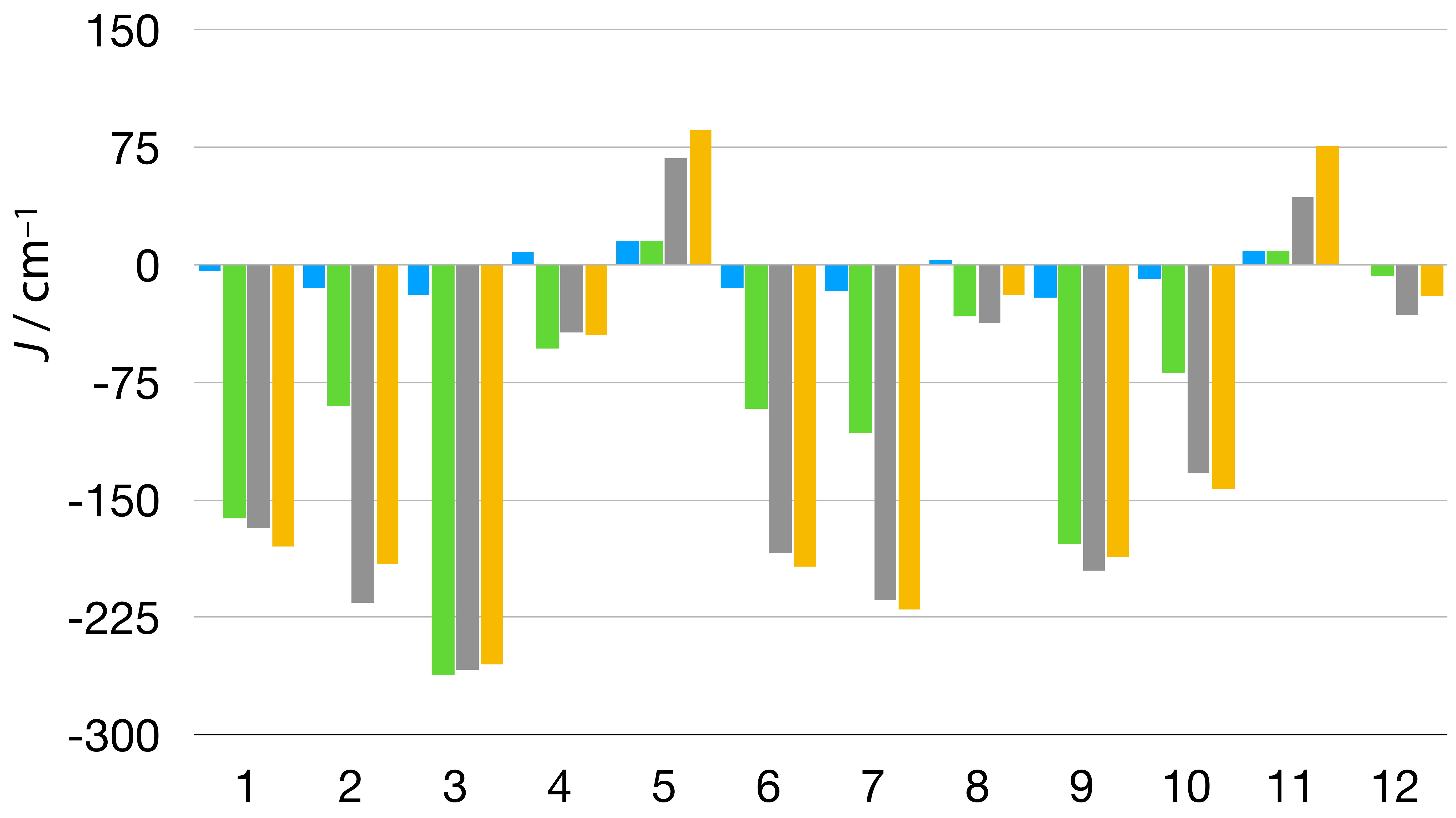
1. S. Ghosh, C. J. Cramer, D. G. Truhlar, L. Gagliardi, *Chem. Sci.* **8**, 2741 (2017).
2. R. Zuzak, et al., *Angew. Chem. Int. Ed.* **63**, e202317091 (2024).

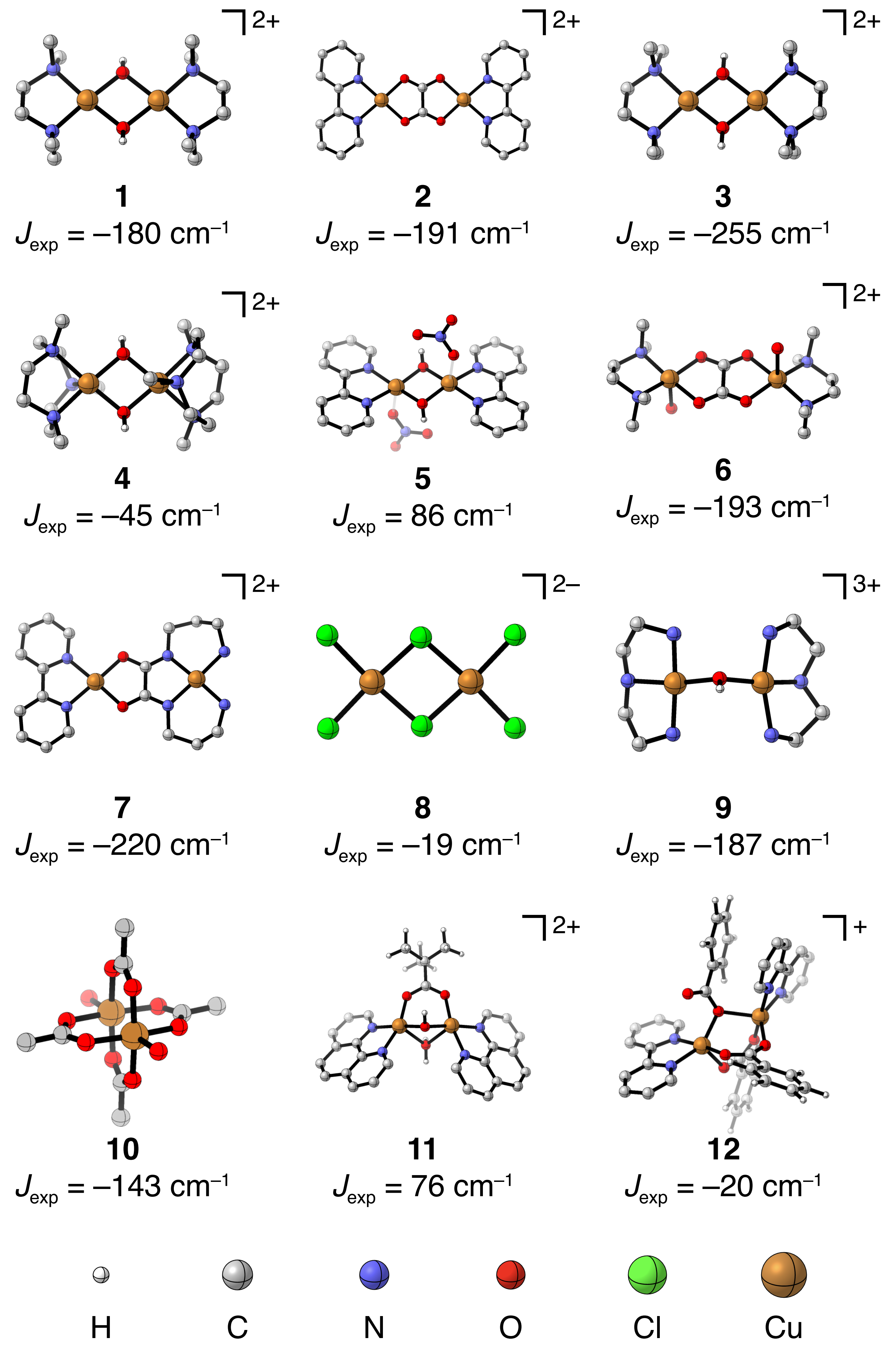
C. Li, X. Wang, H. Zhai, W.-H. Fang, *J. Chem. Theory Comput.* (2025).

Exchange couplings in bimetallic compounds

CAS(2,2) for Cu(II) Complexes

	CASSCF	SA-DSRG-PT2	DDCI	Exp
MRE / %	–96	–30	–6	
MARE / %	96	46	22	



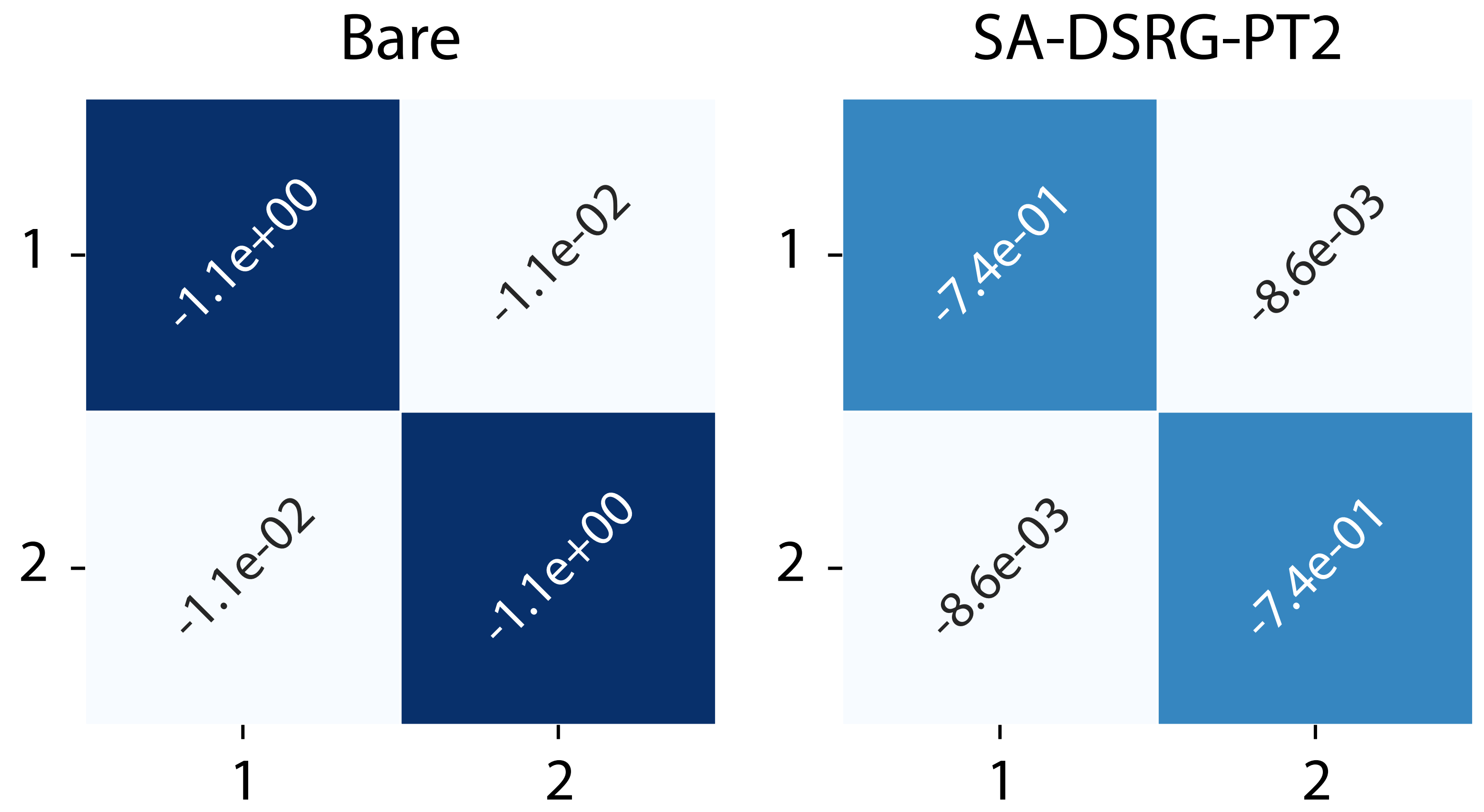


geometries from crystallographic data
def2-SVP for DDCI, def2-TZVP otherwise

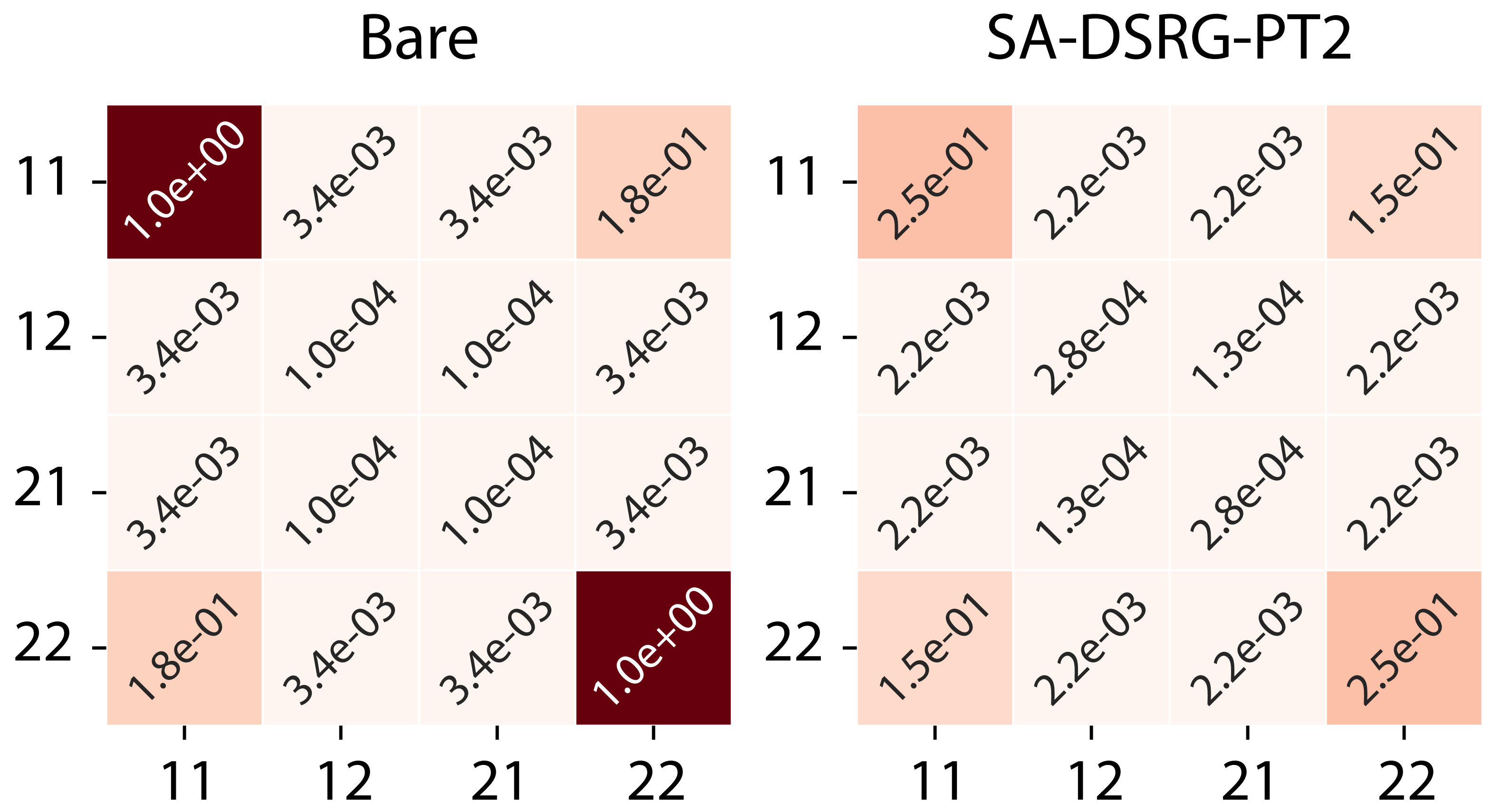
Z. Hu and C. Li, *Inorg. Chem.* (2026).

Analysis of the CAS(2,2) Integrals for Complex 1

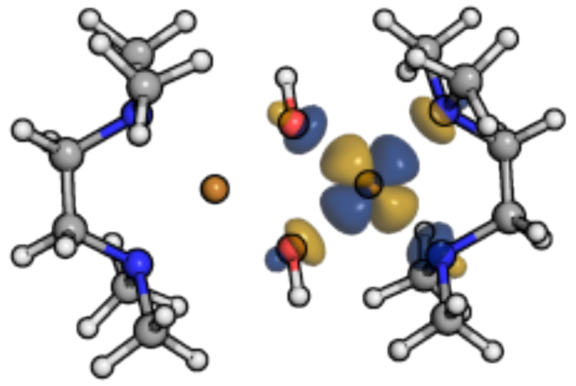
one-body integrals



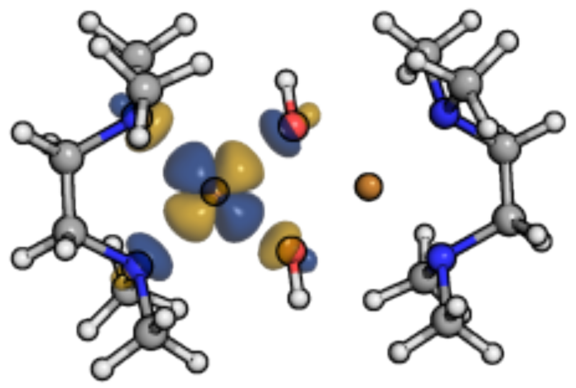
two-body integrals $(pq|rs)$



orbital 1



orbital 2



$$J = \frac{1}{4}(3K_1 + K_2 + U) - \frac{1}{4}\sqrt{K_-(K_- + 2U) + U^2 + 16t^2}$$

$$\approx K - 2t^2/U$$

	$t \times 10^3$	$U \times 10$	$U/\|t\| \times 0.1$
Bare	-7.22	8.59	11.9
SA-DSRG-PT2	-6.41	0.93	1.4

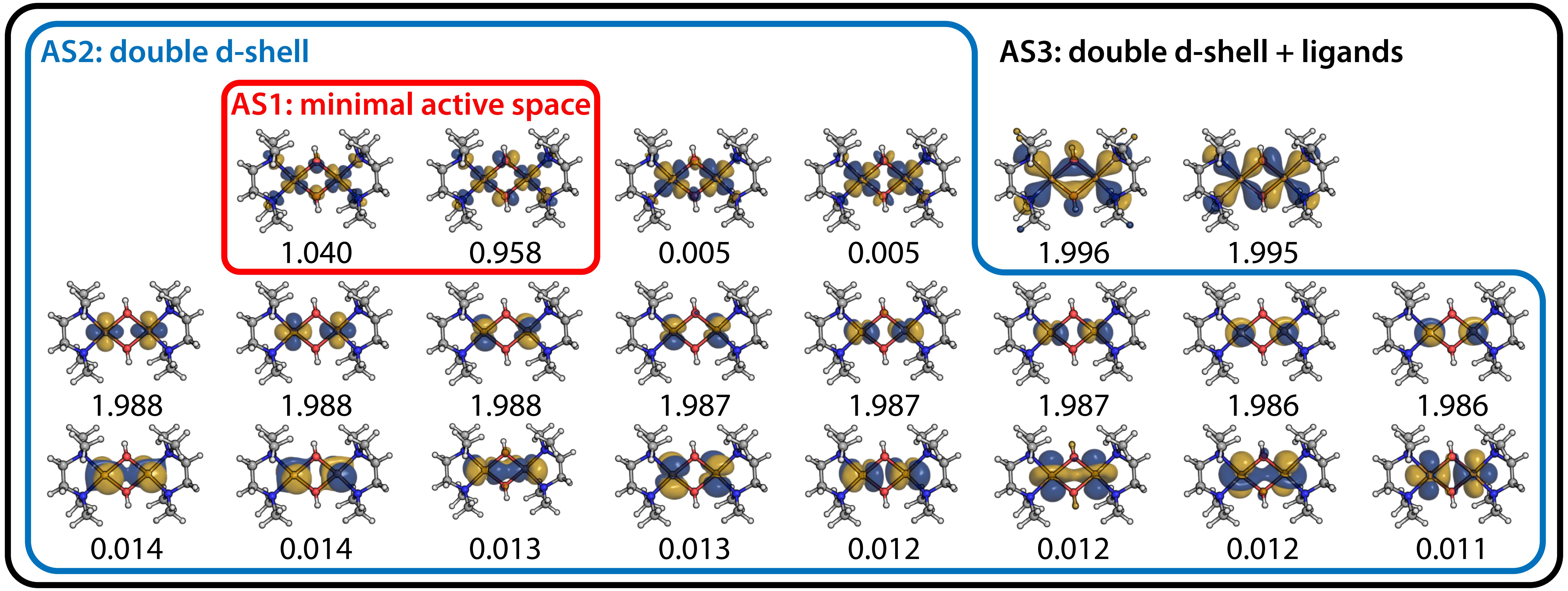
- K_1 is dominant in direct exchange
- $K_1 = K_2$ for bare integrals, but $\bar{K}_1 \neq \bar{K}_2$ for DSRG integrals
- $K \sim \bar{K}, t \sim \bar{t}, U \gg \bar{U},\ U/|t| \downarrow \Rightarrow J \downarrow$

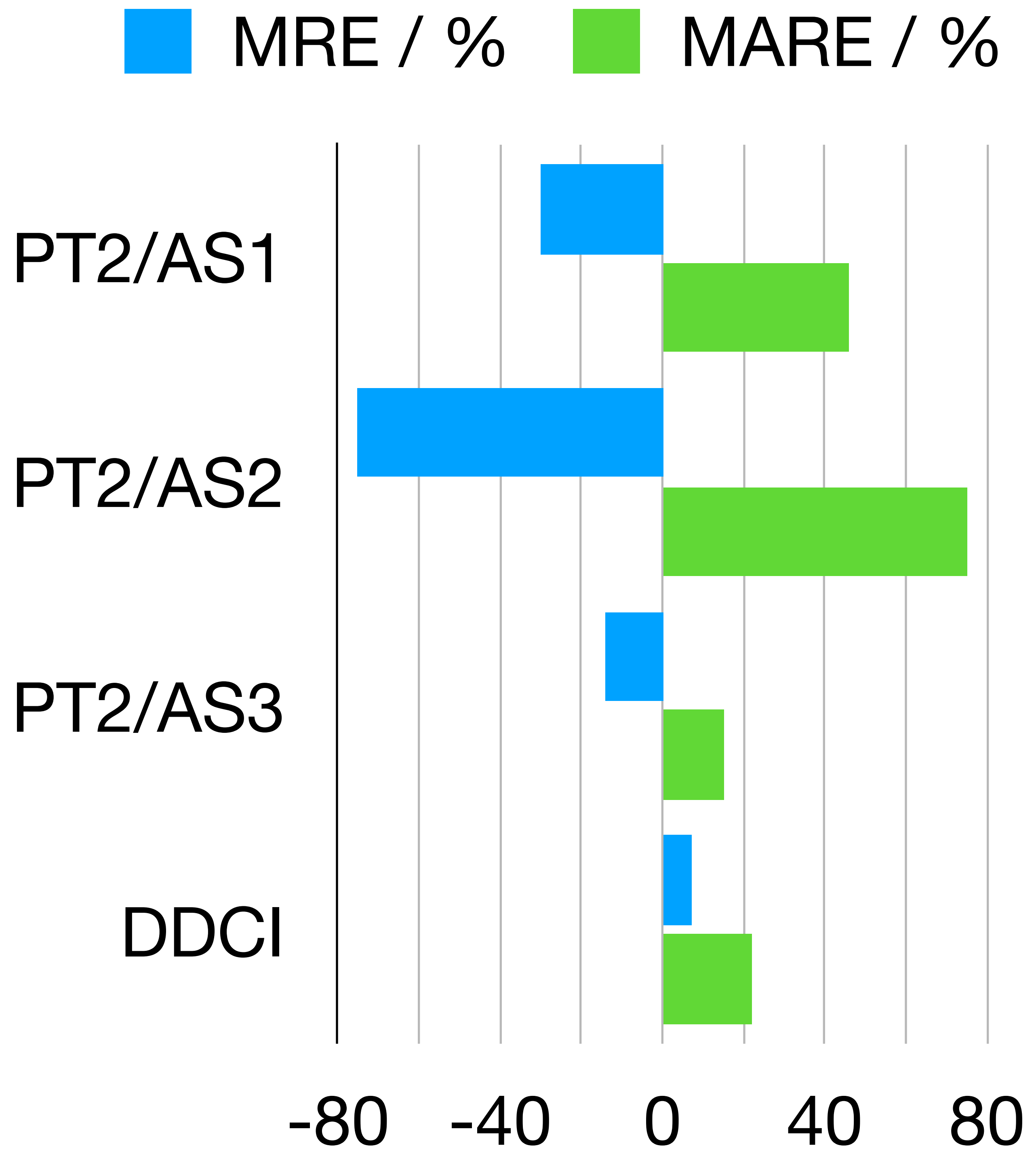
$K_1 = (12|21), K_2 = (12|12), K_- = K_2 - K_1, t = f^{c}_{12} + (12|22), U = f^{c}_{11} - f^{c}_{22} + (11|11) - (11|22)$

Z. Hu and C. Li, *Inorg. Chem.* (2026).

Expanding the Active Space for Cu(II) Complexes

- Atomic valence active space protocol[1]
  - High-spin ROHF orbitals with non-negligible overlaps with metal 3d and 4d
- Equal-weighted state-averaged DMRG-SCF



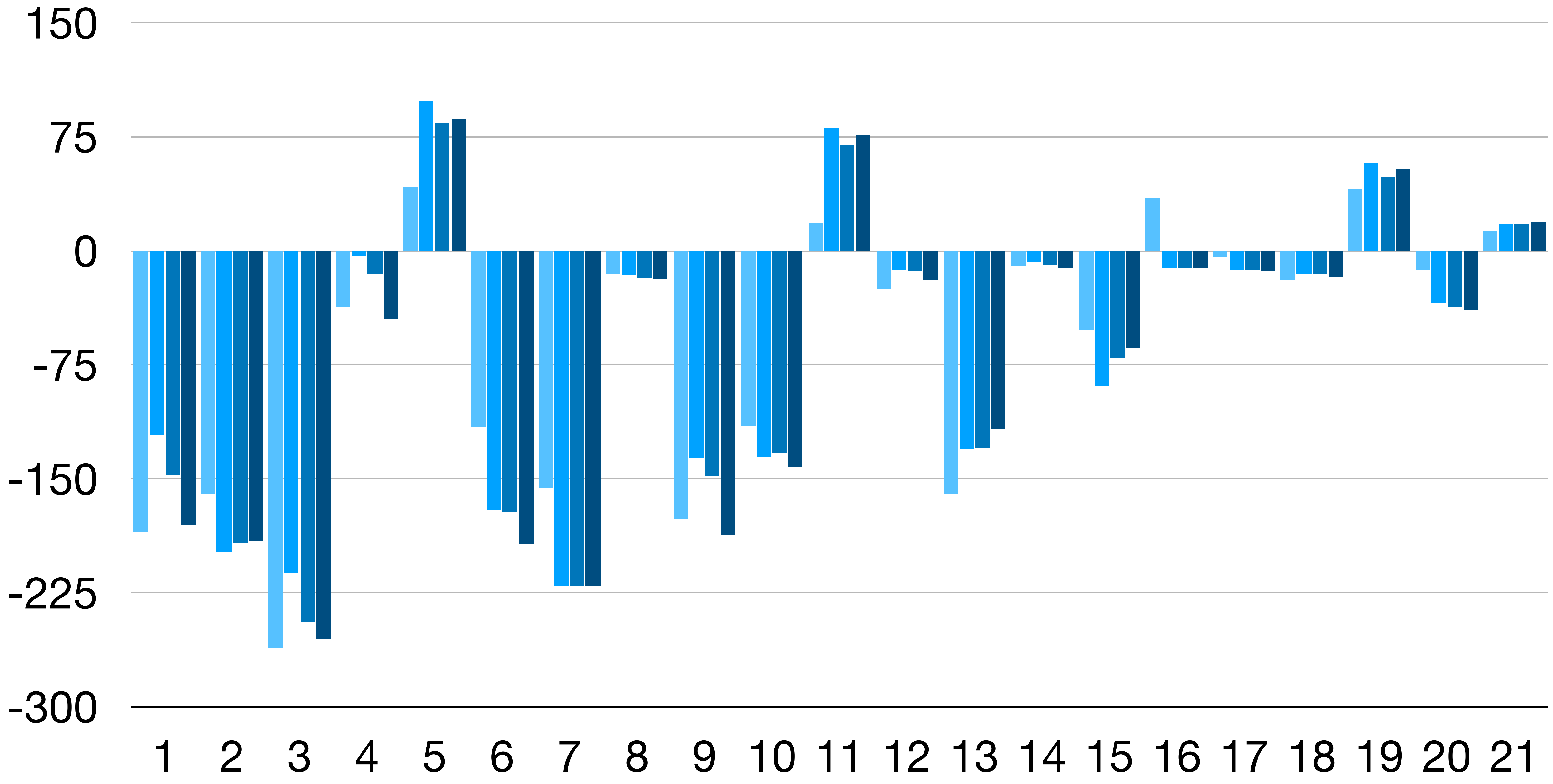


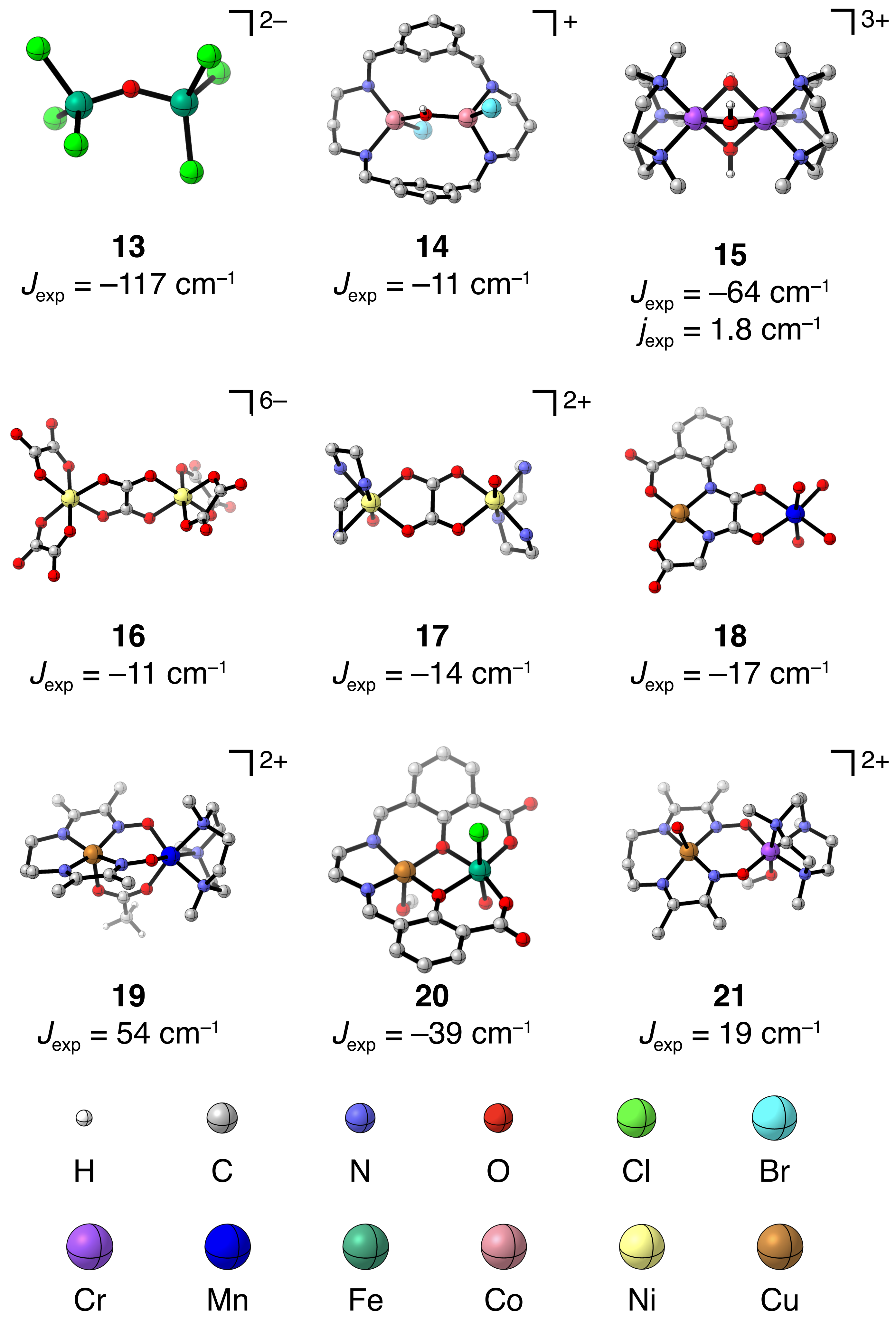
1. Sayfutyarova, Sun, Chan, Knizia, *J. Chem. Theory Comput.* **13**, 4063–4078 (2017).

Z. Hu and C. Li, *Inorg. Chem.* (2026).

More Bimetallic Molecules

	cu4-CASPT2	SS-DSRG-PT2	SA-DSRG-PT2	Exp
MRE / %	−39	−11	−10	
MARE / %	47	18	12	



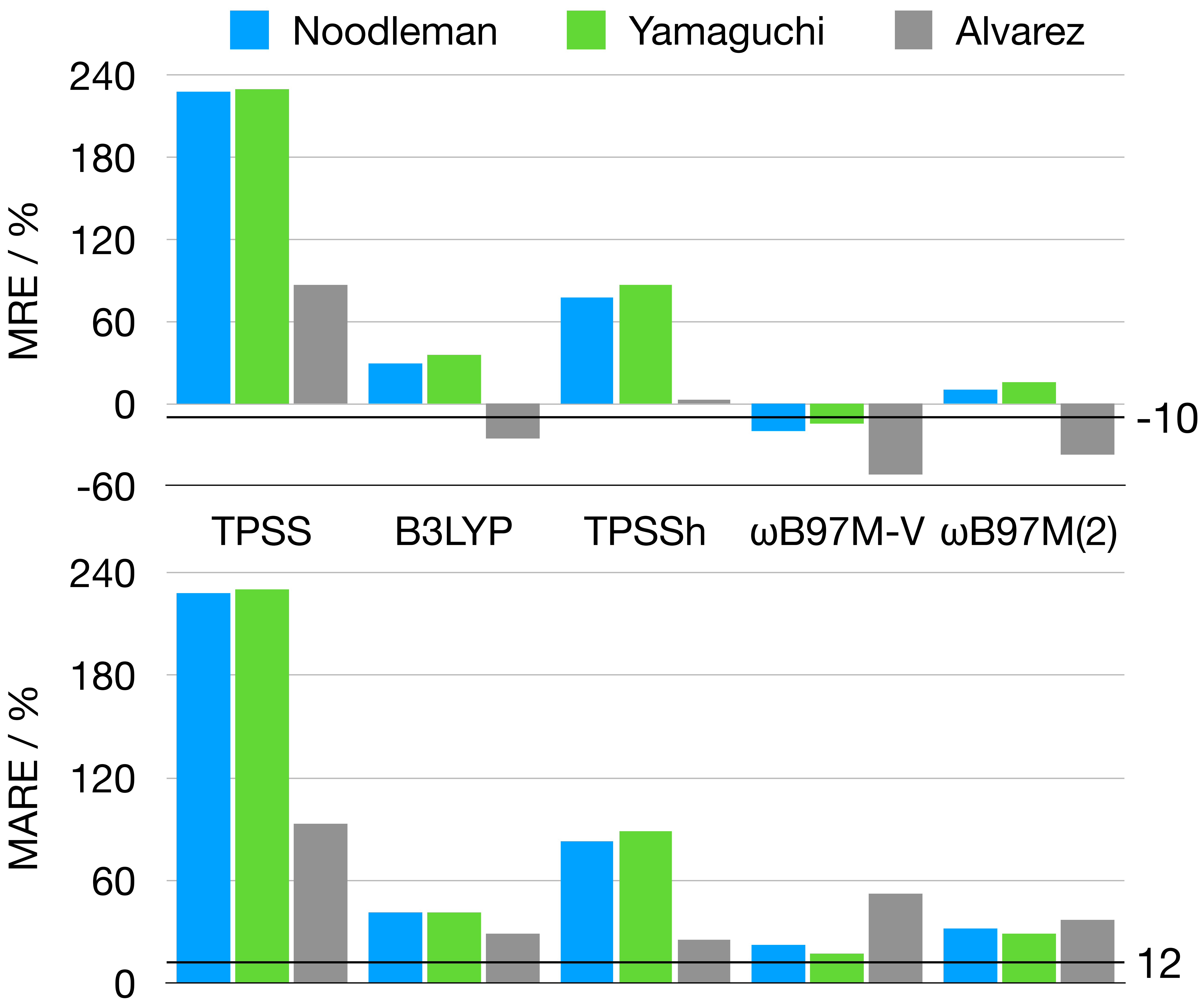


geometries from crystallographic data, def2-TZVP basis set, AS3 active space

Z. Hu and C. Li, *Inorg. Chem.* (2026).

Comparison to BS-DFT Results

- Noodleman:[1] $J_N = \frac{E_{BS} - E_{HS}}{S_{max}^2}$
- Yamaguchi:[2] $J_Y = \frac{E_{BS} - E_{HS}}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}}$
- Alvarez:[3] $J_A = \frac{E_{BS} - E_{HS}}{S_{max}(S_{max} + 1)}$
- Best BS-DFT MARE: J_Y(ωB97M-V) = 17%
- Require careful benchmarking for predictive reliability[4]

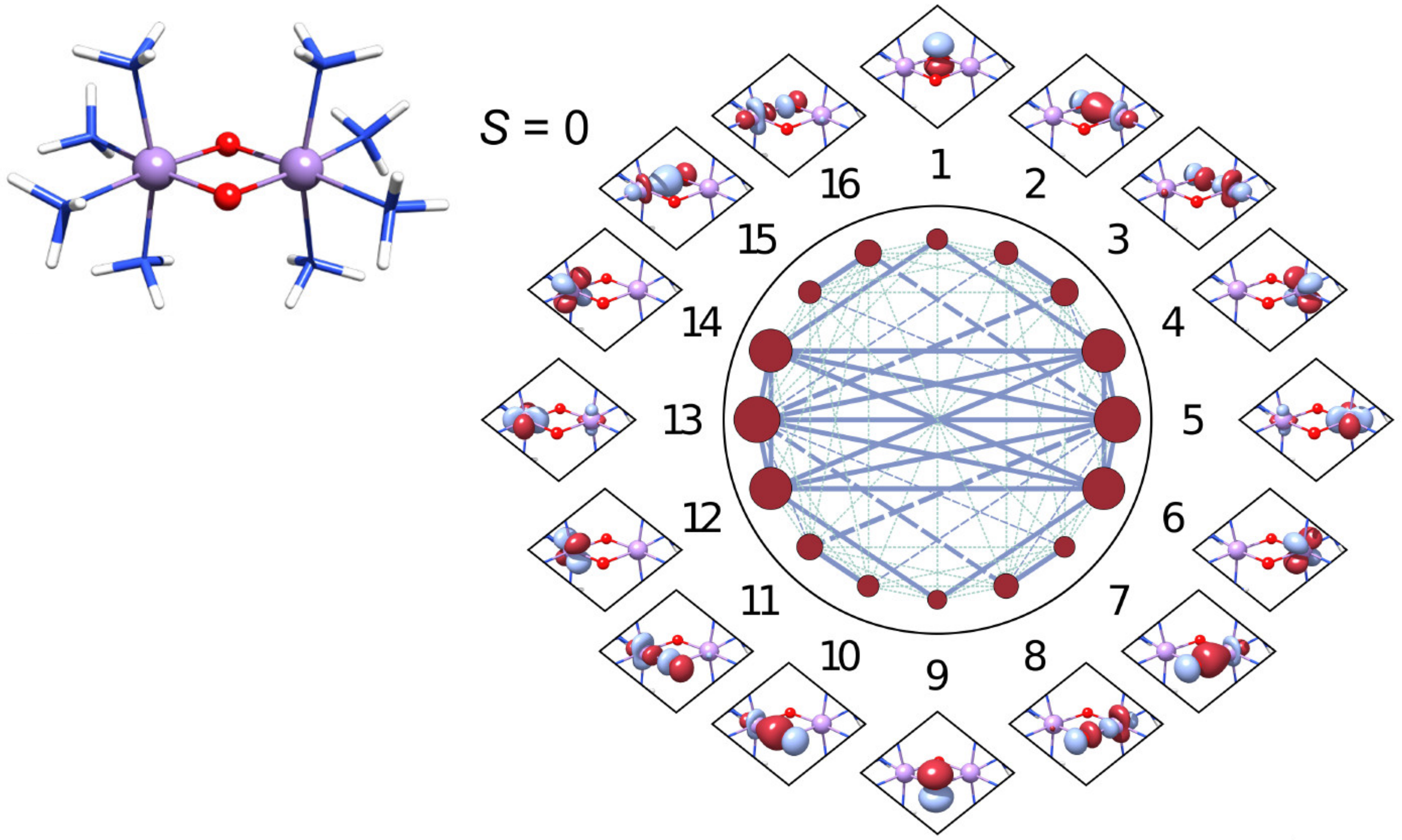


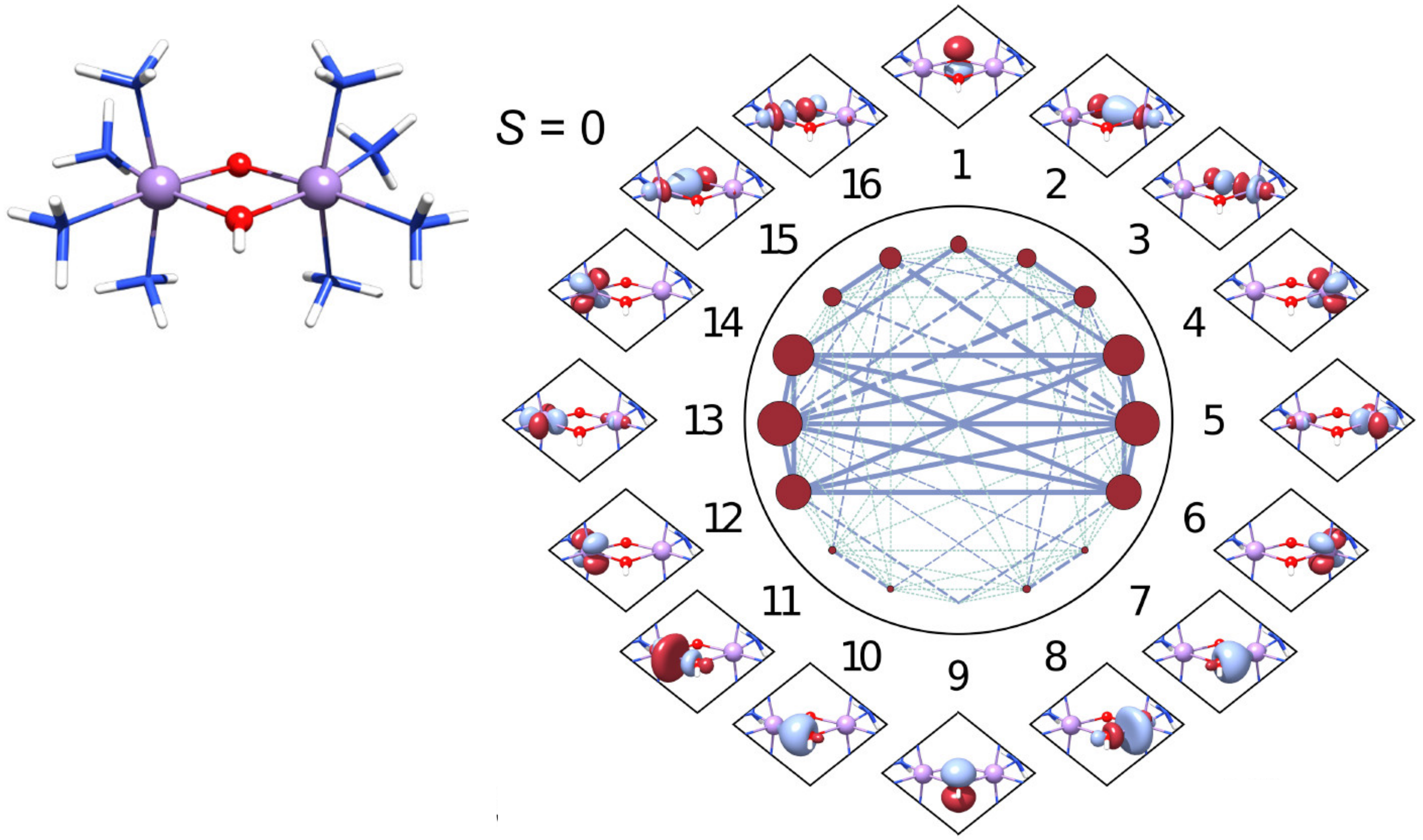
1. Noodleman, *J. Chem. Phys.* **74**, 5737 (1981).
2. Yamanaka, Kawakami, Nagao, Yamaguchi, *Chem. Phys. Lett.* **231**, 25 (1994).
3. Ruiz, Cano, Alvarez, Alemany, *J. Comput. Chem.* **20**, 1391 (1999).
4. Pantazis, *Inorganics*, **7**, 57 (2019).

Z. Hu and C. Li, *Inorg. Chem.* (2026).

Characterization of Coupling Pathways

- Orbital entanglement analysis[1]
  - Based on mutual information $I_{ij} = \frac{1}{2}[s_i(1) + s_j(1) - s_{ij}(2)](1 - \delta_{ij})$ under local orbital basis
  - Computing the two-orbital entropy $s_{ij}(2)$ requires certain elements of 4-RDMs
  - Intuitive picture that aligns with concepts for interpreting magnetic interactions





1. Stein, Pantazis, Krewald, *J. Phys. Chem. Lett.* **10**, 6762 (2019).

Characterization of Coupling Pathways

- Mutual correlation[1]
  - Quantify correlation using Frobenius norm of 2-cumulant $\mathscr{C} = \frac{1}{4}\sum_{pqrs} |\lambda^{pq}_{rs}|^2$
  - Two-body mutual correlation:

$$\mathscr{M}_{AB} = \sum_{p \in A} \sum_{qrs \in B} |\lambda^{pq}_{rs}|^2 + \frac{1}{2} \sum_{pq \in A} \sum_{rs \in B} |\lambda^{pq}_{rs}|^2 + \sum_{pr \in A} \sum_{qs \in B} |\lambda^{pq}_{rs}|^2 + \sum_{pqr \in A} \sum_{s \in B} |\lambda^{pq}_{rs}|^2$$

  - For orbital pairs $A_P = \{\phi_P, \bar{\phi}_P\}, B_Q = \{\phi_Q, \bar{\phi}_Q\}$:

$$\mathscr{M}_{PQ} = (\Lambda^2)^{PQ}_{QQ} + \frac{1}{2}(\Lambda^2)^{PP}_{QQ} + (\Lambda^2)^{PQ}_{PQ} + (\Lambda^2)^{PP}_{QP},\ (\Lambda^2)^{PQ}_{RS} = \sum_{\sigma\tau\mu\nu} |\lambda^{p_\sigma q_\tau}_{r_\mu s_\nu}|^2$$

  - Alternative to orbital mutual information

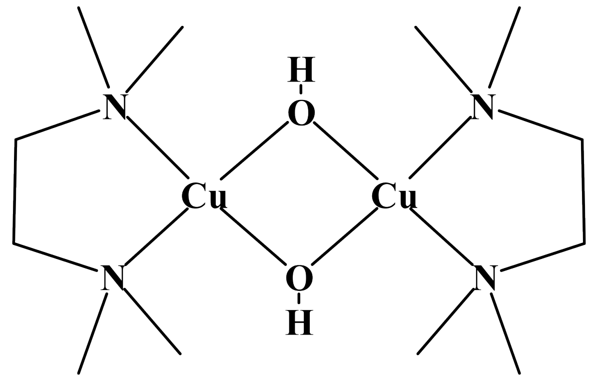
1. Evangelista, *J. Chem. Theory Comput.* **21**, 7471 (2025).

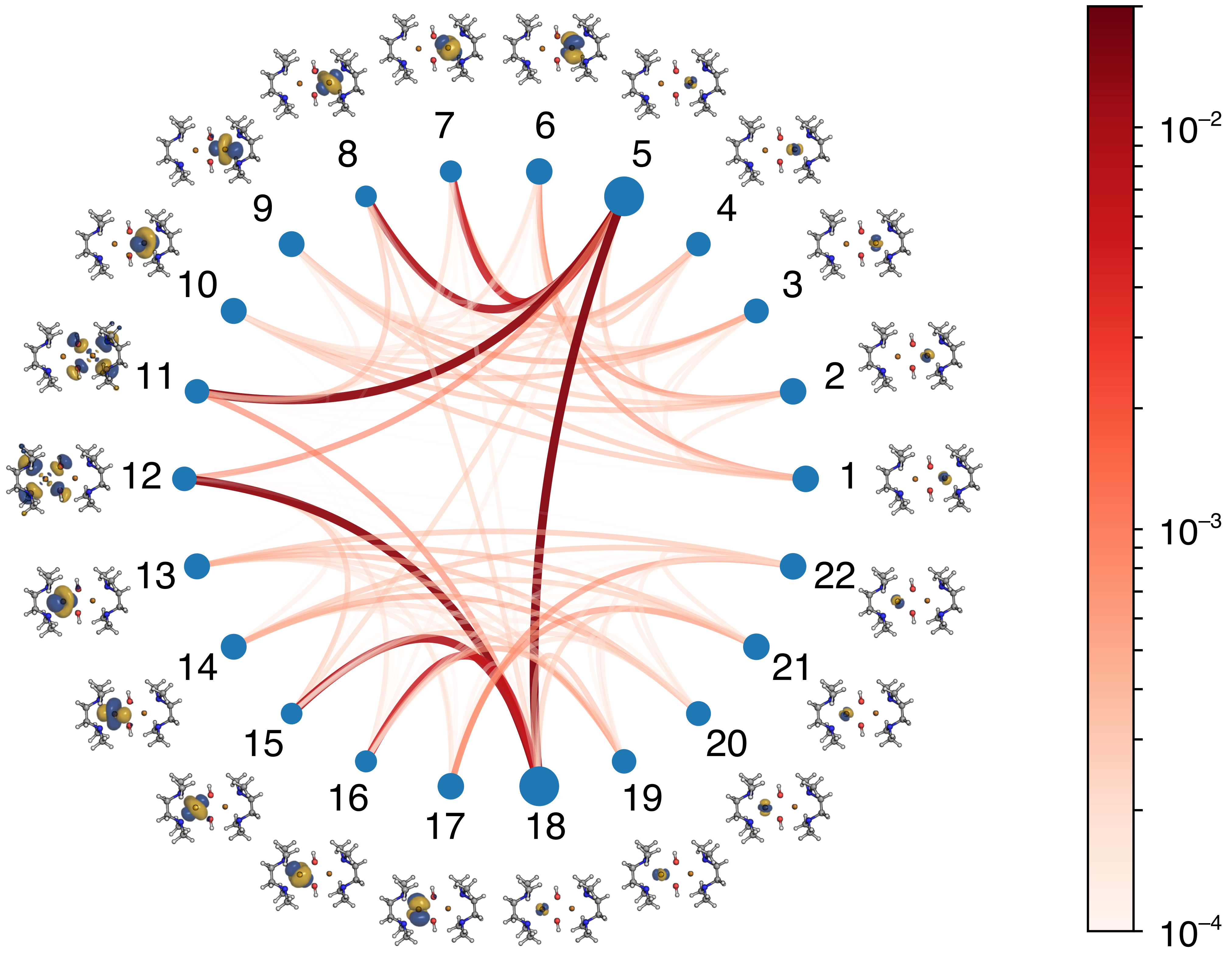
Orbital Mutual Correlation for CAS(2,2)

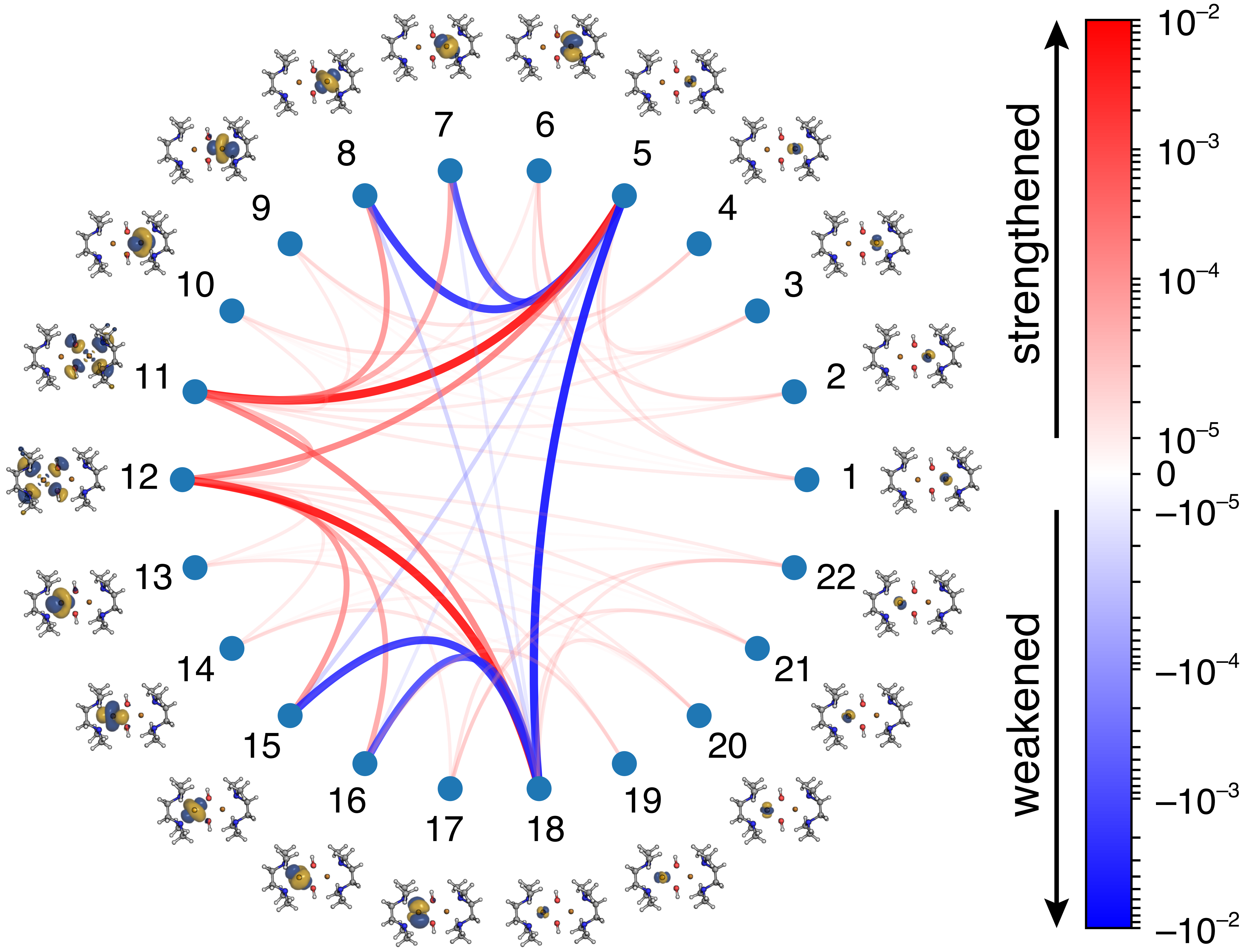
- Triplet state
    - $|\Psi_\mathrm{T}\rangle = \big(|\phi_{1\uparrow}\phi_{2\downarrow}\rangle - |\phi_{2\uparrow}\phi_{1\downarrow}\rangle\big)/\sqrt{2}$, $\mathscr{M}_{1,2}^{\mathrm{T}} = 3/4$
- Singlet state
    - $|\Psi_\mathrm{S}\rangle = N_\mathrm{S}\big[c\big(|\phi_{1\uparrow}\phi_{2\downarrow}\rangle + |\phi_{2\uparrow}\phi_{1\downarrow}\rangle\big) + \big(|\phi_{1\uparrow}\phi_{1\downarrow}\rangle + |\phi_{2\uparrow}\phi_{2\downarrow}\rangle\big)\big]$
    - $c = -(U + \sqrt{U^2 + 16t^2})/(4t) \overset{U \gg 4|t|}{\approx} -U/(2t) - 2t/U$
    - $\mathscr{M}_{1,2}^{\mathrm{S}} = 3(c^4+1)(c^2-1)^2/[4(c^2+1)^4]$
    - $\max \mathscr{M}_{1,2}^{\mathrm{S}} = 3/4$ at $c = 0, \pm\infty$; $\min \mathscr{M}_{1,2}^{\mathrm{S}} = 0$ at $c = \pm 1$
- Equal-weighted state averaging
    - $\mathscr{M}_{1,2}^{\mathrm{SA}} = (2c^8 - 4c^6 + 2c^2 + 5)/[24(c^2+1)^4]$
    - $\max \mathscr{M}_{1,2}^{\mathrm{SA}} = 5/24$ at $c = 0$; $\min \mathscr{M}_{1,2}^{\mathrm{SA}} = 4.24 \times 10^{-3}$ at $c = 1.3285$; $\mathscr{M}_{1,2}^{\mathrm{SA}}(c \to \infty) = 1/12$

Z. Hu and C. Li, *Inorg. Chem.* (2026).

Orbital Mutual Correlation Plot for Cu(II) Complex 1



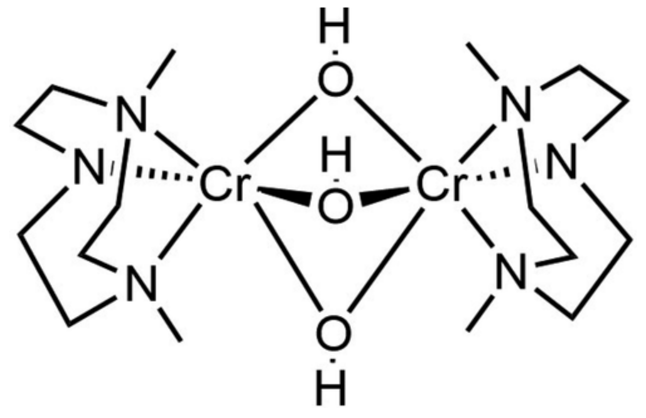


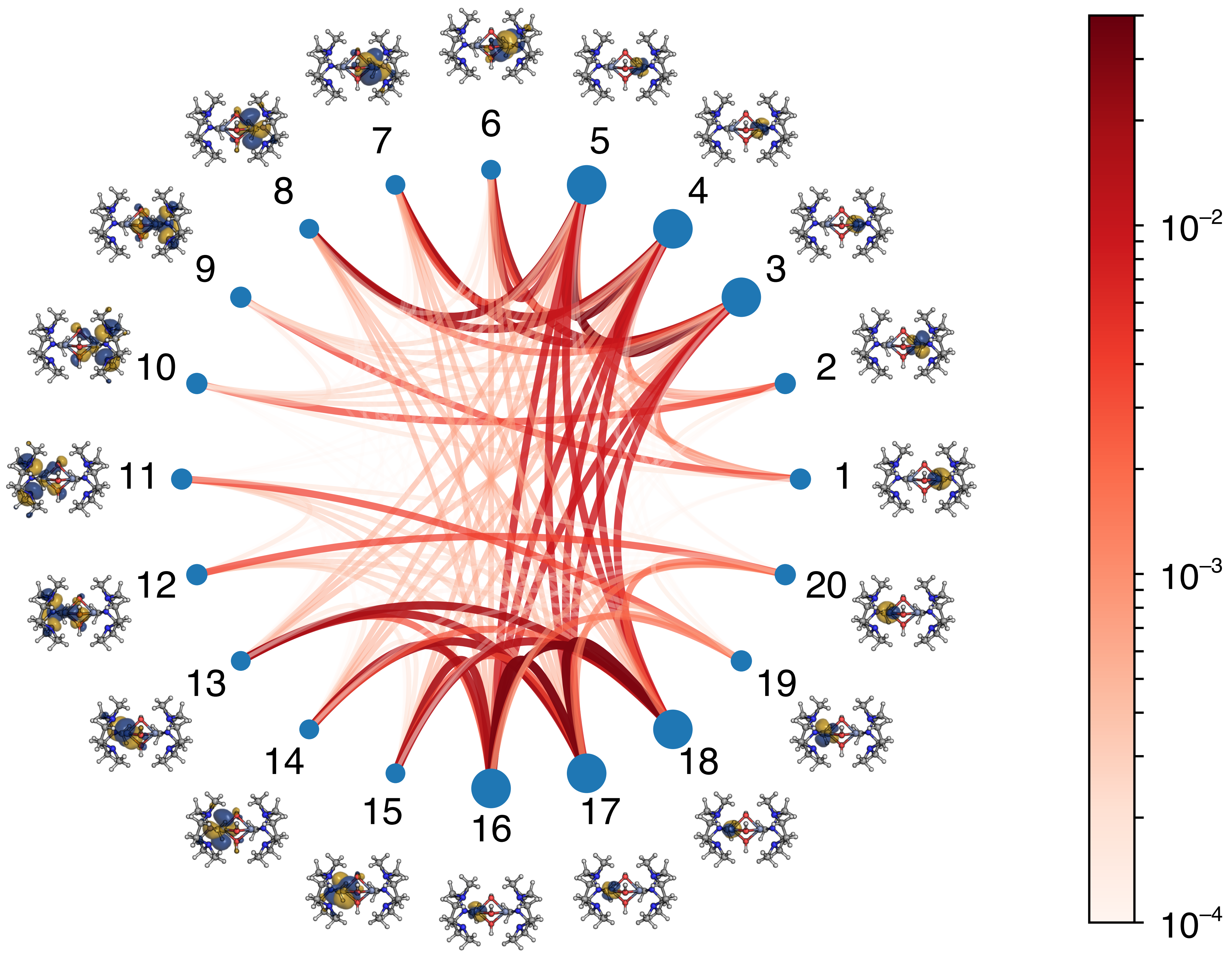


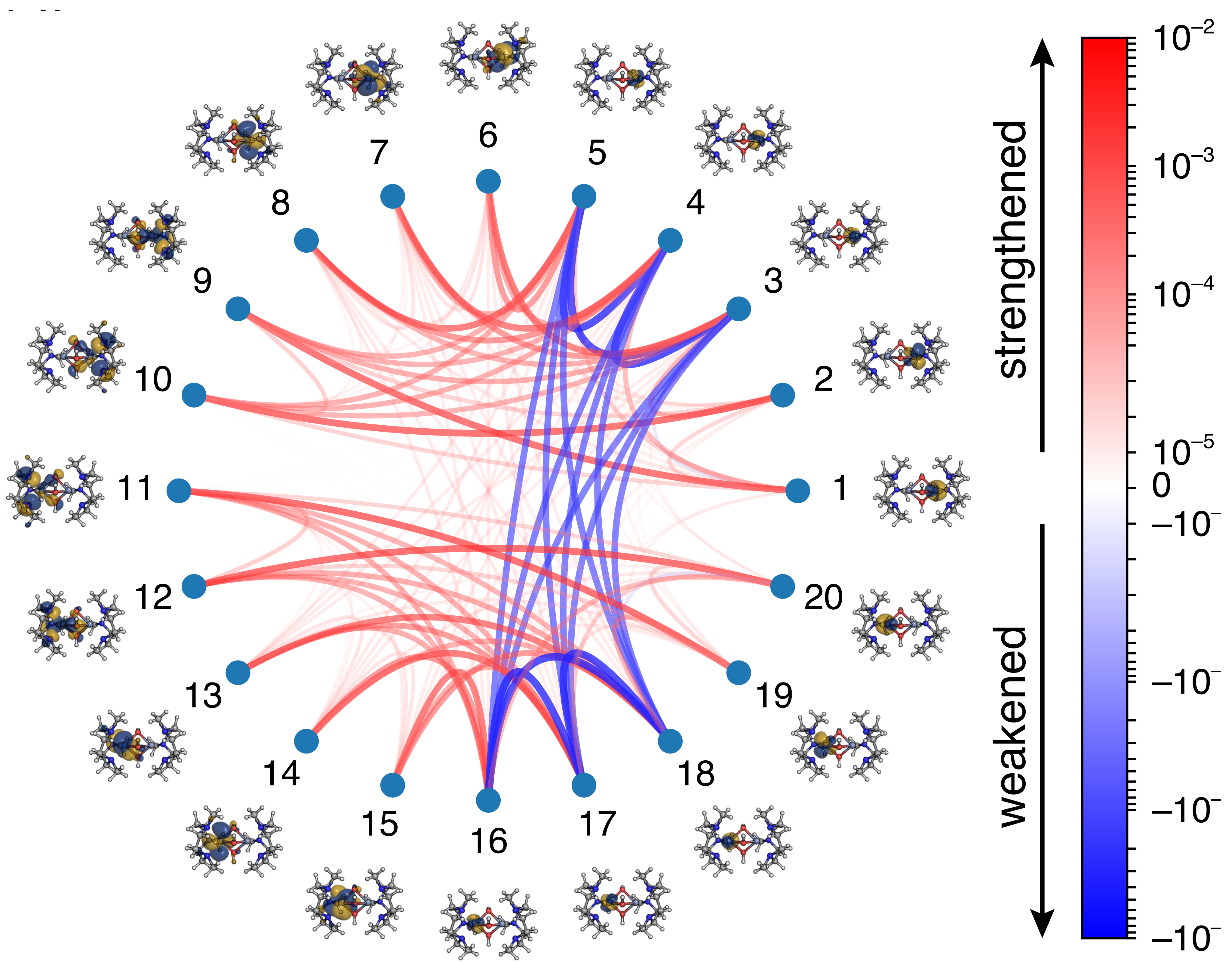
- The correlation of ligand-metal orbital pairs is enhanced by dynamical correlation.

Z. Hu and C. Li, *Inorg. Chem.* (2026).

Orbital Mutual Correlation Plot for Cr(III) Complex 15







- The correlation between magnetic orbitals are slightly enhanced by dynamical correlation.
- $\mathscr{M}^{\mathrm{SA}}_{3,4} : \mathscr{M}^{\mathrm{SA}}_{3,18} : \mathscr{M}^{\mathrm{SA}}_{2,10} = 7.4 : 2.1 : 1 \quad \xrightarrow{\text{DSRG}} \quad 4.7 : 1.3 : 1$

Z. Hu and C. Li, *Inorg. Chem.* (2026).

Conclusions

- SA-DSRG-PT2/DMRG-SCF can accurately compute exchange couplings for bimetallic systems.
- AVAS selection of active space appear useful for these systems.
- Orbital mutual correlation also provides intuitive pictures for interpreting magnetic interactions.

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Thank you for listening!