

Recent developments of density-matrix based quantum embedding approaches to strongly correlated systems

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Outline

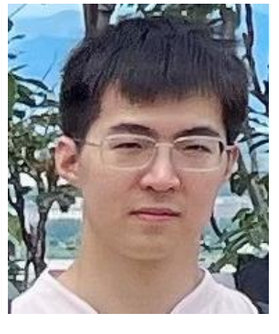
- Introduction: Quantum embedding approaches to strongly correlated systems
- Density-matrix embedding theory (DMET): a short overview
- DMET+CAS-SISO for 3d/4f single-ion magnets
- Non-orthogonal atomic orbitals based DMET (AO-DMET) and further developments
- Concluding remarks

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Dr. Qimin Sun (ByteDance©)

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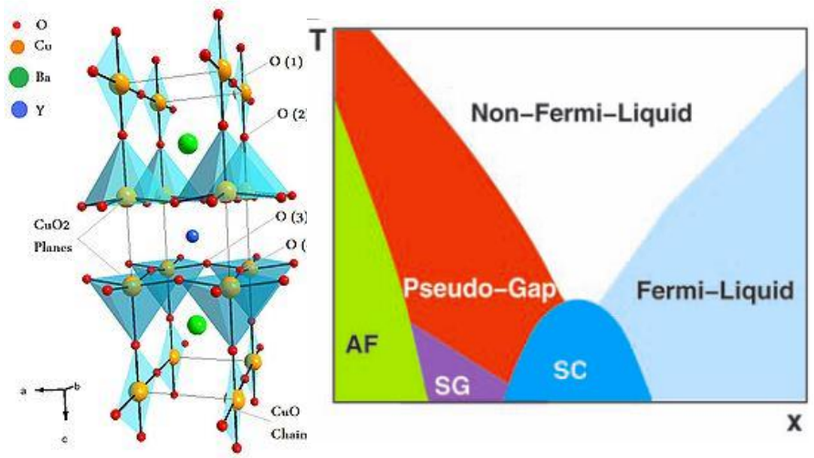




Introduction: quantum embedding approaches to strongly correlated systems

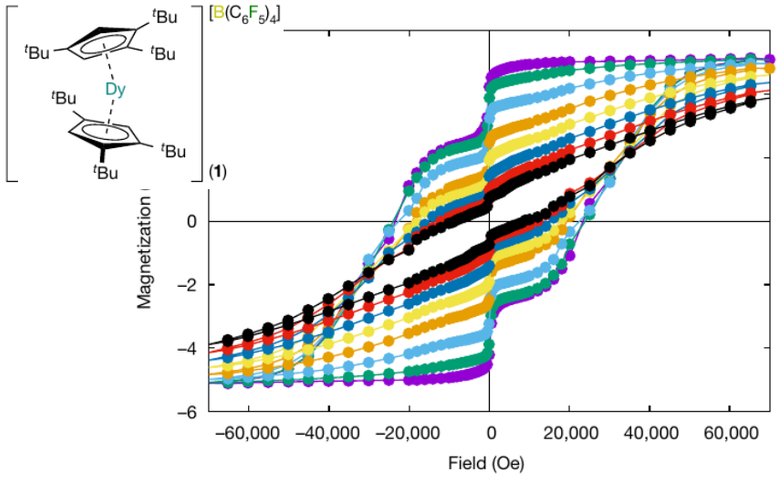
Strongly correlated systems (SCSs)

High-Tc superconductors



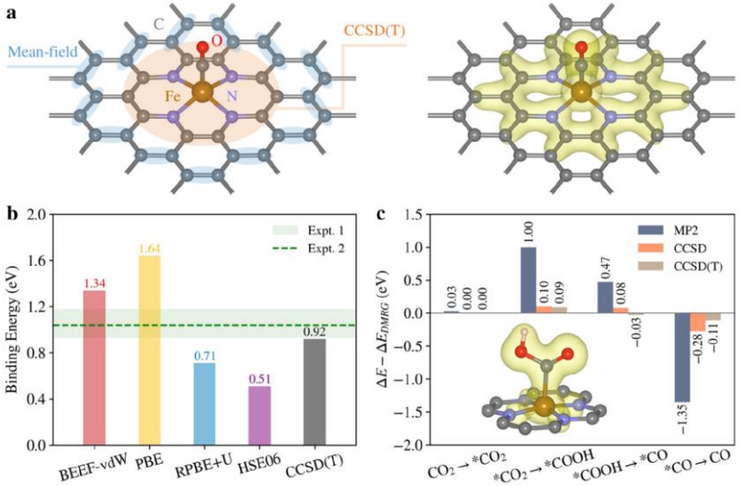
E. Dagotto, *Science* **309**, 257 (2005)

Single molecular magnets (SMMs)



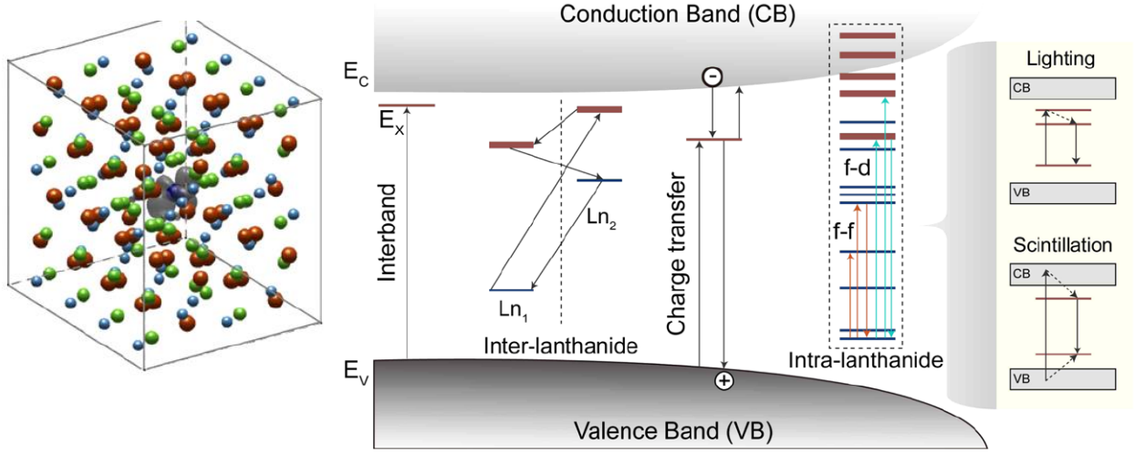
C. A. P. Goodwin et al, *Nature*, **548**, 439 (2018).

Single-atom catalysis



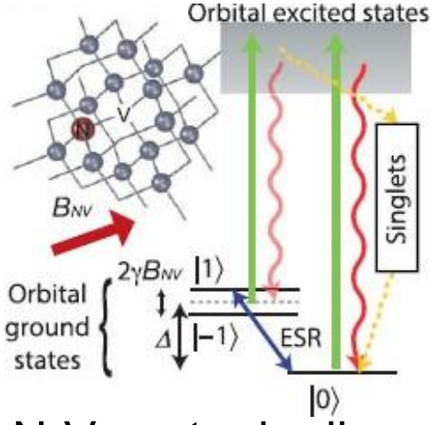
Lei and Zhu, *ACS Catal.* **14**, 3933 (2024).

Lanthanide luminescent materials



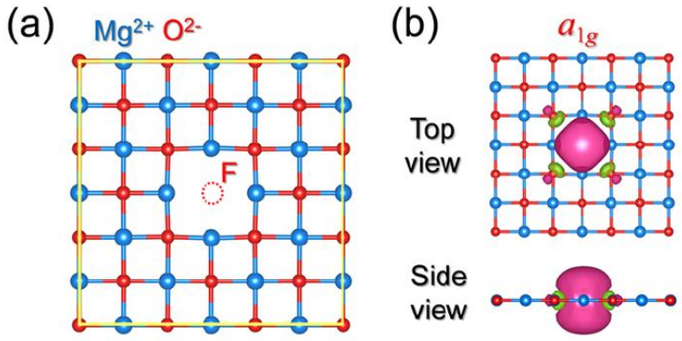
X. Qin, et al. *Chem. Rev.* 117, 4488 (2017).

Defects in solids and surfaces



N-V center in diamond

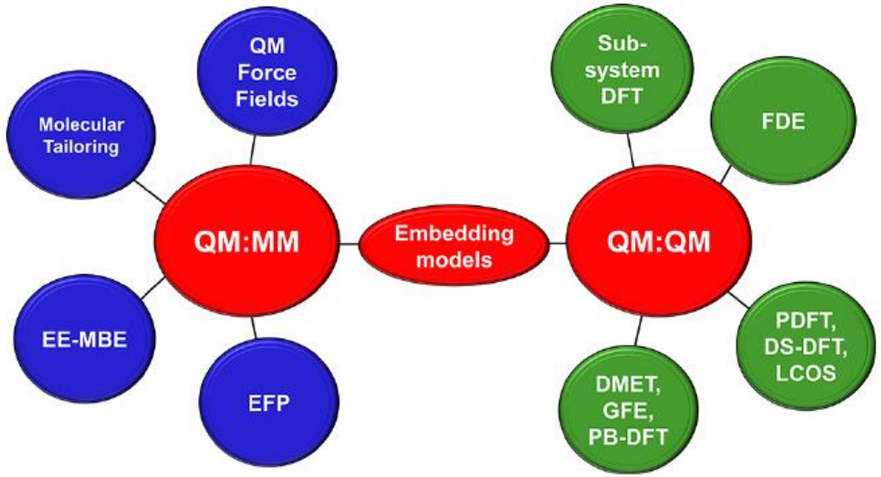
S. Hong *et al. MRS Bulletin*, **38**, 155 (2013)



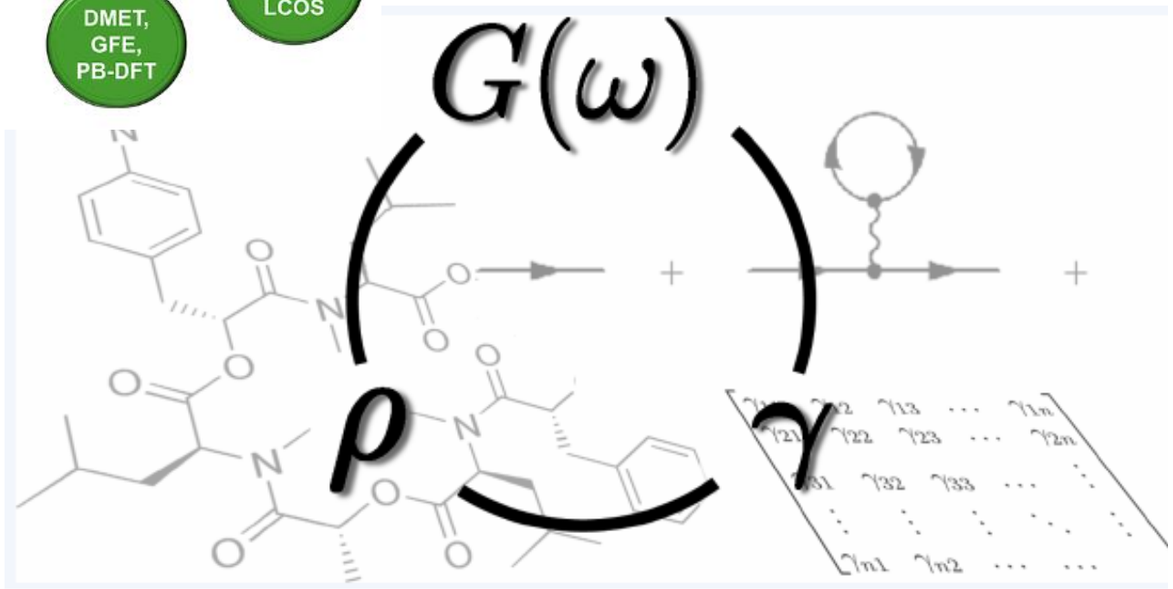
Color center in MgO

A. Mitra et al, : JPCL, 12, 11688 (2021).

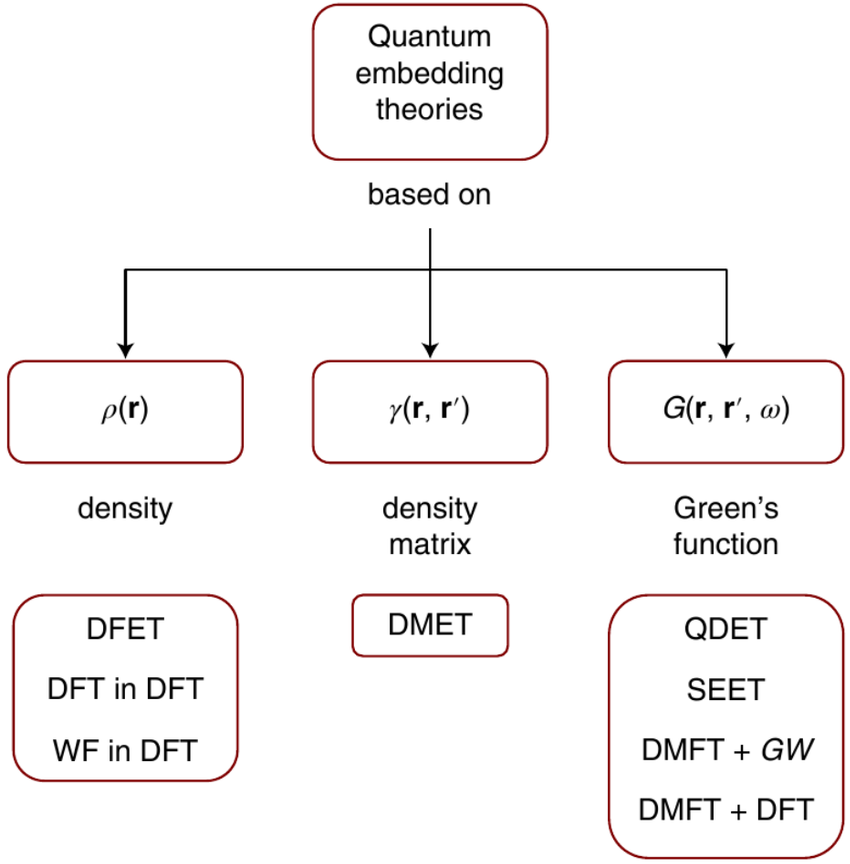
General approaches: embedding-based methods



L. O. J. Jones et al. J. Am. Chem. Soc., 142, 3281(2020)

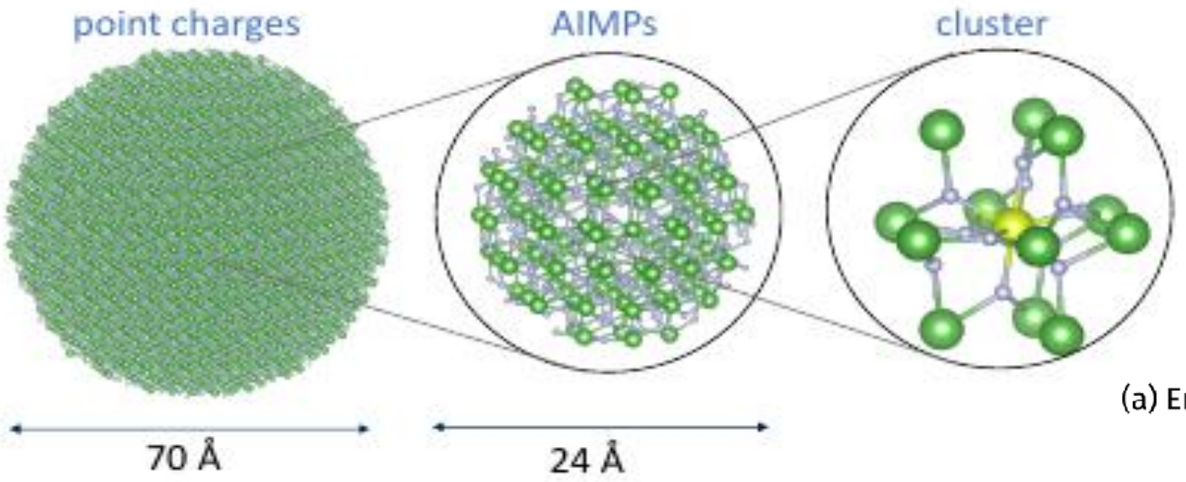


Q. Sun, G. K.-L. Garnet, Acc. Chem. Res. 49, 2705 (2016).



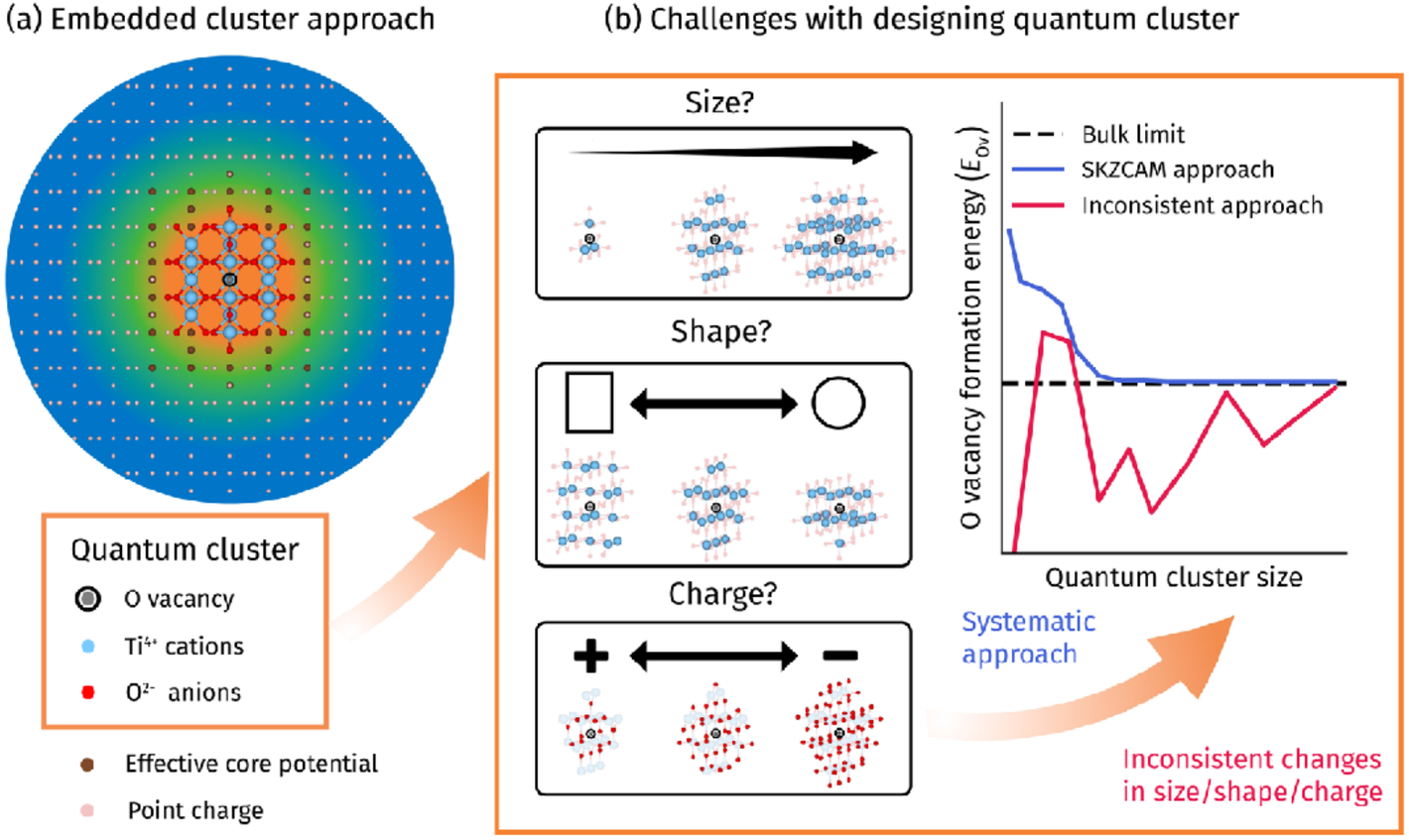
Vorwerk et al. Nature Comput. Sci. 2, 424 (2022).

“Simplistic” embedded cluster models



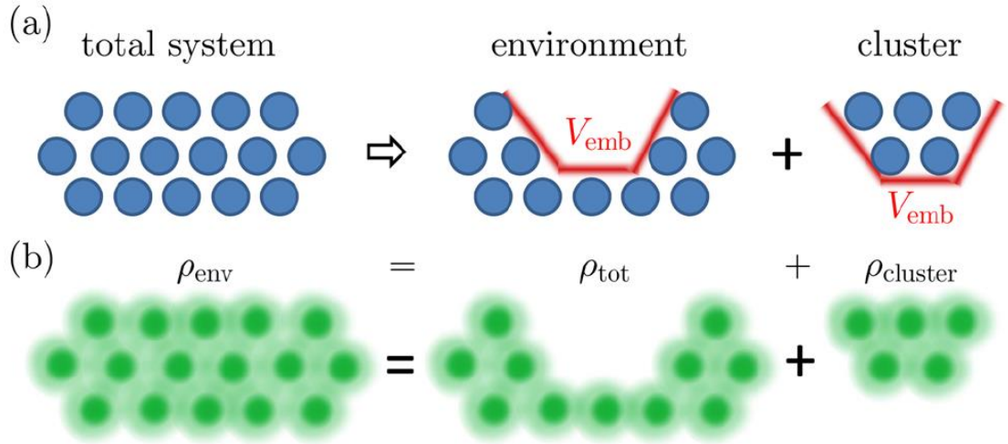
Joos, et al., *Inorg. Chem. Front.*, 7, 871 (2020).
H.-Y. Sun, S.-X. Li, H. Jiang*, *J. Ch. Chem. Soc.* 70, 604 (2023).

B. X. Shi et al. *J. Chem. Phys.* 156, 124704 (2022)



Density-based embedding methods

Density functional embedding theory (DFET) and variants.

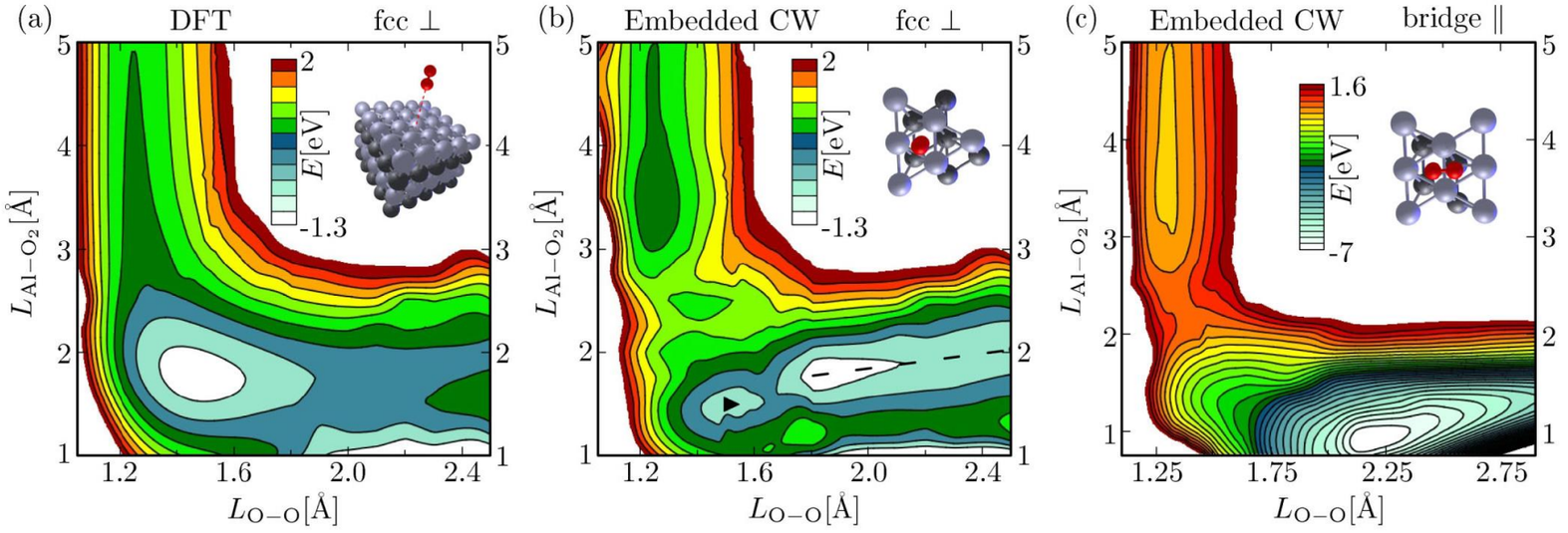


$$E_{tot} = E_{cluster}[\rho_{cluster}] + E_{env}[\rho_{env}] + E_{int}[\rho_{cluster}, \rho_{env}]$$

$$\frac{\delta E_{int}}{\delta \rho_{cluster}} = V_{emb}^{cluster}, \qquad \frac{\delta E_{int}}{\delta \rho_{env}} = V_{emb}^{env}$$

$$E_{tot} = E_{tot}^{DFT} + (E_{emb,cluster}^{CW} - E_{emb,cluster}^{DFT})$$

O_2/Al(111)



Libisch et al, PRL, 109, 198303 (2012).

Recommended reviews:

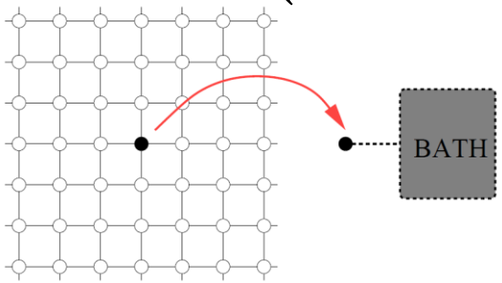
C. R. Jacob and J. Neugebauer, WIRES Comput. Mol. Sci. 14, e1700 (2024).

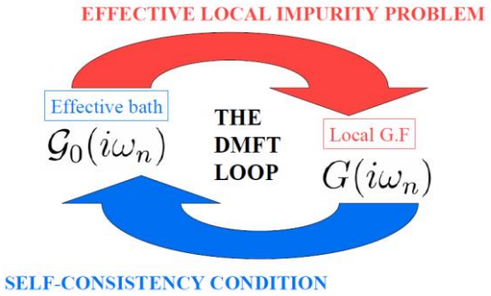
T. A. Wesolowski et al. Chem. Rev. 115, 5891 (2015).

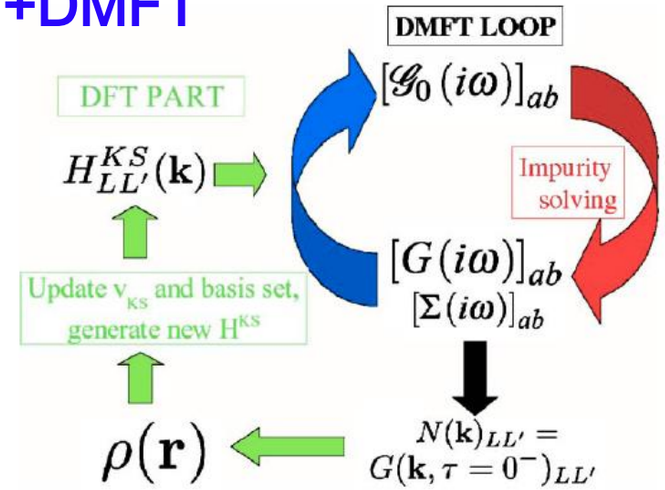
F. Libisch et al Acc. Chem. Res. 47, 2768 (2014).

Green's function based embedding: DFT/GW+DMFT

Dynamical mean-field theory (DMFT): a quantum embedding approach to lattice (Hubbard) Hamiltonian

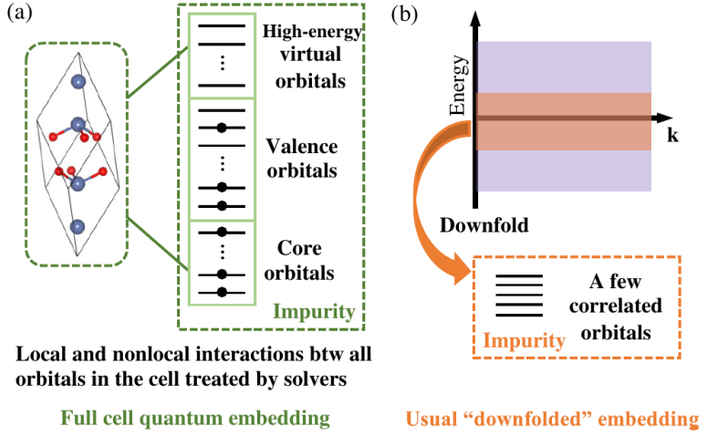




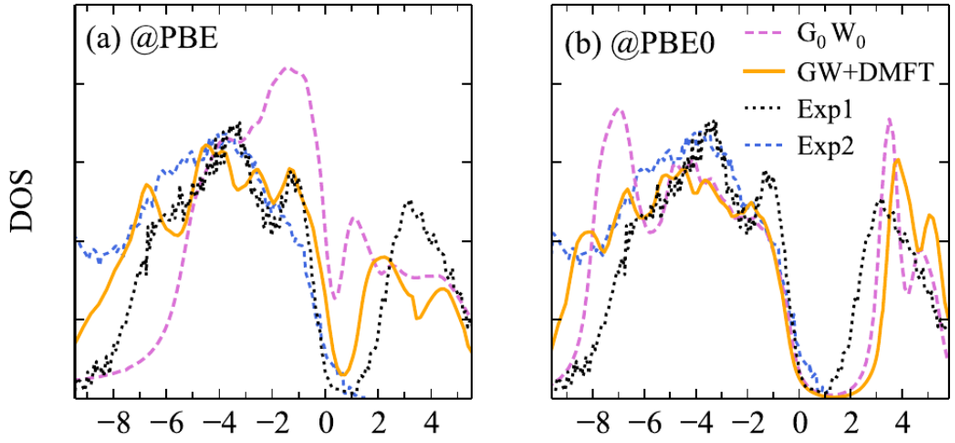


A. Georges, arXiv: cond-mat/0403123 (2004)

Zhu and Chan: full-cell GW+DMFT (PRX 11, 021006 (2021))

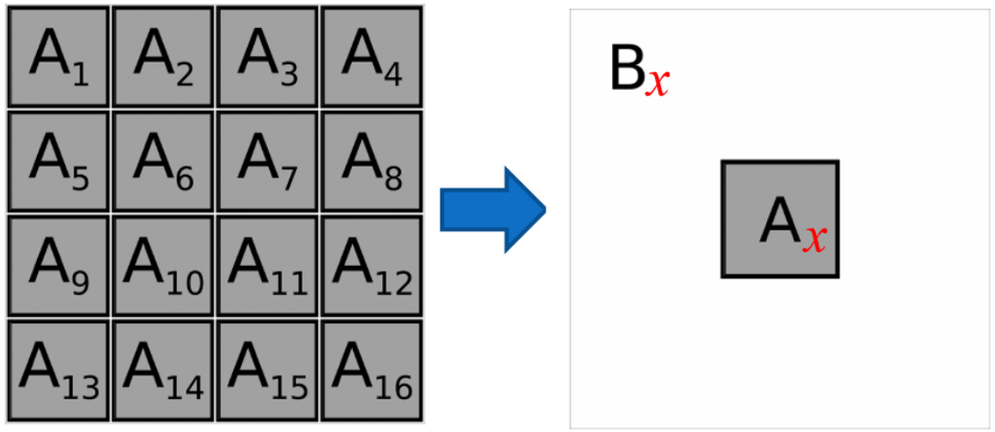


Pourovskii et al. PRB 76, 235101 (2007)



Mainly for electronic band structures, very expensive energetic properties.

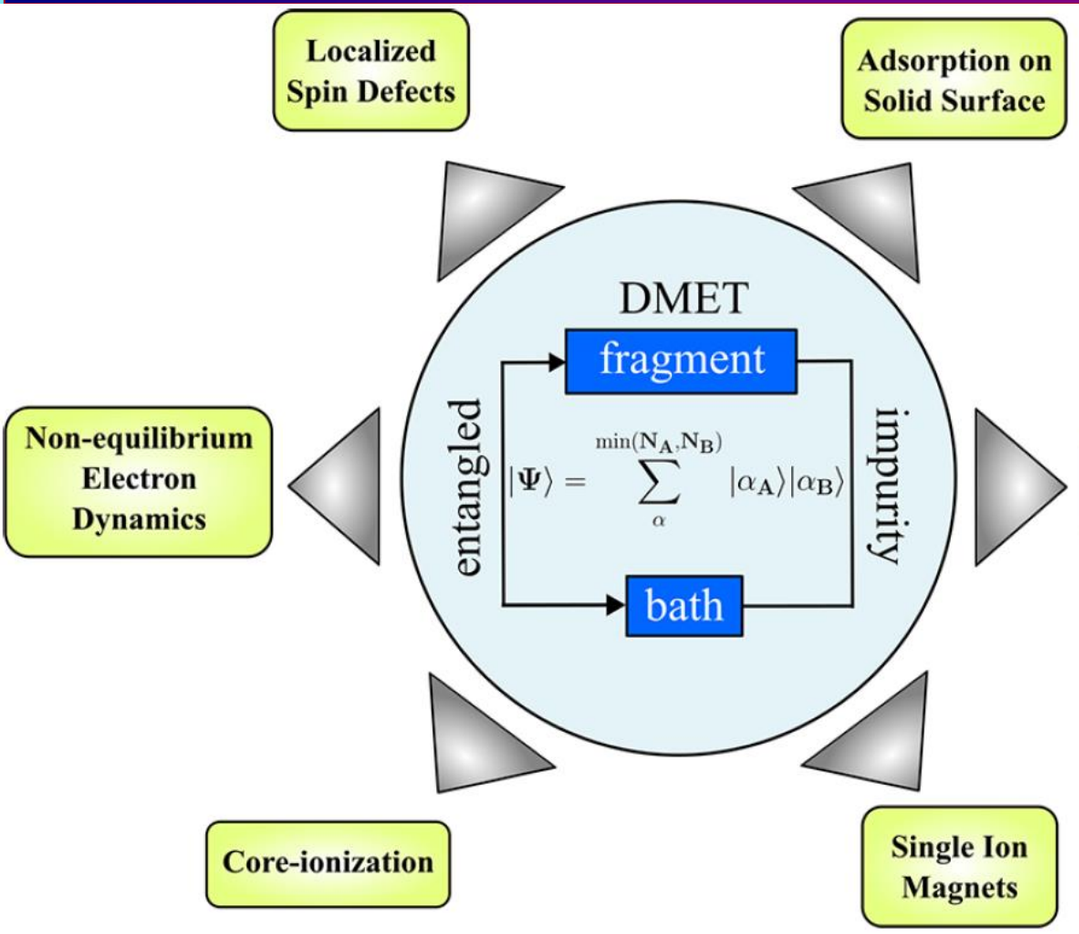
Density-matrix embedding theory (DMET): a short overview

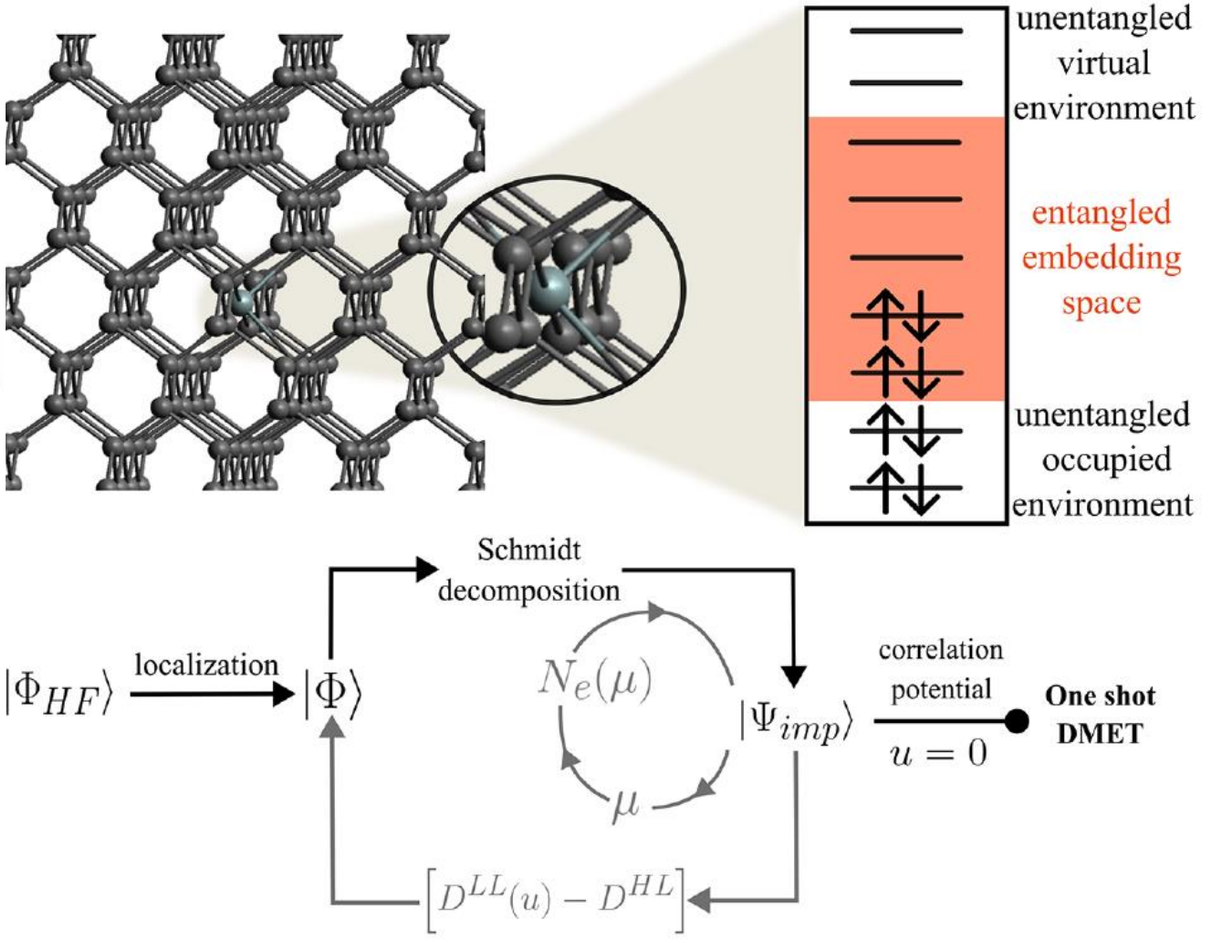


S. Wouters, …,G. K.-L. Chan, JCTC, 12, 2706 (2016).

S. Verma et al. Chem. Rev. 126, 184 (2026).

Density matrix embedding theory (DMET): an overview



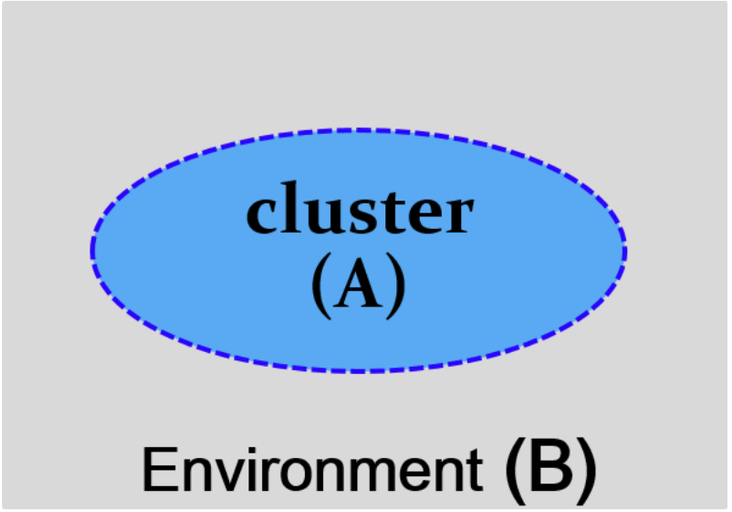


S. Verma et al. Chem. Rev. 126, 184 (2026).

Schmidt decomposition of a many-electron wave-function

$$|\Psi\rangle = \sum_{i}^{L_A}\sum_{j}^{L_B} C_{ij}\,|A_i\rangle \otimes |B_j\rangle$$

L_X: the size of the **Fock space** X spanned by N_X **orthonormal local orbitals** centered within X (X=A or B).



Single-value decomposition (SVD) of C

$$\mathbf{C}_{N_A\times N_B} = \mathbf{U}_{N_A\times N_A}\,\Lambda_{N_A\times N_B}\,\mathbf{V}^{\dagger}_{N_B\times N_B}$$

$$|\Psi\rangle = \sum_{i}^{L_A}\sum_{j}^{L_B}\left(\sum_{\alpha}^{L_A} U_{i\alpha}\lambda_\alpha V^{\dagger}_{\alpha j}\right)|A_i\rangle\otimes|B_j\rangle = \sum_{\alpha}^{L_A}\lambda_\alpha\,|\tilde{A}_\alpha\rangle\otimes|\tilde{B}_\alpha\rangle$$

$\mathbf{U}, \mathbf{V}$: unitary matrix

$\Lambda_{ij} = \lambda_i \delta_{ij}$

assuming $N_A < N_B$

$$\hat{H}_{\text{emb}} \equiv \hat{P}\hat{H}\hat{P}, \qquad \hat{P} = \sum_{\alpha,\beta}^{L_A} |\tilde{A}_\alpha\tilde{B}_\beta\rangle\langle\tilde{A}_\alpha\tilde{B}_\beta|$$

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad\Rightarrow\quad \hat{H}_{\text{emb}}|\Psi\rangle = E|\Psi\rangle$$

G. Knizia, G. K.-L. Chan, PRL, 109, 186404 (2012).

S. Wouters, …,G. K.-L. Chan, JCTC, 12, 2706 (2016).

Schmidt decomposition of a Slater determinant

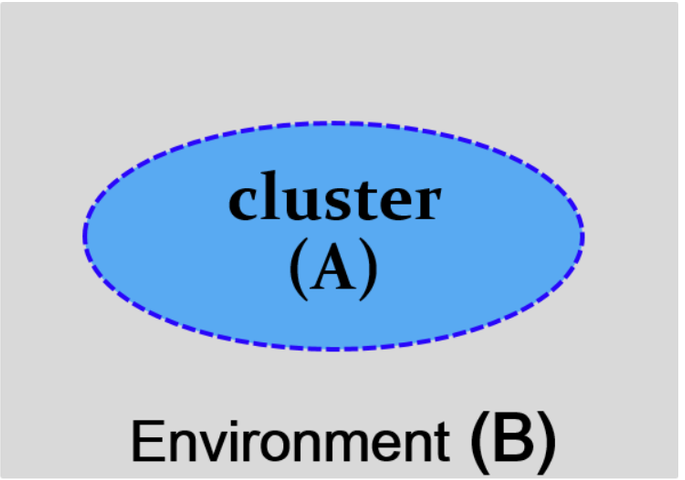
$$|\Phi\rangle = \prod_{i}^{N_{\text{occ}}} \hat{a}_i^\dagger |\text{vac}\rangle, \quad \hat{a}_i^\dagger = \sum_{\mu \in A,B} C_{\mu i} \hat{a}_\mu^\dagger$$

$\left\{ \hat{a}_\mu^\dagger \right\}$ orthonormal atomic basis, (i.e. Löwdin orthonogalized AOs

$$C_{\mu i}\left(\mu \in \text{A}\right) = \sum_{m}^{N_\text{A}} U_{\mu m} \lambda_m V_{mi}^\dagger \qquad \text{(assuming } N_\text{A} < N_\text{occ} < N_B\text{)}$$

$$\hat{a}_m^\dagger = \sum_{i}^{N_\text{occ}} V_{im} \hat{a}_i^\dagger = \sum_{i}^{N_\text{occ}} \sum_{\mu \in \text{A,B}} V_{im} C_{\mu i} \hat{a}_\mu^\dagger = \sum_{\mu \in \text{A}} \hat{a}_\mu^\dagger \tilde{C}_{\mu m} + \sum_{\mu \in \text{B}} \hat{a}_\mu^\dagger \tilde{C}_{\mu m}$$

$$\tilde{C}_{\mu m}\left(\mu \in \text{A}\right) = \begin{cases} U_{\mu m}\lambda_m & m \le N_\text{A} \\ 0 & N_\text{A} < m \le N_\text{occ} \end{cases}$$



$m \le N_A$: $\quad \hat{a}_m^\dagger = |\lambda_m| \hat{a}_{m,\text{A}}^\dagger + \left(1 - |\lambda_m|^2\right)^{1/2} \hat{a}_{m,\text{B}}^\dagger$

$$\hat{a}_{m,\text{A}}^\dagger = |\lambda_m|^{-1} \sum_{\mu \in \text{A}} \hat{a}_\mu^\dagger \tilde{C}_{\mu m}, \quad \hat{a}_{m,\text{B}}^\dagger = \left(1 - |\lambda_m|^2\right)^{-1/2} \sum_{\mu \in \text{B}} \hat{a}_\mu^\dagger \tilde{C}_{\mu m}$$

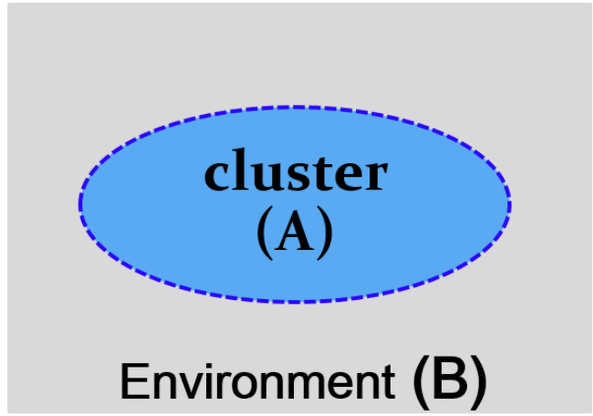
$N_A < m \le N_\text{occ}$: $\quad \hat{a}_m^\dagger = \sum_{\mu \in \text{B}} \hat{a}_\mu^\dagger \tilde{C}_{\mu m}$

G. Knizia, G. K.-L. Chan, PRL, 109, 186404 (2012).
S. Wouters et al., JCTC, 12, 2706 (2016).

Embedded cluster Hamiltonian

$$|\Phi\rangle = \prod_{i}^{N_{\mathrm{occ}}} \hat{a}_i^\dagger |\mathrm{vac}\rangle = \prod_{m}^{N_A} \left[|\lambda_m| \hat{a}_{m,\mathrm{A}}^\dagger + \left(1 - |\lambda_m|^2\right)^{1/2} \hat{a}_{m,\mathrm{B}}^\dagger \right] \prod_{N_\mathrm{A} < m \le N_{occ}} \hat{a}_m^\dagger |\mathrm{vac}\rangle$$

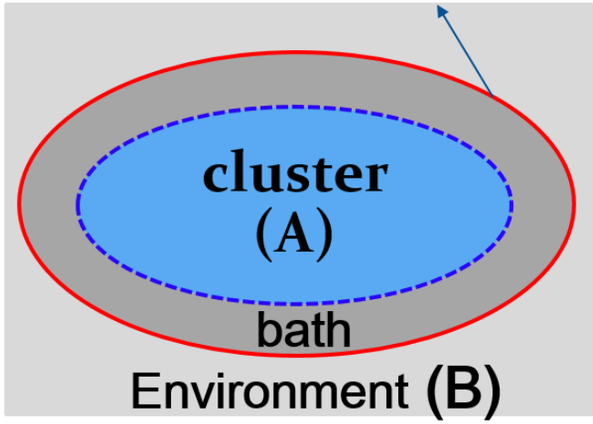
$$= \sum_{\alpha}^{L_A} \tilde{\lambda}_\alpha \left|\tilde{\Psi}_\alpha^{\mathrm{A}}\right\rangle \otimes \left|\tilde{\Psi}_\alpha^{\mathrm{B}}\right\rangle \otimes \left|\Phi_{\mathrm{core}}^{\mathrm{B}}\right\rangle$$



Embedded cluster space: $\mathcal{A} = \left\{\hat{a}_{\mu\in\mathrm{A}}^\dagger\right\} \oplus \left\{\hat{a}_{m,\mathrm{B}}^\dagger\right\}$

"DMET ansatz" $|\Psi\rangle = |\Psi_{\mathcal{A}}\rangle \otimes \left|\Phi_{\mathrm{core}}^{\mathrm{B}}\right\rangle$

Embedded cluster space ($\mathcal{A}$)



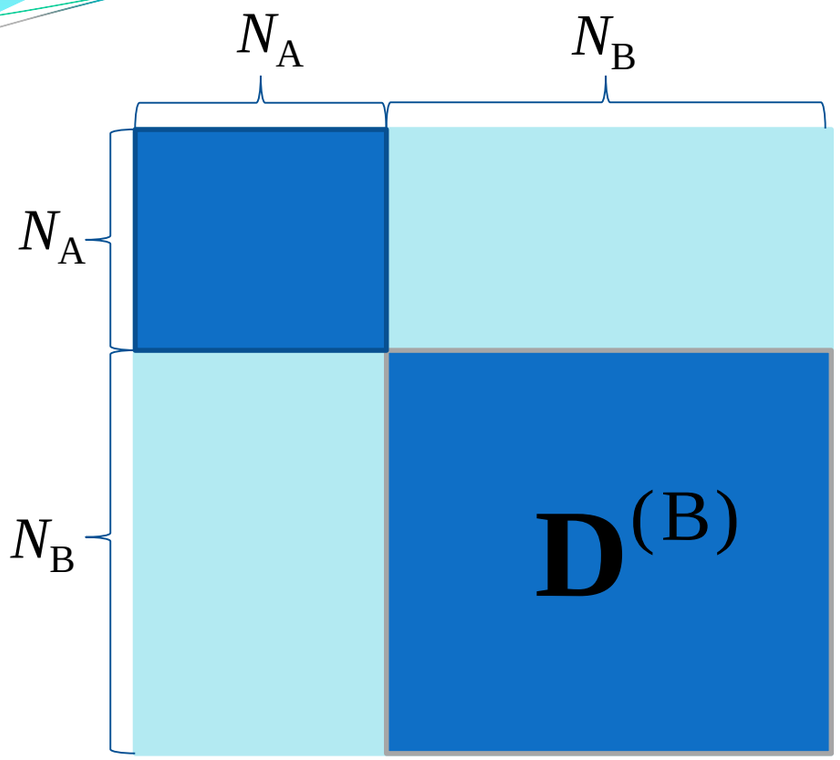
Embedded cluster Hamiltonian

$$\hat{H}^{\mathcal{A}} = \sum_{\mu,\nu\in\mathcal{A}} \sum_{\sigma} h_{\mu\nu}^{\mathcal{A}} c_{\mu\sigma}^\dagger c_{\nu\sigma} + \frac{1}{2} \sum_{\mu,\nu,\lambda,\eta\in\mathcal{A}} \sum_{\sigma,\sigma'} \langle\mu\nu|\lambda\eta\rangle c_{\mu\sigma}^\dagger c_{\nu\sigma'}^\dagger c_{\eta\sigma'} c_{\lambda\sigma}$$

$$h_{\mu\nu}^{\mathcal{A}} = -\frac{1}{2}\nabla^2 - \sum_{I\in\mathrm{A,B}} \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} + \sum_{b\in\mathrm{B_{core}}} \left(2\hat{J}_b - \hat{K}_b\right)$$

S. Wouters et al., JCTC, 12, 2706 (2016).
H. Q. Pham et al, JCTC, 14, 1960 (2018).

Bath orbitals from projected low-level density matrix



$$D_{\mu\nu} = \langle \Phi_0 | a_\nu^\dagger a_\mu | \Phi_0 \rangle$$

$$\mathbf{D}^{(\mathrm{B})} = \left(D_{\mu,\nu\in\mathrm{B}} \right)_{N_\mathrm{B}\times N_\mathrm{B}}$$

$$\mathbf{D}^{(\mathrm{B})}\mathbf{b}_m = \zeta_m \mathbf{b}_m$$

$$\zeta_m = \begin{cases} (0,1) & \text{Entangled (bath) orbitals} \\ 1 & \text{Unentangled (core) occupied orbitals} \\ 0 & \text{Unentangled virtual orbitals} \end{cases}$$

In practice:

$$\varepsilon < \zeta_m < 1 - \varepsilon$$

$$\hat{a}_{m,\mathrm{B}}^\dagger = \sum_{\mu\in\mathrm{B}} b_{\mu m} \hat{a}_\mu^\dagger$$

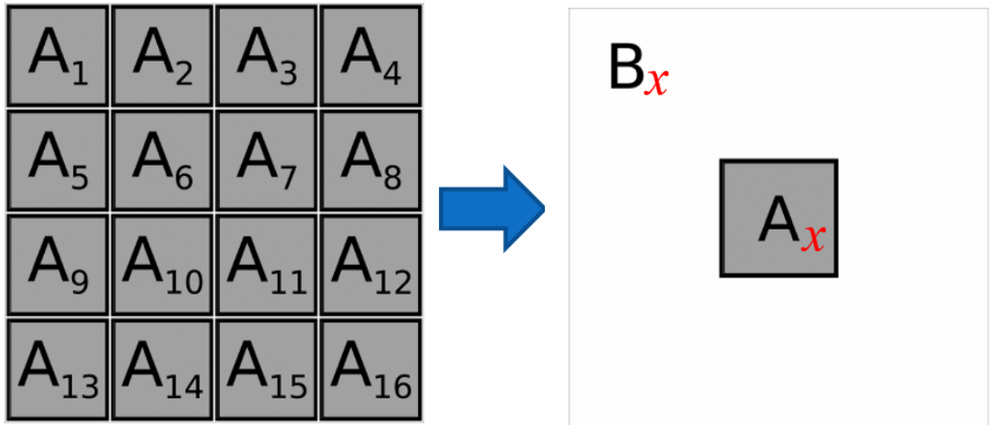
S. Wouters et al., JCTC, 12, 2706 (2016).

Self-consistent DMET for multiple-impurity systems

$$\hat{h}' = \hat{h} + \sum_x \hat{C}_x \qquad \hat{C}_x = \sum_{kl \in A_x} u_{kl}^x \hat{a}_k^\dagger \hat{a}_l$$

$$\hat{H}_{emb}^x = P\hat{H}P = \sum_{rs}^{L_{A_x}+L_{B_x}} \tilde{h}_{rs}^x \hat{a}_r^\dagger \hat{a}_s + \sum_{pqrs}^{L_{A_x}+L_{B_x}} (pq|rs)\hat{a}_p^\dagger \hat{a}_r^\dagger \hat{a}_s \hat{a}_q$$

$$\hat{h}^x = \sum_{kl} [t_{kl} + \sum_{mn}^{L} [(kl|mn) - (kn|ml)]D_{mn}^{\mathrm{env,x}}]\hat{a}_k^\dagger \hat{a}_l$$



Self-consistent condition:

$$\mathrm{CF}_{\mathrm{frag}}(u) = \sum_x \sum_{rs \in A_x} (D_{rs}^x - D_{rs}^{\mathrm{mf}}(u))^2$$

Challenges:

- SC condition not uniquely defined!
- Convergence not guaranteed
- No underlying variation principle available!
- ……

S. Wouters,..., G. K.-L. Chan, JCTC, **12**, 2706(2016); X. Wu, ..., L. Lin Phys. Rev. B 102, 085123 (2020); A. Negre et al, arXiv 2503.09881v1

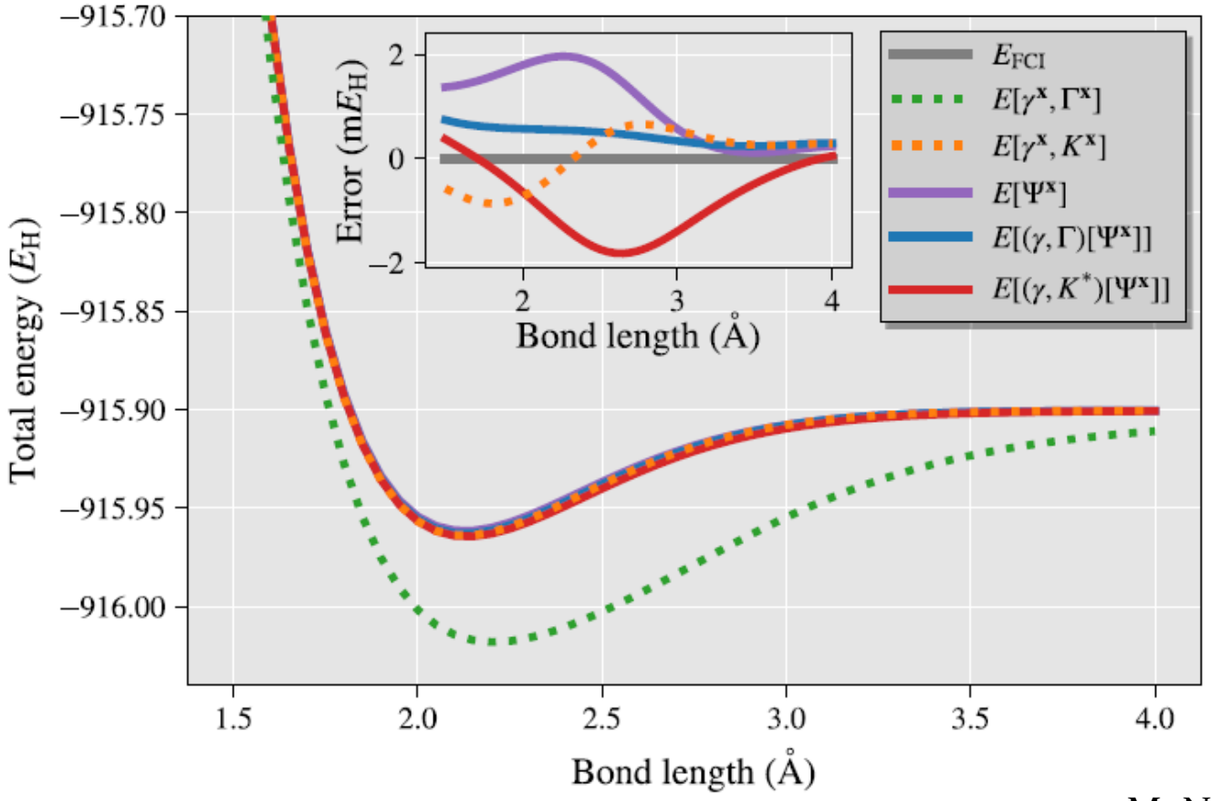
How to obtain global quantities

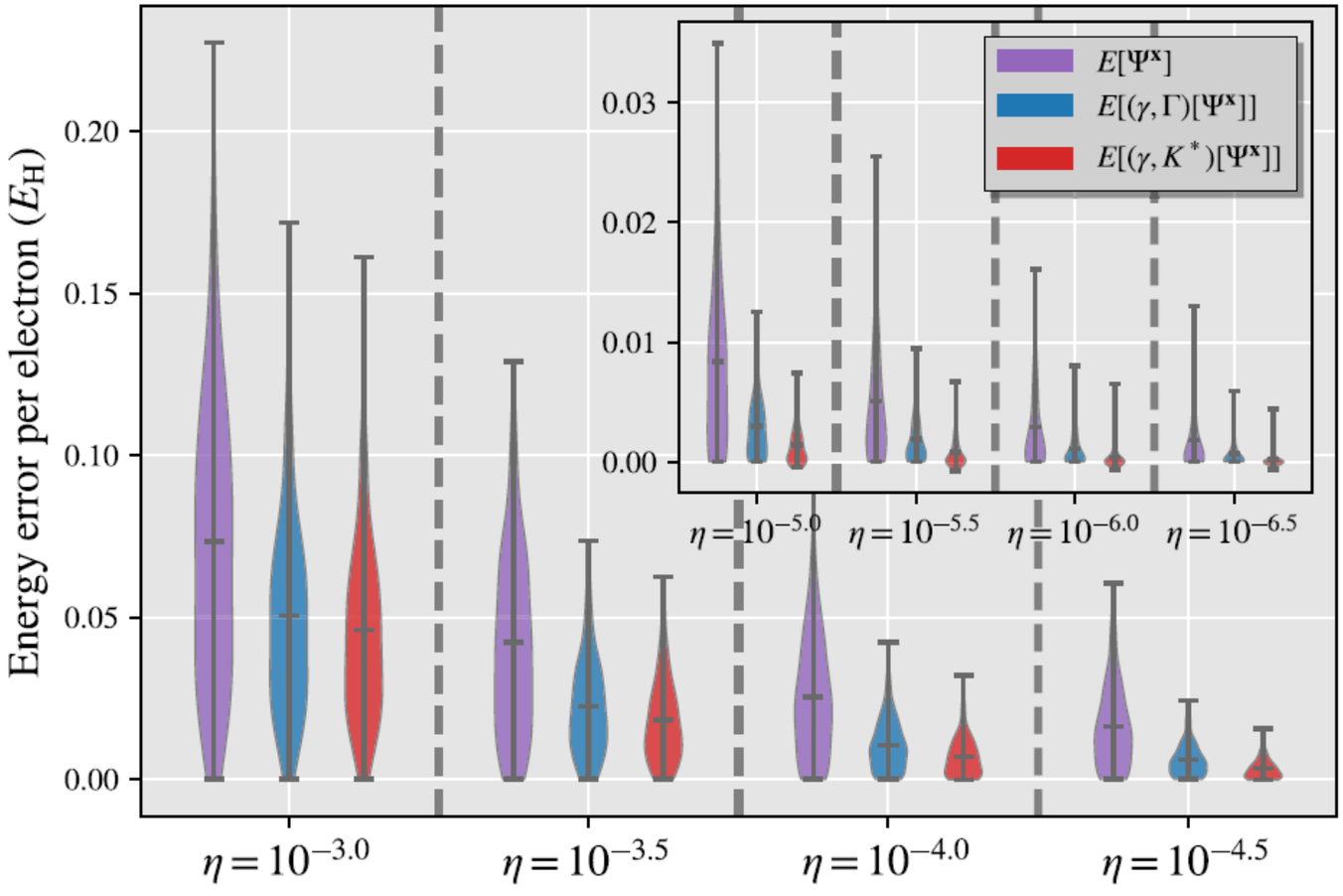
$$E_{\text{tot}} = E_{\text{nuc}} + \sum_x E_x$$

$$E_x = \sum_{k \in A_x} \left(\sum_l^L t_{kl} D_{lk}^{\text{tot}} + \frac{1}{2} \sum_{lmn}^L (kl|mn) P_{lk|nm}^{\text{tot}} \right)$$

$$|\Psi\rangle = |\Phi\rangle + \sum_{\mathbf{x}}^{N_{\text{frag}}} \hat{P}^{\mathbf{x}} |\Delta\Psi^{\mathbf{x}}\rangle \qquad |\Delta\Psi^{\mathbf{x}}\rangle = |\Psi^{\mathbf{x}}\rangle - |\Phi\rangle$$

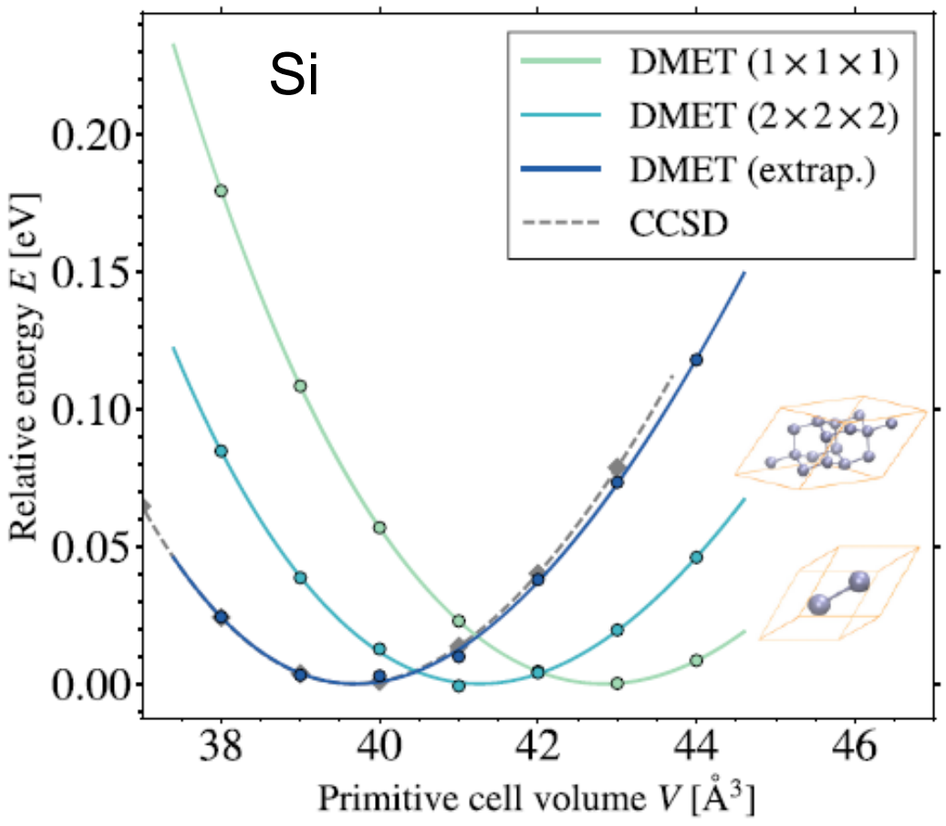
S. Wouters et al JCTC **12**, 2706(2016).

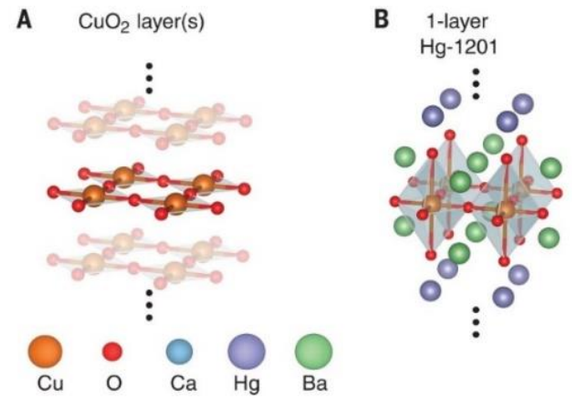


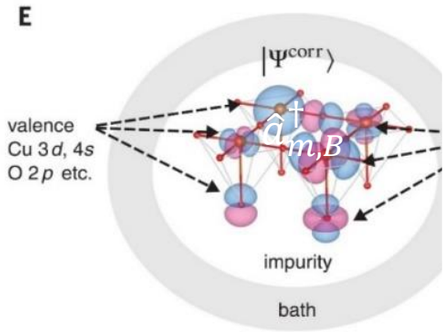


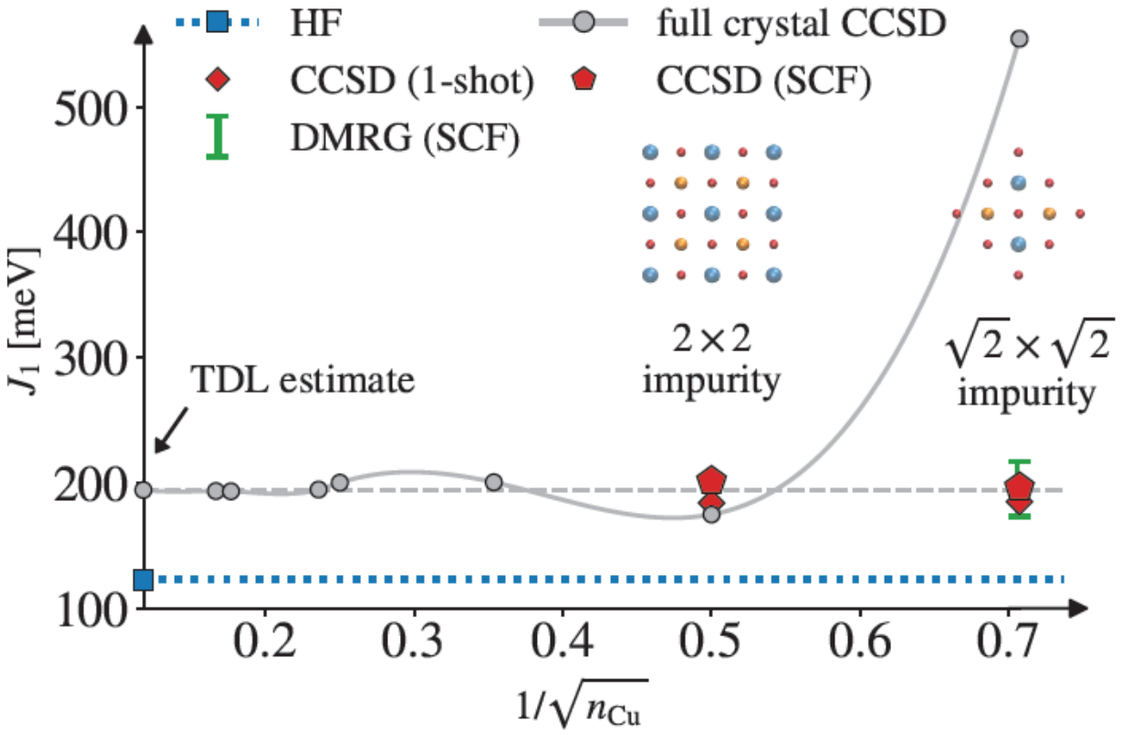
M. Nusspickel, B. Ibrahim, G. H. Booth, *J. Chem. Theory Comput.* 19, 2769 (2023).

DMET+DMRG/CCSD for solids





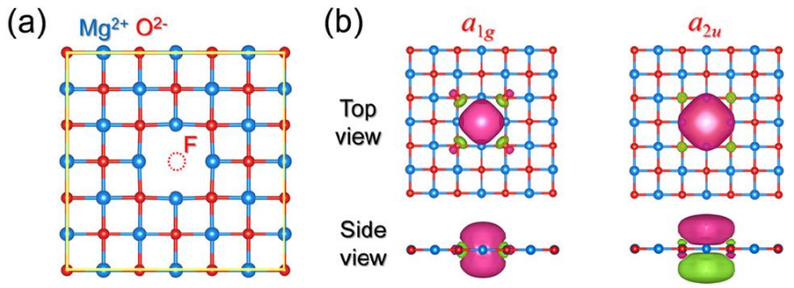




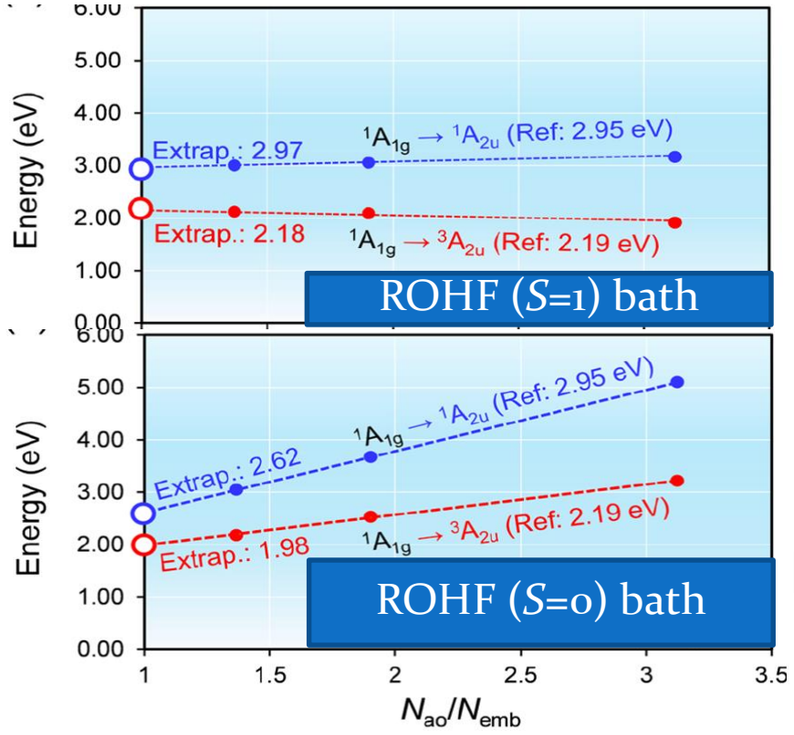
Z.-H. Cui, ..., G. K.-L. Chan, J. Chem. Theory Comput. 16, 119 (2020).

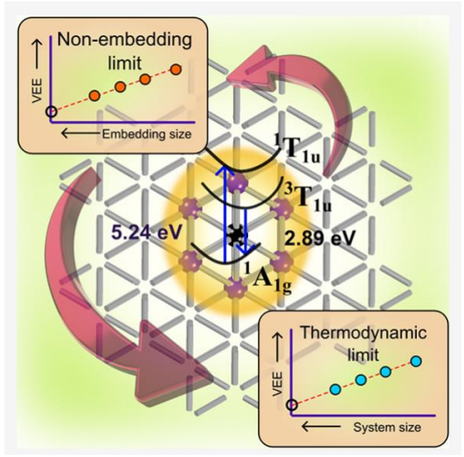
Z.-H. Cui et al, Science, 377, 1192 (2022).

DMET for excited states in extended systems



- Periodic TD-hybrid for excited state structural optimization.
- DMET+CAS/PT2@ROHF
- Extrapolation w.r.t. embedding space size and supercell size





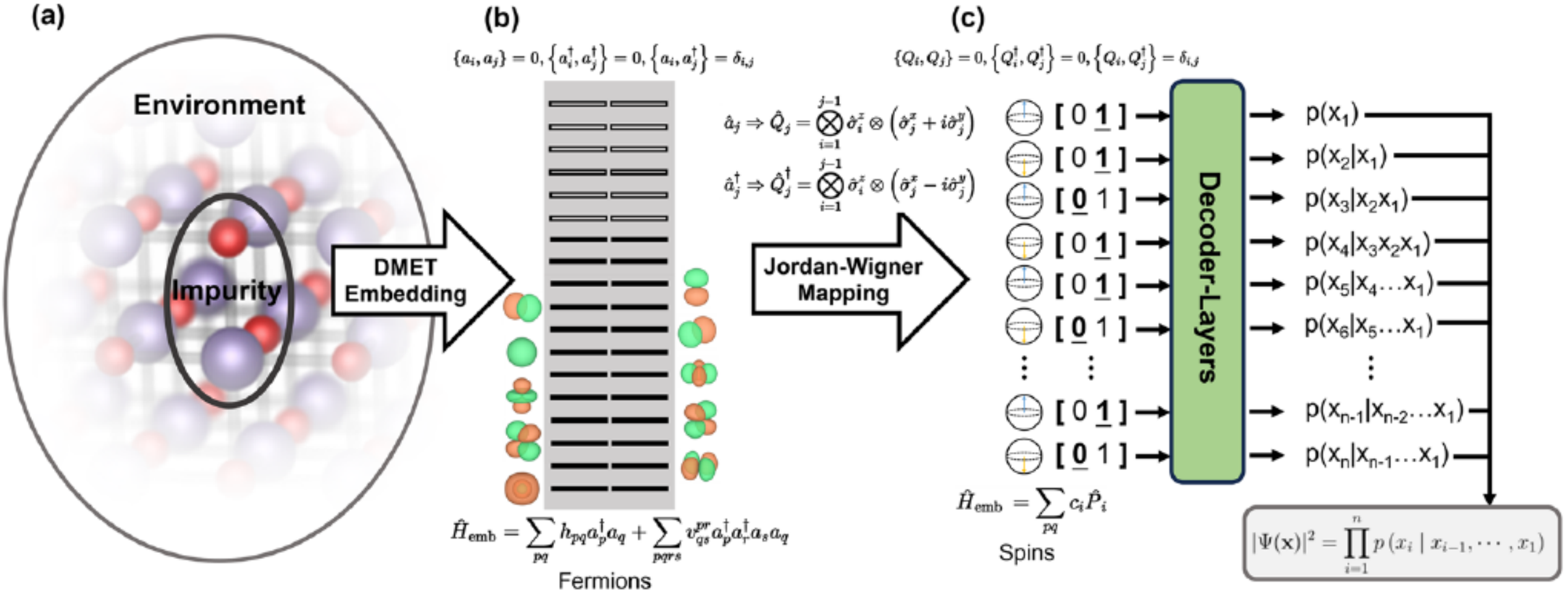
F^0-center in MgO

method	absorption $^1A_{1g} \rightarrow {}^1T_{1u}$	absorption $^1A_{1g} \rightarrow {}^1CBM$	emission $^3T_{1u} \rightarrow {}^1A_{1g}$
CAS-DMET@ROHF	6.26		2.74
NEVPT2-DMET@ROHF	5.24		2.89
CASPT2-cluster[6]	5.44		4.09
EE-EOM-CCSD[7]	5.28		3.66
embedded-EOM-CCSD[62]	5.31		
embedded-BSE@DDH[12]	5.23		2.93*
G_0W_0@LDA-BSE[9]		4.95	3.40*
GW@PBE[10]		5.20	
QMC (FN-DMC)[8]		5.0	3.8*

[a]The experimental absorption energy is 5.03 eV, and the emission occurs at 2.4 eV. All the energies are in units of eV. Emission energies marked with an asterisk (*) do not involve the $^3T_{1u}$ state.

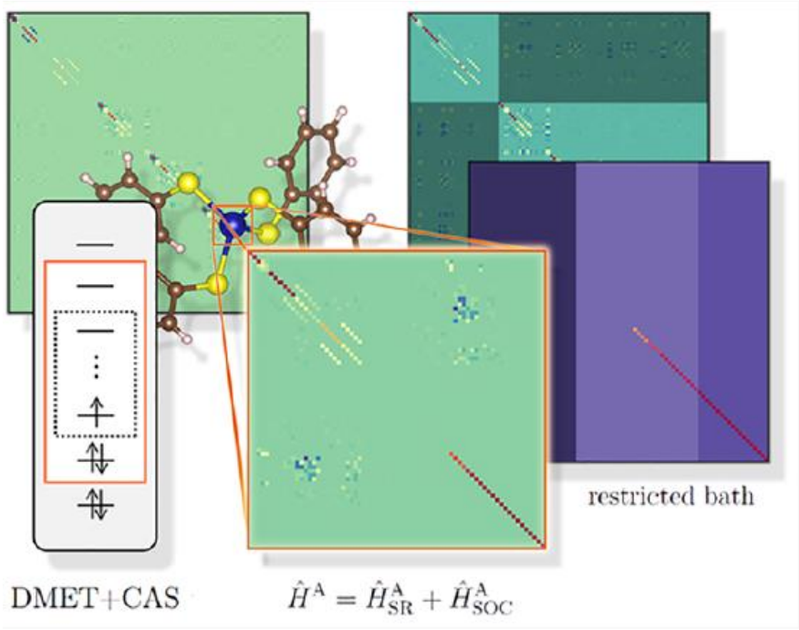
Mitra et al, **JPCL** 12, 11688 (2021); Haldar et al, **JPCL** 14, 4273 (2023).
Verma et al, JPCL, 14, 7703 (2023); A. Mitra et al. **JCTC**, 19, 3498 (2023).

DMET+ Neural Network Quantum States NNQS



H. Ma, H. Shang, J. Yang, npj Comput. Mater. 10, 220 (2024).

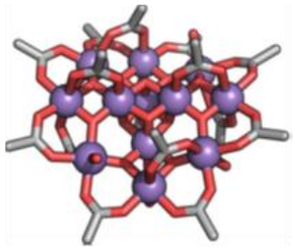
DMET+CAS-SISO approach to 3d/4f single-ion magnets

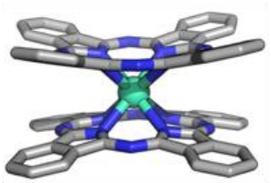


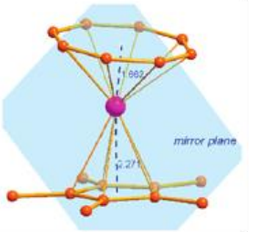
Y. Ai, Q. Sun, H. Jiang, ***J. Phys. Chem. Lett.*** 13, 10627 (2022).
Z. Guan, H. Jiang, ***J. Chem. Phys.*** 162, 224111 (2025).
Y. Ai, Z.W. Li, Z.-B. Guan, H. Jiang, ***J. Chem. Theory Comput.***, 21, 9631 (2025).

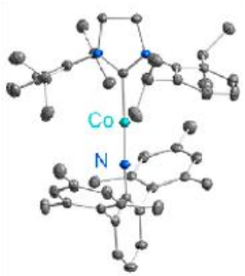
Importance of Single-molecule magnets (SMMs)

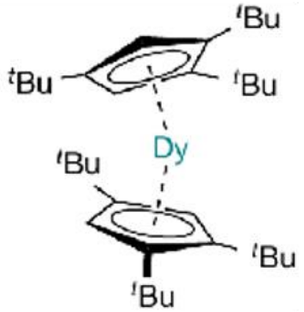
	1993	2003	2011	2017	2022	2025
U_{eff}	46 cm^{-1}	230 cm^{-1}	224 cm^{-1}	413 cm^{-1}	1541 cm^{-1}	1631 cm^{-1}	1843 cm^{-1}
T_B	3 K	1.7 K	5 K	~9.5 K	80 K	72 K	100 K

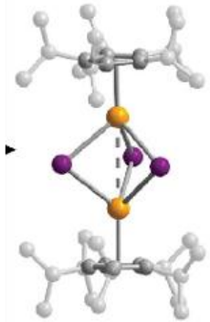


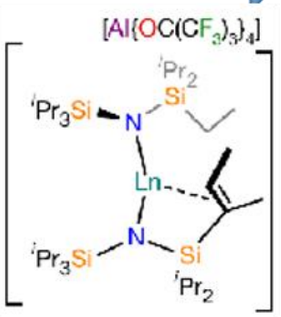








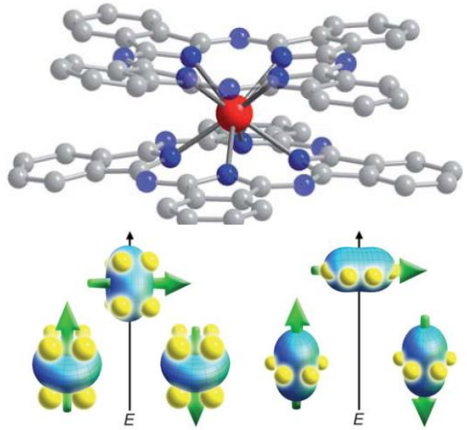


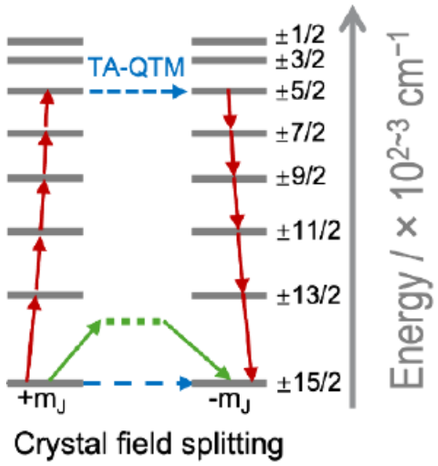


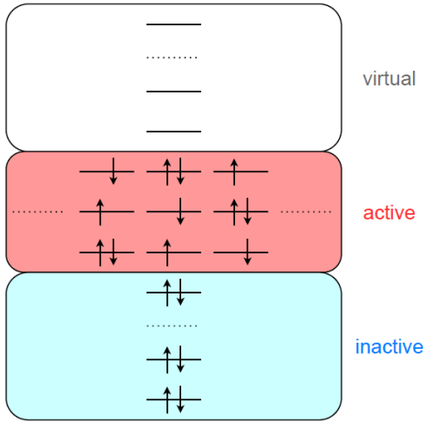
Nature (1993) JACS (2003) JACS(2011) ACIE (2017) Nature(2017) Science (2022) Nature(2025)

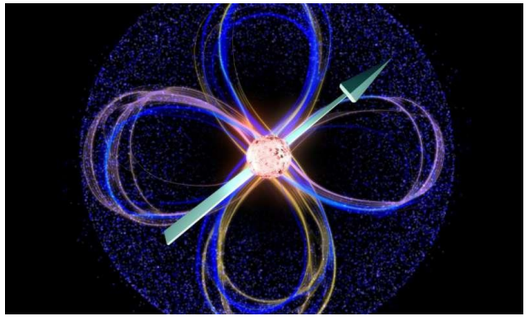
- **Foundations for future new-edge technologies**: high-density information storage, molecular spintronics, quantum sensing, quantum computing, …
- **Inspiring new design strategies** for next-generation rare-earth permanent magnets
- **"test-bed" for novel quantum physics**: quantum tunneling, decoherence, entanglement, …

Challenges of first principles theoretical study of SMMs









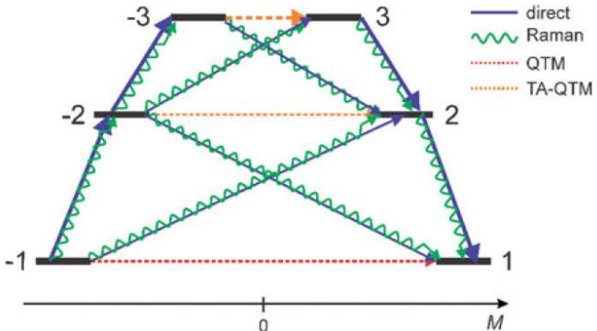
Fine energetic splitting in complex ligand field (required precision: ~10 cm

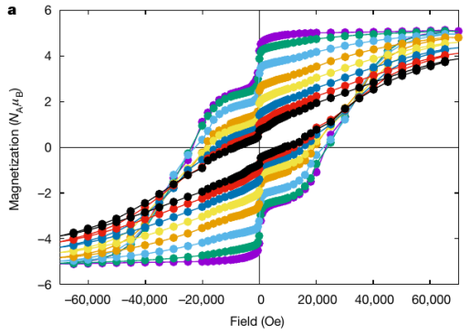
Strong correlation & relativistic effects ($10^{2\text{-}3}$ spin states + SISO)

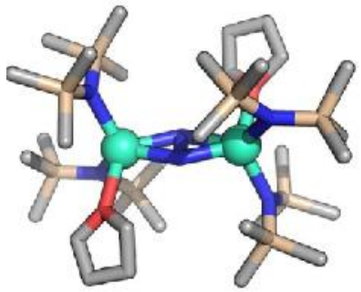
Theoretical study of Ln-SMMs

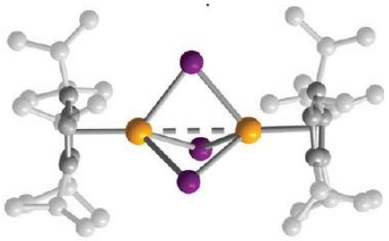
ab initio spin relaxation dynamics ($10^{3\text{-}5}$ high-level calc.)

Coupled multi-nuclear systems: large active space (50o-100o)









Gould et al. *Science* (2022).

Single-shot DMET based CASSI-SO approach to SIMs

This work: single-shot DMET → "DMET ansatz" $|\Psi\rangle = |\Psi_{\mathcal{A}}\rangle \otimes |\Phi^{\mathrm{B}}_{\mathrm{core}}\rangle$

Low level solver: restricted open-shell Hartree-Fock **(ROHF) with properly converged SCF solution**

High-level solver: Complete active space state interaction with spin-orbit coupling (**CASSI-SO**)

$$\hat{H}^{\mathcal{A}} = \hat{H}^{\mathcal{A}}_{\mathrm{SR}} + \hat{H}^{\mathcal{A}}_{\mathrm{SOC}} \qquad \hat{H}^{\mathcal{A}}_{\mathrm{SR}} = \sum_{\mu,\nu\in\mathcal{A}} \sum_{\sigma} h^{\mathcal{A}}_{\mu\nu} c^{\dagger}_{\mu\sigma} c_{\nu\sigma} + \frac{1}{2} \sum_{\mu,\nu,\lambda,\eta\in\mathcal{A}} \sum_{\sigma,\sigma'} \langle \mu\nu | \lambda\eta \rangle c^{\dagger}_{\mu\sigma} c^{\dagger}_{\nu\sigma'} c_{\eta\sigma'} c_{\lambda\sigma}$$

$$h^{\mathcal{A}}_{\mu\nu} = -\frac{1}{2}\nabla^2 - \sum_{I\in\mathrm{A,B}} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} + \sum_{b\in\mathrm{B_{core}}} \left(2\hat{J}_b - \hat{K}_b\right)$$

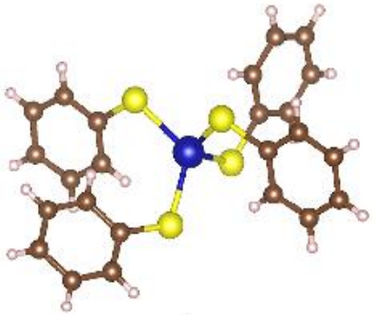
Two-step approach to SOC:

$\hat{H}^{\mathcal{A}}_{\mathrm{SR}}$: state-average CAS self-consistent field (SA-CASSCF)

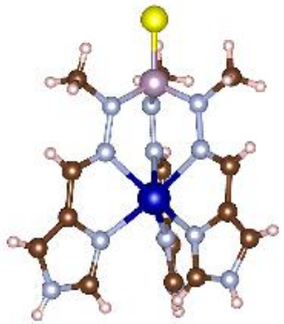
$\hat{H}^{\mathcal{A}}_{\mathrm{SOC}}$: quasi-degenerate perturbation theory (QDPT) based on **mean-field approx. to Breit-Pauli Hamiltonian (SOMF)**

B. A. Hess, et al, Chem. Phys. Lett. 251, 365 (1996);
F. Neese, J. Chem. Phys. 122, 034107 (2005).

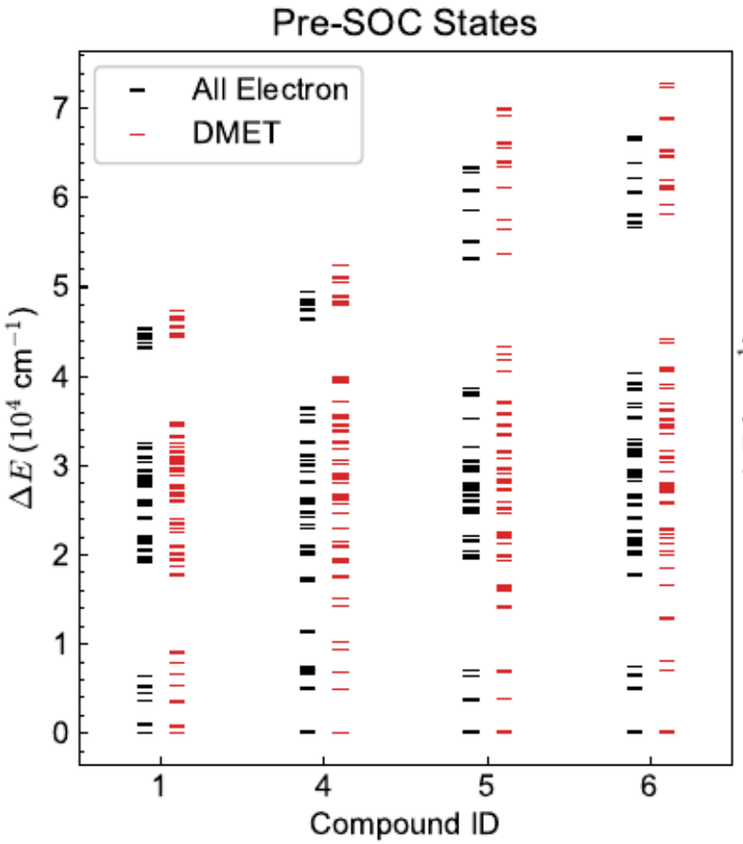
DMET+CASSI-SO approach to SIMs

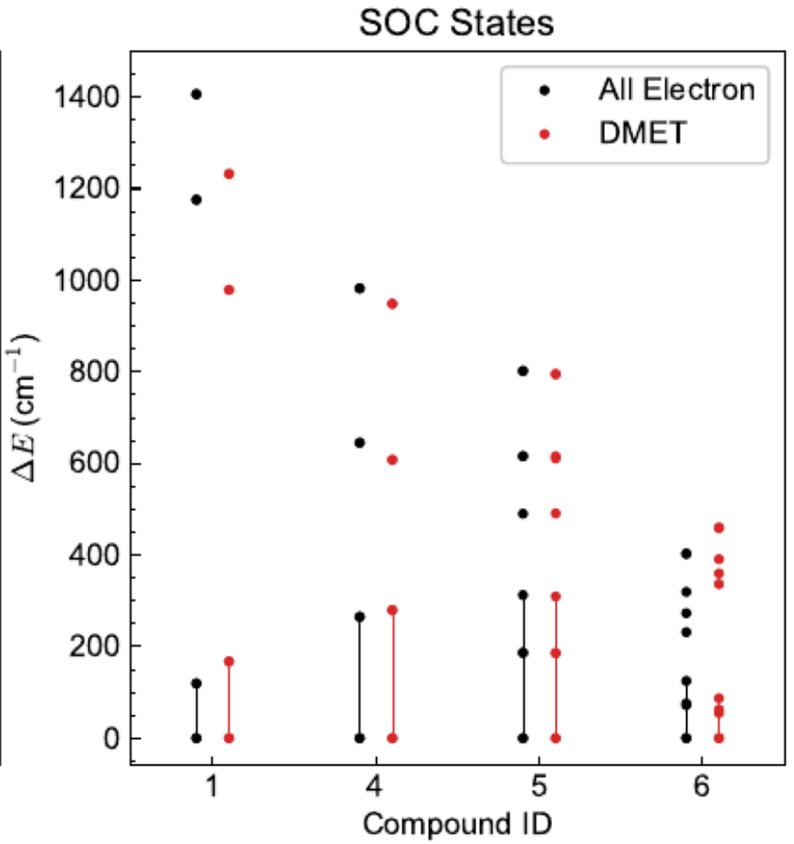


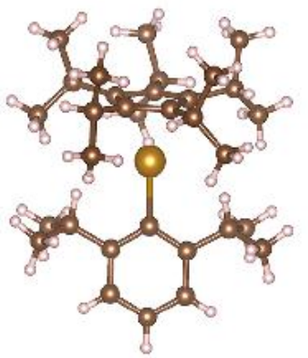
1



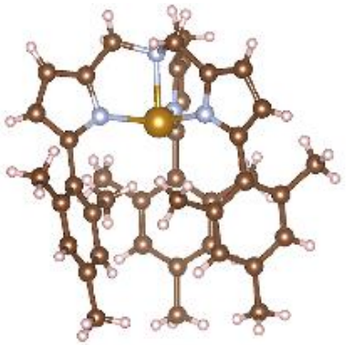
4







5



6

$$\hat{H}_{\mathrm{ZFS}} = D\left(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right)$$

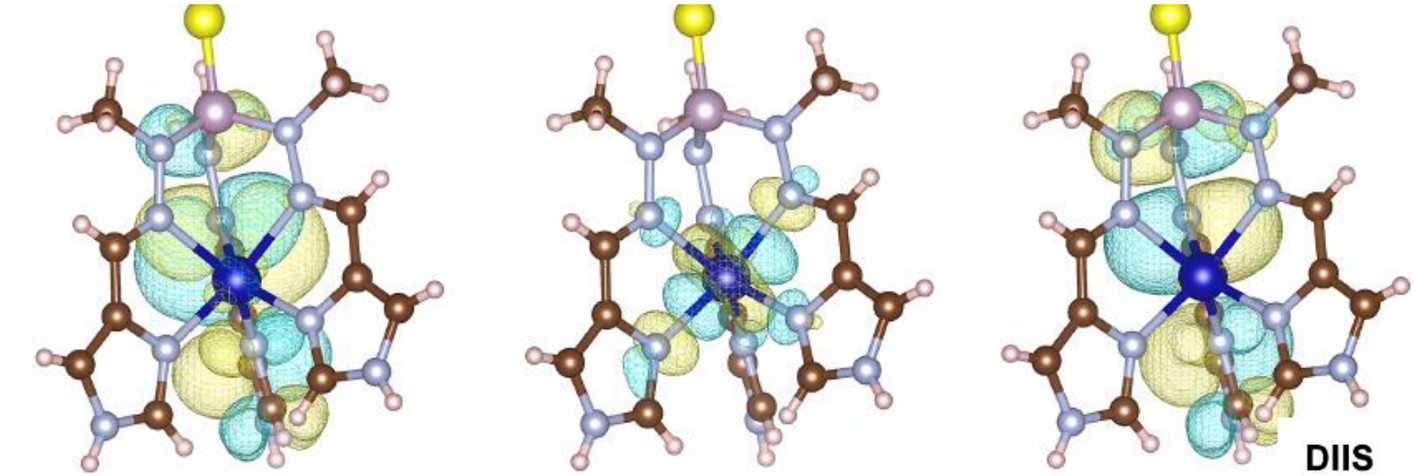
$$D' = D - E$$

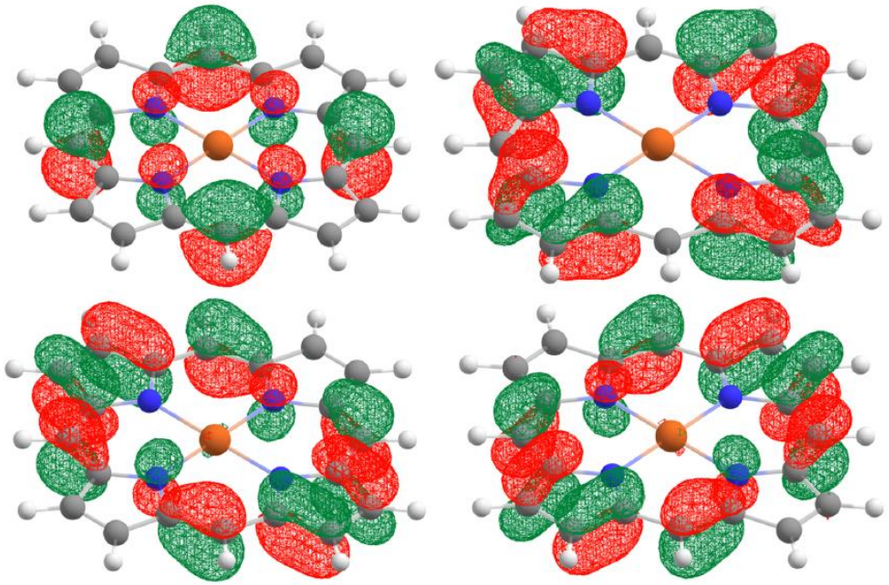
Unit: cm^{-1}

Compound	DIIS	R-DIIS	All Electron	Exp.
1[a]	−83.7	−62.7	−59.5	−55
4	−140	−132	−132	−73
5	−69.2	−66.0	−69.7	−51.4
6	−20.5	−33.6	−27.7	−37.5

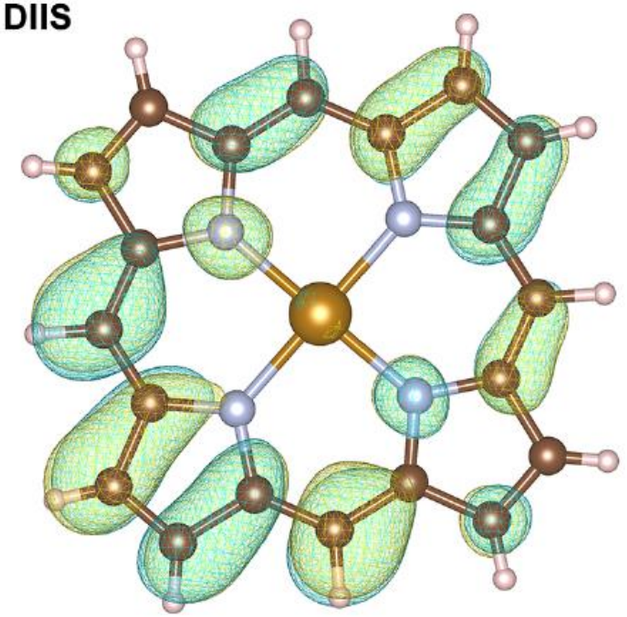
What's going wrong?

Singly occupied ROHF MOs obtained by DIIS-SCF for compound 4.





L. Gagliardi and coworkers, *J. Phys. Chem. Lett.* **10**, 5507 (2019)



Fe-P (this work)

DIIS technique for SCF convergence

DIIS: direct inversion in iterative subspace

SCF is equivalent to solve the iterative equation $\mathbf{x} = f(\mathbf{x})$

$$\mathbf{x}_k^{(\mathrm{in})} = \sum_{i=1}^{m} c_i \mathbf{x}_i, \qquad \mathbf{x}_i \equiv \mathbf{x}_{k-i}^{(\mathrm{out})}$$

Error vector: $\mathbf{e}(\mathbf{x}_i) \equiv \mathbf{x}_i - f(\mathbf{x}_i) \equiv \mathbf{e}_i$

$$\{c_i\} = \arg\min_{\sum_i c_i = 1} \left|\mathbf{e}\left(\mathbf{x}_k^{(\mathrm{in})}\right)\right|^2 \cong \arg\min_{\sum_i c_i = 1} \left|\sum_{i=1}^{m} c_i \mathbf{e}(\mathbf{x}_i)\right|^2$$

$$\begin{bmatrix} B_{11} & \cdots & B_{1m} & -1 \\ \vdots & \cdots & B_{2m} & -1 \\ B_{m1} & \cdots & B_{mm} & -1 \\ -1 & \cdots & -1 & 0 \end{bmatrix} \begin{bmatrix} c_1 \\ \vdots \\ c_m \\ \lambda \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{bmatrix}$$

Error vector in SCF :

$$\mathbf{e}(\mathbf{D}) = \mathbf{SDF}(\mathbf{D}) - \mathbf{F}(\mathbf{D})\mathbf{DS}$$

$$B_{ij} \equiv \mathbf{e}_i \cdot \mathbf{e}_j$$

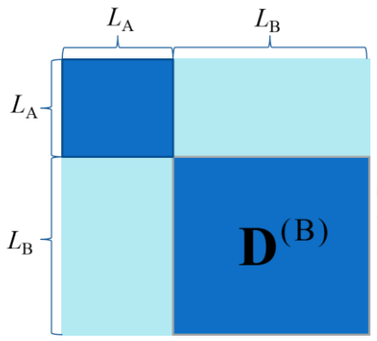
P. Pulay, *Chem. Phys. Lett.* **73**, 393 (1980); *J. Comput. Chem.* 3, 556 (1982).

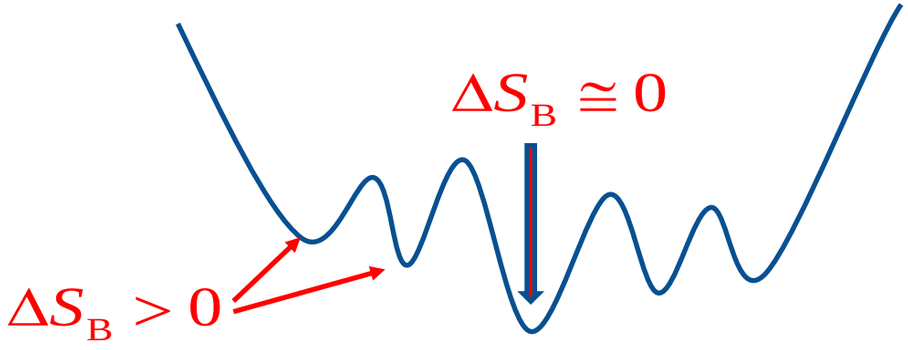
Regularized DIIS: a “blocking” strategy

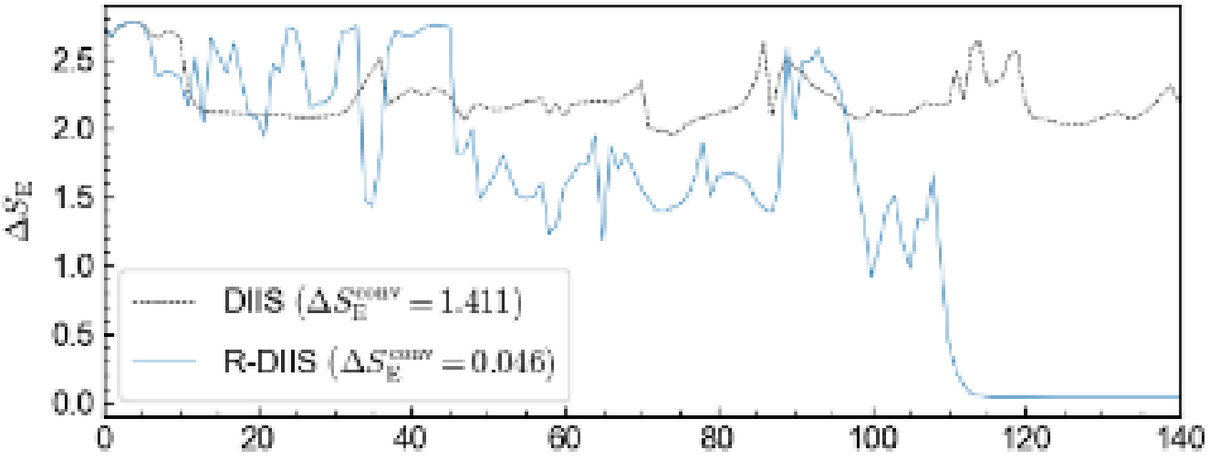
A modified error vector with a blocking term (**R-DIIS**)

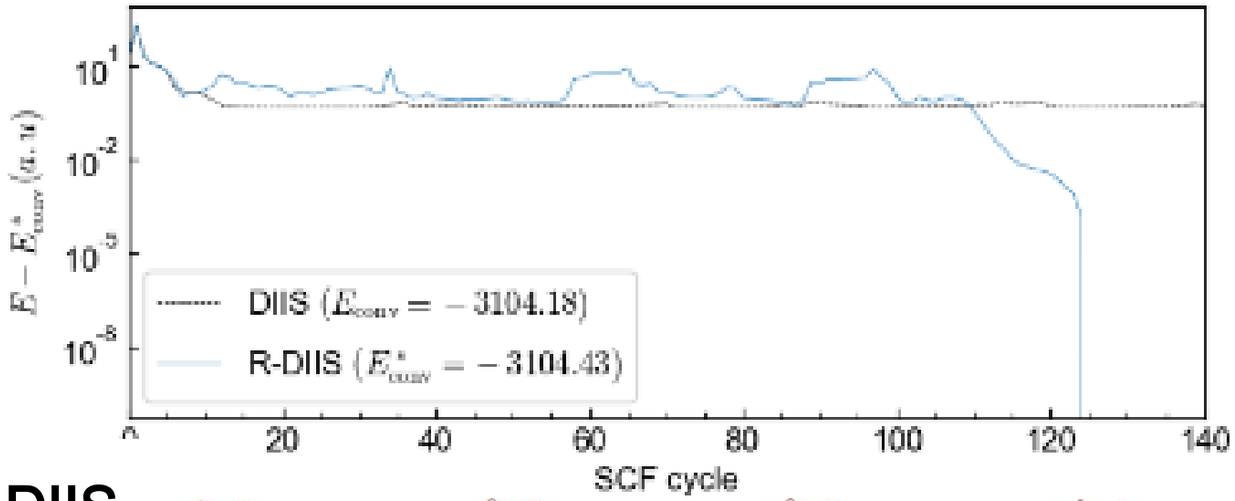
$$\mathbf{e} = \mathbf{SDF} - \mathbf{FDS} + \lambda \Delta S_{\mathrm{B}} \mathbf{I}$$

$$\Delta S_{\mathrm{B}} = \sum_{\sigma=\alpha,\beta} \mathrm{Tr}\, \mathbf{D}_{\sigma}^{(\mathrm{B})} \ln \mathbf{D}_{\sigma}^{(\mathrm{B})} - 2\,\mathrm{Tr}\, \frac{\mathbf{D}^{(\mathrm{B})}}{2} \ln \frac{\mathbf{D}^{(\mathrm{B})}}{2}$$

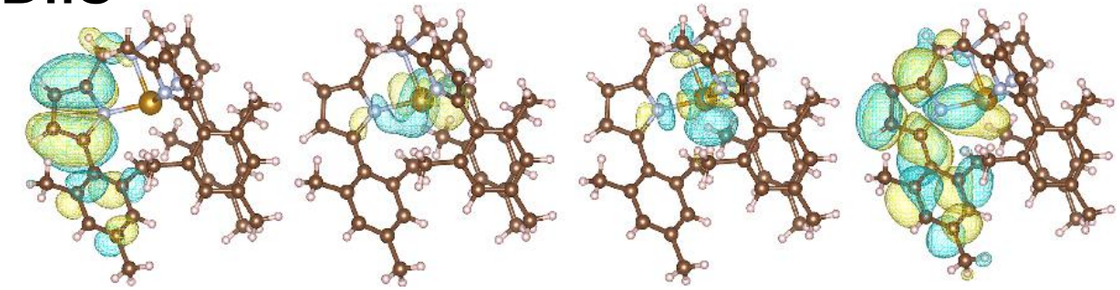




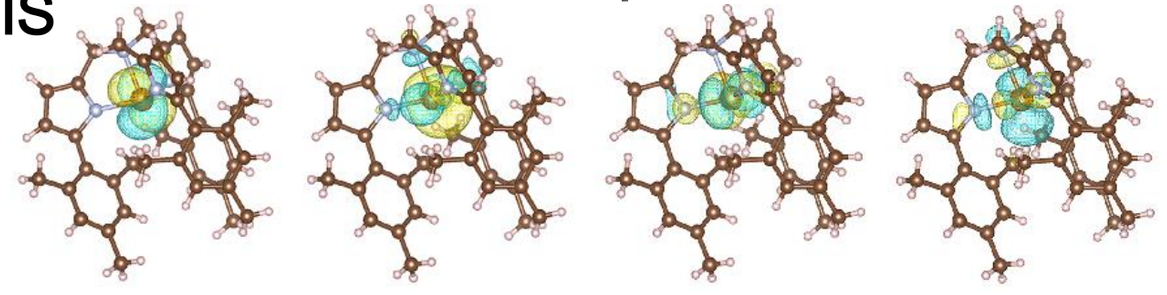




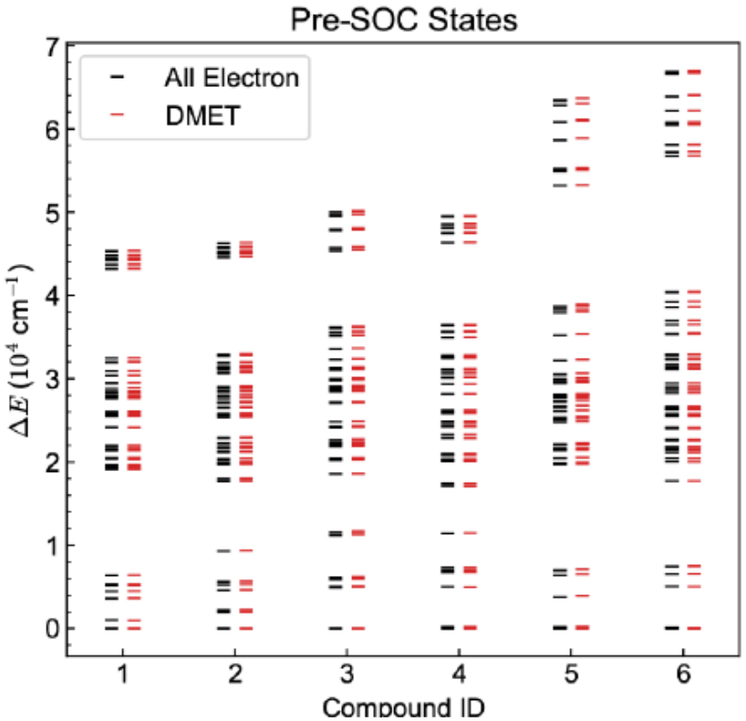
DIIS

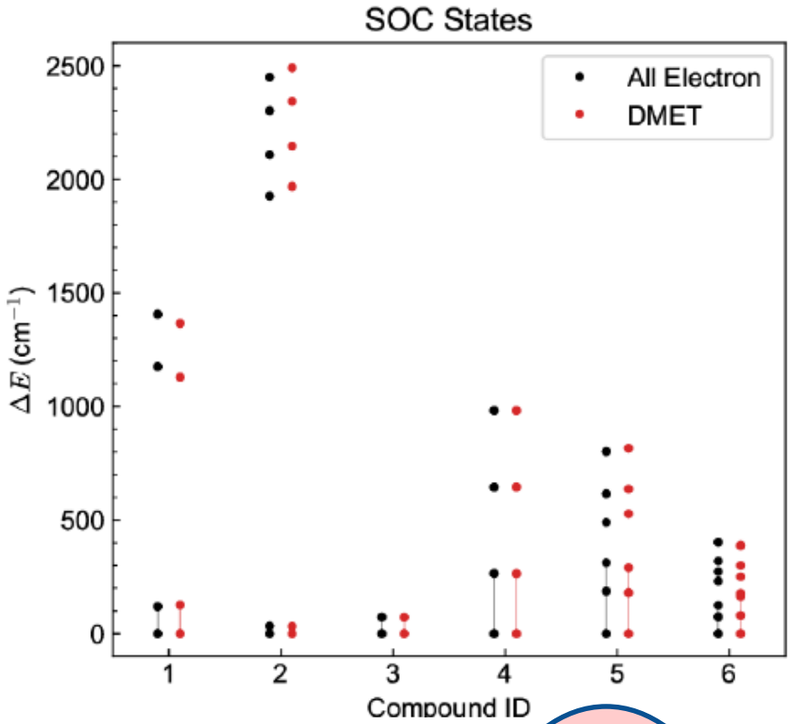


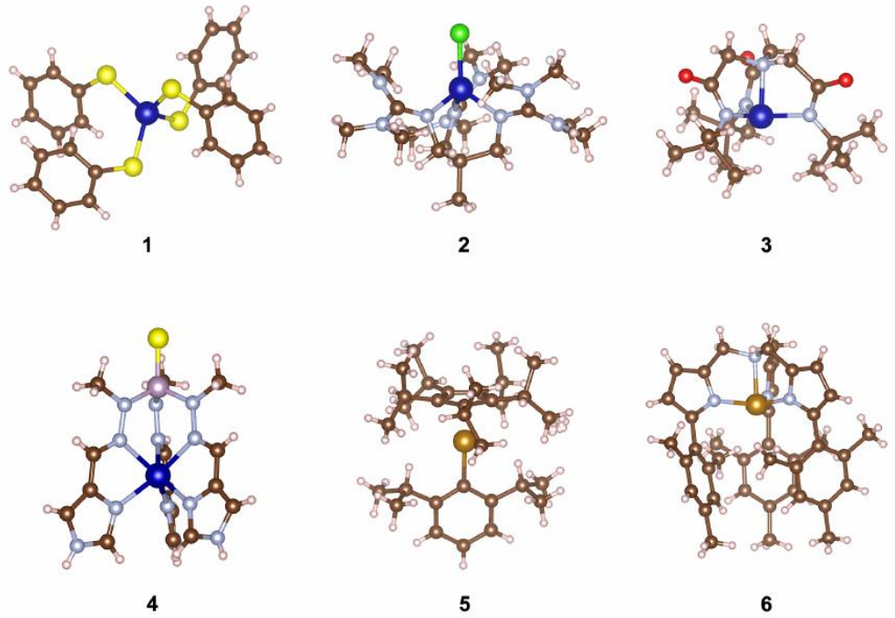
R-DIIS



DMET+CASSI-SO: applications to 3d-SIMs

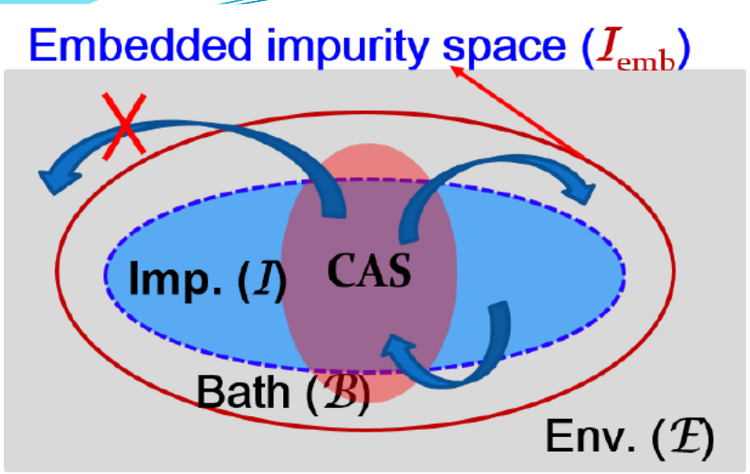






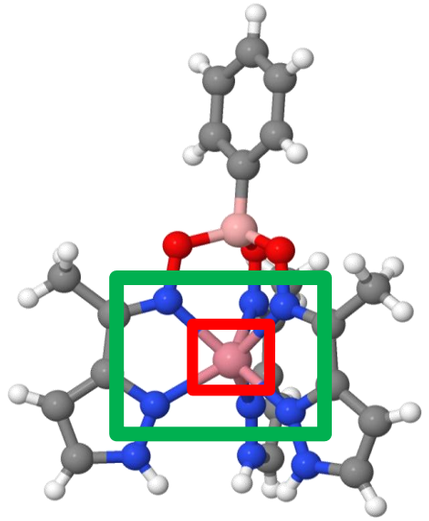
Compound	Size Compression	ΔS_{E}	All Electron	DMET	Calc.[a]	Exp.
1	$569 \rightarrow 100$	0.020	-59.7	-63.5	-59.1[56]	-55[56]
2	$629 \rightarrow 98$	0.022	$+16.8$	$+16.2$	$+17.0$[10]	$+12.9$[57]
3	$529 \rightarrow 97$	0.023	$+36.4$	$+36.1$	$+36.9$[10]	$+16$[61]
4	$641 \rightarrow 102$	0.014	-132	-132	-141[10]	-73[62]
5	$699 \rightarrow 99$	0.044	-69.7	-66.0	-72.9[10]	-51.4[59]
6	$847 \rightarrow 107$	0.031	-27.7	-33.6	-28.4[58]	-37.5[58,60]

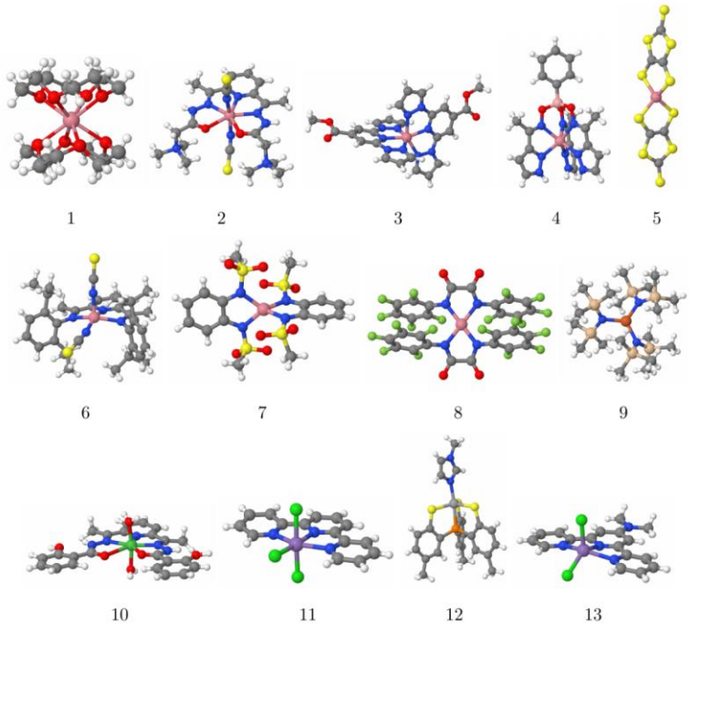
DMET+NEVPT2 for SIMs: considering dynamical correlation

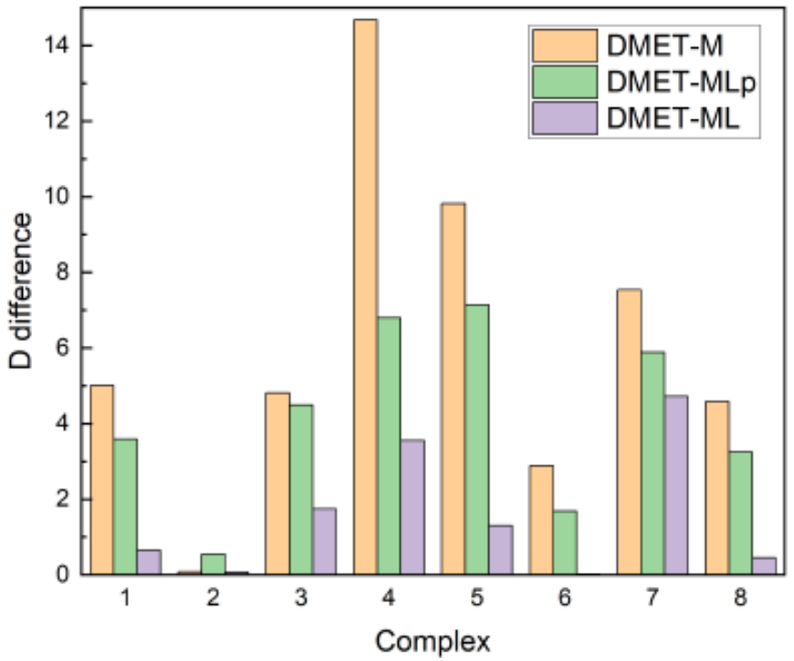


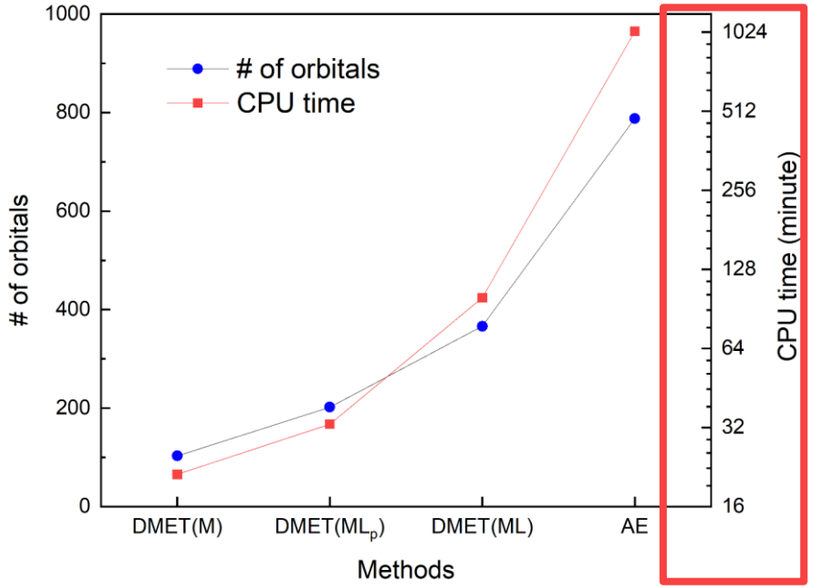
Different choice of A:

- DMET(M): TM atom as A
- DMET(ML_p): TM atom + p-orbitals of coordinating atom as A
- DMET(ML): TM atom + coordinating atoms





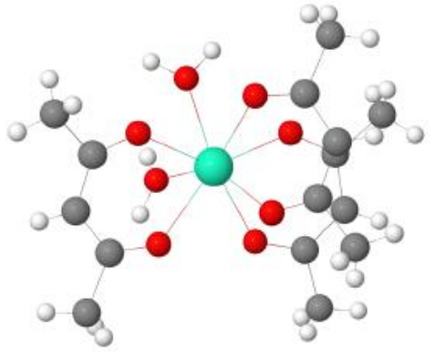




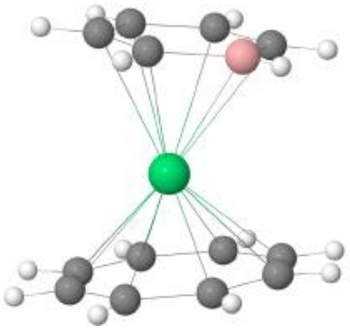
Z. Guan, H. Jiang, *J. Chem. Phys.* 162, 224111 (2025).

DMET+CASSI-SO for 4f SIMs

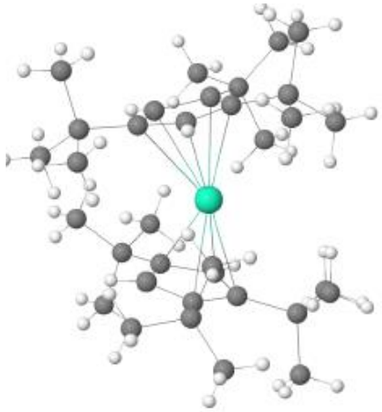
1Dy

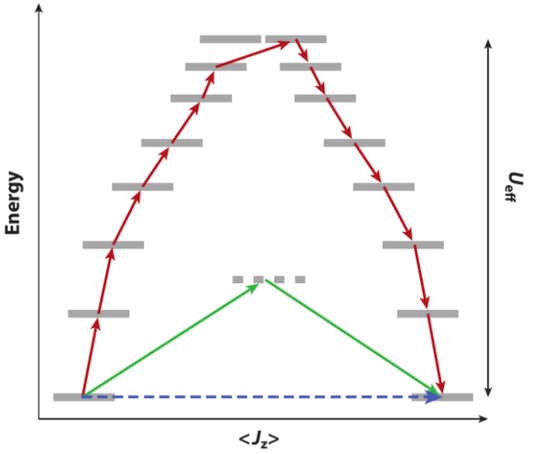


2Er



3Dy





CASSCF+SO

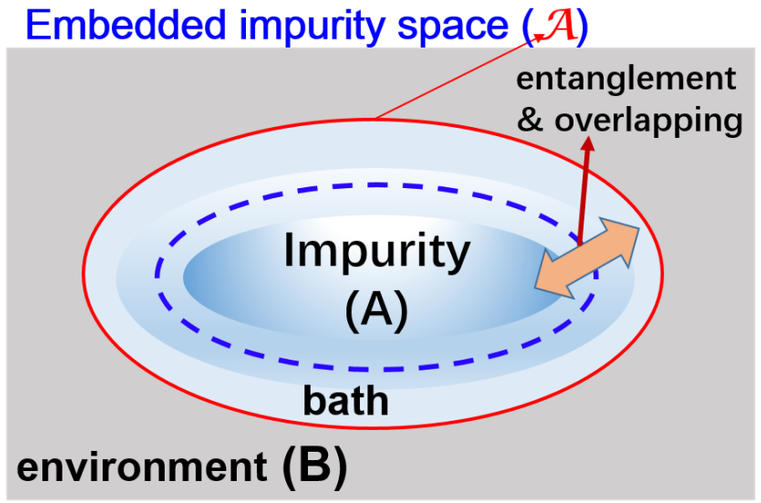
State	1Dy DMET (214)	1Dy AE (679)	2Er DMET (188)	2Er AE (386)	3Dy DMET (218)	3Dy AE (1030)
1	0.0	0.0	0.0	0.0	0.0	0.0
2	156.2	153.2	144.7	144.4	488.1	486.2
3	232.9	228.3	191.4	190.9	772.9	768.8
4	286.7	281.2	205.9	205.5	955.5	949.4
5	321.3	313.3	232.5	231.7	1119.4	1111.9
6	417.5	406.1	242.8	242.1	1276.9	1268.3
7	477.3	465.0	263.7	262.9	1402.1	1392.6
8	540.2	530.2	290.9	290.1	1484.2	1474.7
MAE	7.8		0.6		6.7	
MARE(%)	2.3		0.3		0.6	

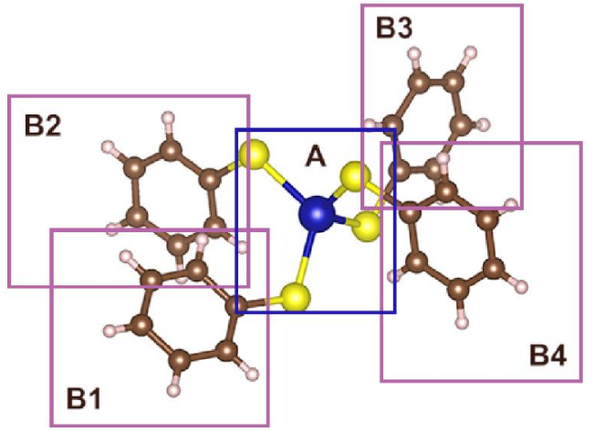
CASSCF+PT2+SO

State	1Dy DMET	1Dy AE	2Er DMET	2Er AE	3Dy DMET	3Dy DMET(ML_n)	3Dy AE
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	155.8	155.6	155.1	146.4	529.8	512.6	507.5
3	238.6	238.0	207.7	201.0	803.2	772.0	762.3
4	307.3	304.7	246.2	238.0	976.0	934.2	921.4
5	344.6	341.2	283.9	275.0	1159.9	1108.0	1093.2
6	456.0	439.8	300.4	291.5	1355.4	1293.5	1277.2
7	550.2	523.8	340.6	333.1	1520.2	1451.4	1434.0
8	612.2	588.4	376.4	363.9	1626.2	1552.3	1536.0
MAE	10.5		8.8		62.7	13.2	
MARE(%)	2.1		3.5		5.7	1.2	

Y. Ai, Z.W. Li, Z.-B. Guan, H. Jiang, *J. Chem. Theory Comput.*, 21, 9631 (2025).

Non-orthogonal atomic orbitals based DMET (AO-DMET) and further developments



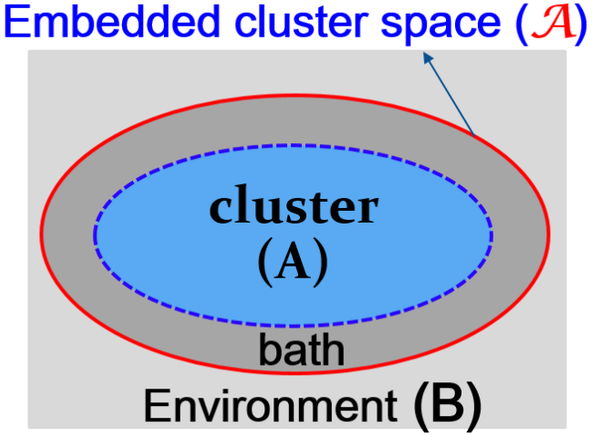


Y. Ai, Z.-W. Li, H. Jiang, *Phys. Rev. Lett.* 135, 026502 (2025) .

Limitations of orthogonal local orbital-based DMET (LO-DMET)

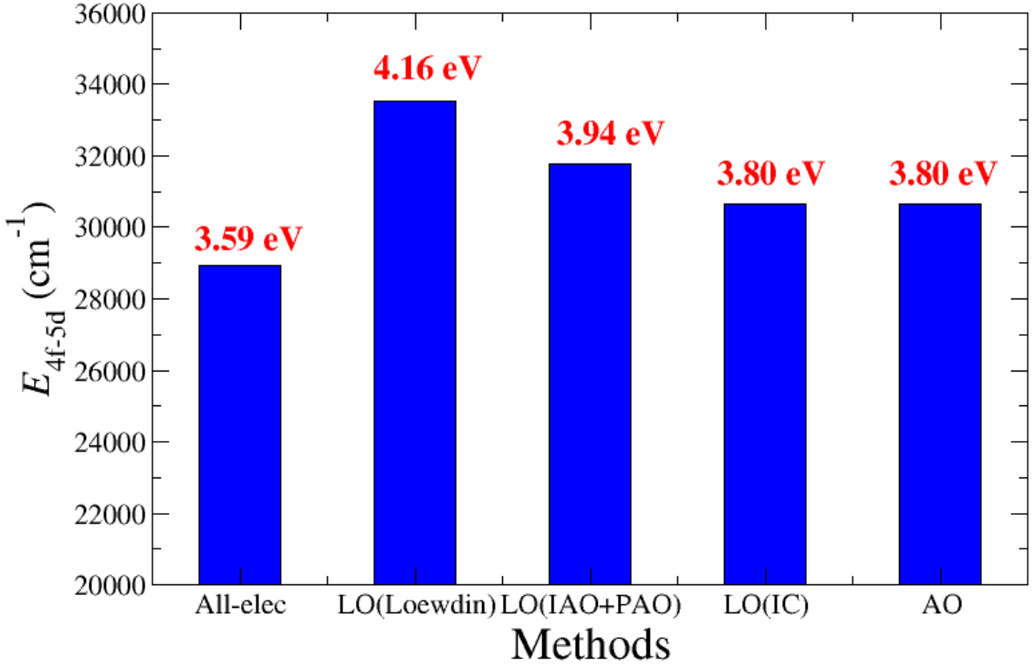
$$\hat{H}^{\mathcal{A}} = \sum_{\mu,\nu\in\mathcal{A}} \sum_{\sigma} h^{\mathcal{A}}_{\mu\nu} c^{\dagger}_{\mu\sigma} c_{\nu\sigma} + \frac{1}{2} \sum_{\mu,\nu,\lambda,\eta\in\mathcal{A}} \sum_{\sigma,\sigma'} \langle \mu\nu | \lambda\eta \rangle c^{\dagger}_{\mu\sigma} c^{\dagger}_{\nu\sigma'} c_{\eta\sigma'} c_{\lambda\sigma}$$

$$h^{\mathcal{A}}_{\mu\nu} = -\frac{1}{2}\nabla^2 - \sum_{I\in \mathrm{A,B}} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} + \sum_{b\in \mathrm{B_{core}}} \left(2\hat{J}_b - \hat{K}_b\right)$$



- Arbitrariness of defining LOs (various bottom-up or top-down schemes) ➔ **significant for DMET accuracy**
- Although $\hat{H}^{\mathcal{A}}$ defined by at most $2N_A$ orbitals, Hamiltonian matrix elements (e.g. SOC) still require two-electron integrals involving AOs in the **full** system.
- Low-level solver (e.g. Hartree-Fock) necessary for the full system (A+B) ➔ expensive for large systems

Ce-Bp **CASSCF-NEVPT2-SISO**



Non-orthogonal decomposition of a Slater determinant

Non-orthogonal atomic orbitals (AO): $\{|\phi'_\mu\rangle\}$

Local orthogonalization with A and B, respectively, $|\phi''_\mu\rangle = \sum_{\mu'} X_{\mu'\mu}|\phi'_{\mu'}\rangle$

$$|\chi_i\rangle = \sum_\alpha [C'']^A_{\alpha i}|\phi''_\alpha\rangle + \sum_\beta [C'']^B_{\beta i}|\phi''_\beta\rangle$$

$\mu=\alpha/\beta$ for orbitals centered in A/B.

Single value decomposition (SVD)

$$[C'']^B_{\beta i} = \sum_j U''_{\beta j}\sigma''_j[V'']^\dagger_{ji}$$

It **can be proven rigorously** that under the assumption $N_B > N_{occ} > 2N_A$

$$\begin{cases} 0 \le \sigma''_i \le 1 \text{ or } \sigma''_i \ge 1 & 1 \le i \le 2N_A; \\ \sigma''_i = 1 & 2N_A + 1 \le i \le N_{\mathrm{OCC}} \end{cases}$$

Y. Ai, Z.-W. Li, H. Jiang, ***Phys. Rev. Lett.*** **135, 026502 (2025)** .

Non-orthogonal atomic orbital(AO)-based DMET (AO-DMET)

Unitary transform of occupied orbitals in terms of **V”**

$$|\tilde{\chi}_i\rangle = \sum_j V''_{ji}|\chi_j\rangle = \sum_\alpha [\tilde{C}'']^A_{\alpha i}|\phi''_\alpha\rangle + \sigma''_i|B''_i\rangle$$

$\sigma''_i = 1 \quad |\tilde{\chi}_i\rangle = |B''_i\rangle$ ➔ core orbitals, orthogonal to *A*

$|B''_i\rangle$ with $0 < \sigma''_i < 1$ or $\sigma''_i > 1$

➔ **Entangled** and **Overlapping** (EO) orbitals, at most $2N_A$

➔ **Further approximation**: using auxiliary orbitals ($\#N_{aux} < 2N_A$)

$$|\Phi\rangle = |\Psi^{A+B_{eo}}\rangle \otimes |\Phi^{B_c}\rangle$$

Y. Ai, Z.-W. Li, H. Jiang, ***Phys. Rev. Lett.*** 135, 026502 (2025) .

Non-orthogonal atomic orbital(AO)-based DMET (AO-DMET)

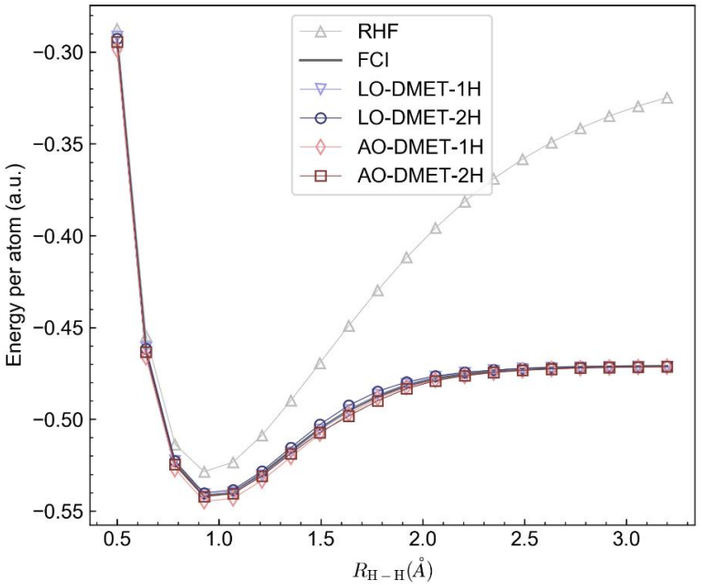
$$|\Phi\rangle = |\Psi^{A+B_{\mathrm{eo}}}\rangle \otimes |\Phi^{B_{\mathrm{c}}}\rangle$$

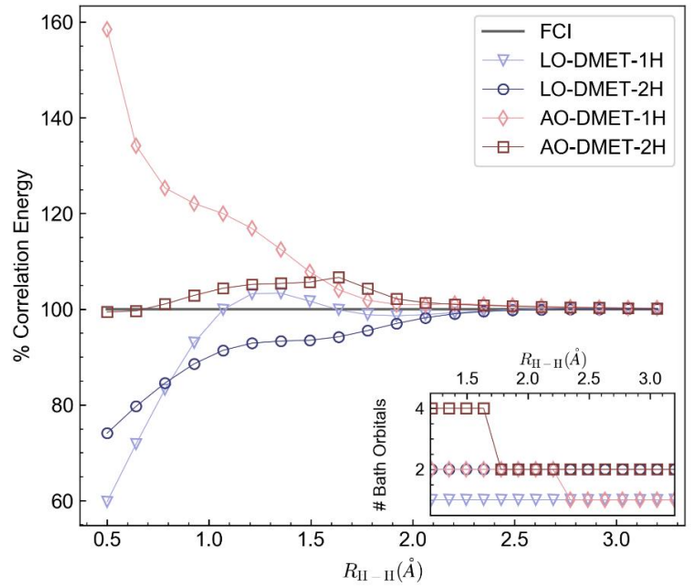
$$\hat{H}^{\mathrm{AO-DMET}}_{\mathrm{imp}} = \sum_{\mu\nu\in A+B_{\mathrm{eo}}} \sum_{\sigma} \bar{h}_{\mu\nu} c^{\dagger}_{\mu\sigma} c_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\lambda\eta\in A+B_{\mathrm{eo}}} \sum_{\sigma\sigma'} \bar{V}_{\mu\nu\lambda\eta} c^{\dagger}_{\mu\sigma} c^{\dagger}_{\nu\sigma'} c_{\eta\sigma'} c_{\lambda\sigma}$$

$$\bar{h}_{\mu\nu} \equiv [\mathbf{S}^{-1}\mathbf{h}\mathbf{S}^{-1}]_{\mu\nu}$$

$$\hat{h} = -\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} + \sum_{b\in B_{\mathrm{c}}} (2\hat{J}_b - \hat{K}_b)$$

$$\bar{V}_{\mu\nu\lambda\eta} \equiv \sum_{\mu'\nu'\lambda'\eta'\in A+B_{\mathrm{eo}}} S^{-1}_{\mu\mu'} S^{-1}_{\nu\nu'} S^{-1}_{\lambda\lambda'} S^{-1}_{\eta\eta'} \langle \mu'\nu'|\lambda'\eta'\rangle$$





Y. Ai, Z.-W. Li, H. Jiang, ***Phys. Rev. Lett.*** **135, 026502 (2025)** .

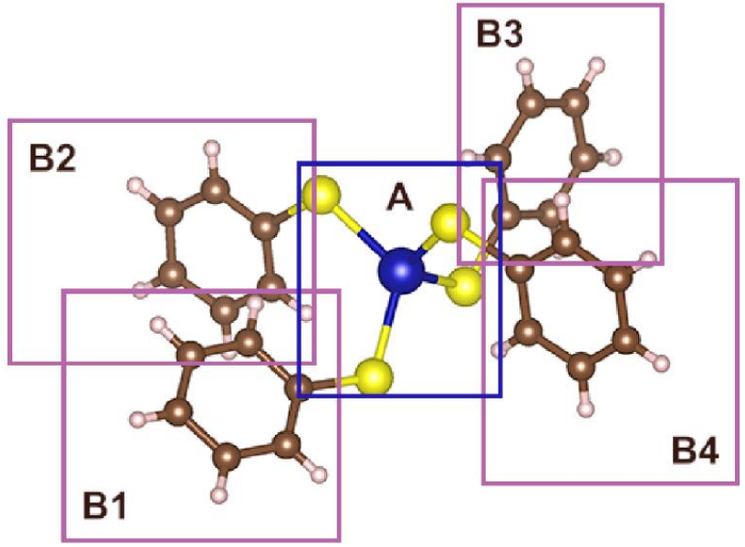
Fragmented AO-DMET (fAO-DMET)

LO-DMET vs AO-DMET: different locality in the transformation matrix between non-orthogonal **atomic orbitals** (**AO**) to **embedded cluster orbitals** (**ECO**)

LO-DMET: $\mathbf{C}^{\mathrm{AO}\to\mathrm{ECO}} = \mathbf{X}\begin{pmatrix}\mathbf{I}^{AA} & \mathbf{0}\\ \mathbf{0} & \mathbf{Y}\end{pmatrix} = \begin{pmatrix}\mathbf{X}^{AA} & \mathbf{X}^{AB}\mathbf{Y}\\ \mathbf{X}^{BA} & \mathbf{X}^{BB}\mathbf{Y}\end{pmatrix}$

AO-DMET: $\tilde{\mathbf{C}}^{\mathrm{AO}\to\mathrm{ECO}} = \begin{pmatrix}\mathbf{I}^{AA} & \mathbf{0}\\ \mathbf{0} & \mathbf{X}'\mathbf{U}''\end{pmatrix}$

For a large system with a fragmented structure $A + \sum_i B^{(i)}$



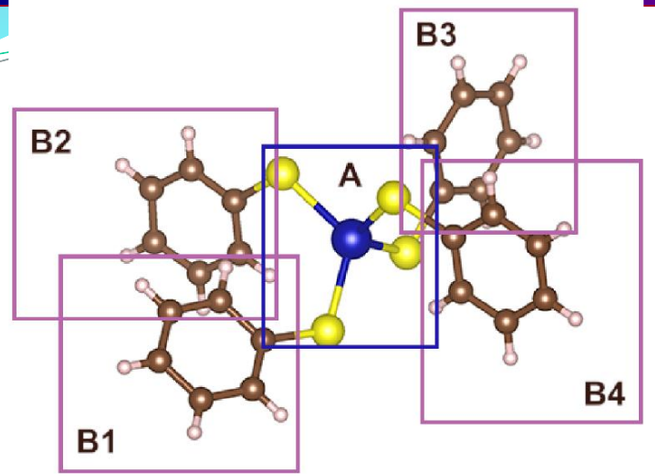
$$A + B^{(i)} \xrightarrow{\text{Hartree-Fock}} \tilde{\mathbf{C}}^{\mathrm{AO}\to\mathrm{ECO}}_{A+B^{(i)}} = \begin{pmatrix}\mathbf{I}^{AA} & \mathbf{0}\\ \mathbf{0} & [\mathbf{X}']^{(i)}[\mathbf{U}'']^{(i)}\end{pmatrix}$$

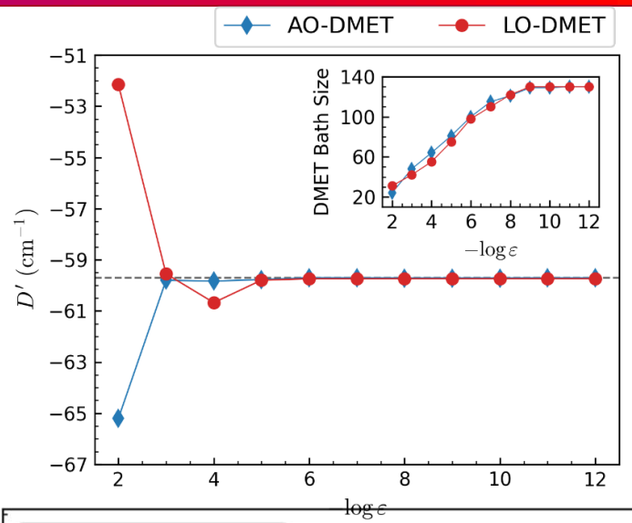
$$A + \sum_i B^{(i)} \qquad \tilde{\mathbf{C}}^{\mathrm{AO}\to\mathrm{ECO}}_{A+\sum_i B^{(i)}} = \begin{pmatrix}\mathbf{I}^{AA} & & & \\ & [\mathbf{X}']^{(1)}[\mathbf{U}'']^{(1)} & & \\ & & \ddots & \\ & & & [\mathbf{X}']^{(M)}[\mathbf{U}'']^{(M)}\end{pmatrix} \qquad A + \sum_i B^{(i)}_{\mathrm{eo}}$$

Limiting case: $B^{(i)}_{\mathrm{eo}}$ is empty ➔ Ab initio model potential (AIMP) embedding

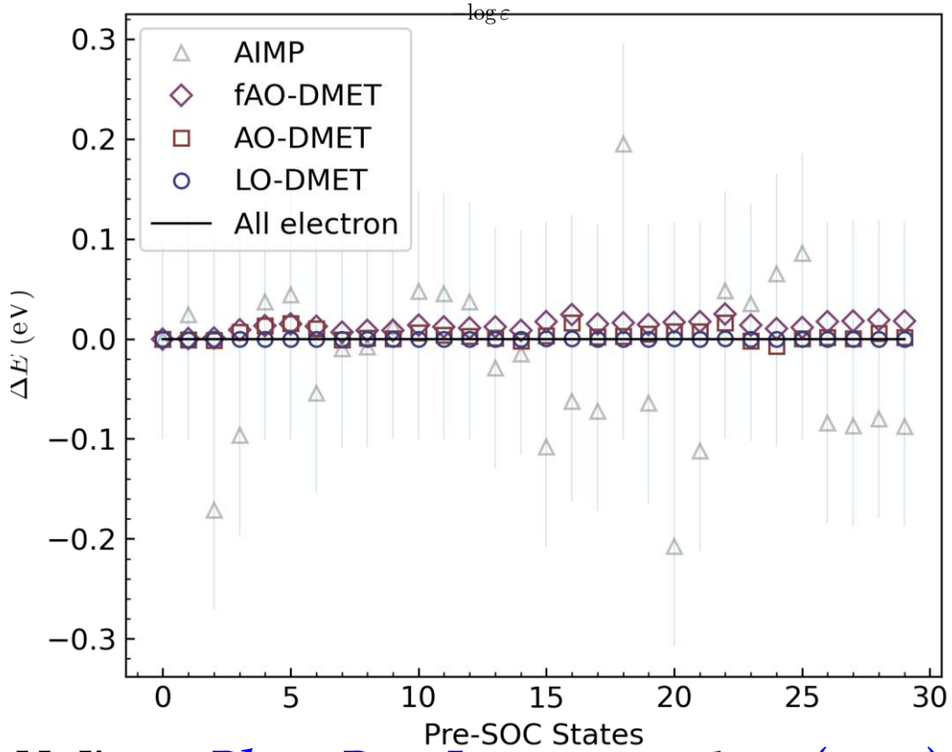
Y. Ai, Z.-W. Li, H. Jiang, ***Phys. Rev. Lett.*** **135, 026502 (2025)**.

Comparison of different approaches: $[Co(SPh)_4]^{2-}$





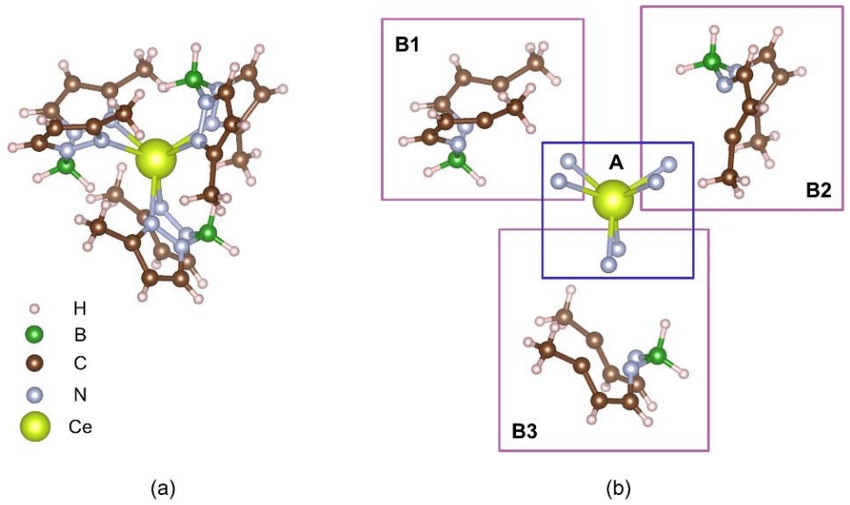
Method	$N_{\mathrm{AO}}^{\mathrm{MF}}$	$N_{\mathrm{AO}}^{\mathrm{HL}}$	N_{EC}	D' (cm^{-1})
All-electron	569	569	569	-59.7
AIMP	94	193	193	-41.5
LO-DMET	569	569	269	-60.0
AO-DMET	569	569	274	-59.8
AO-DMET(aux)	569	333	274	-60.3
fAO-DMET	131	569	265	-58.9
fAO-DMET(aux)	131	333	265	-61.9



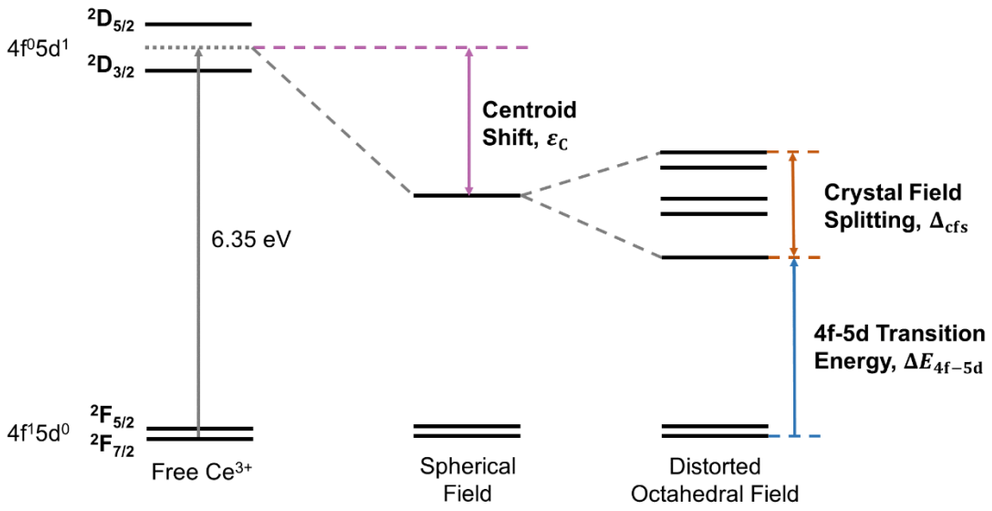
Y. Ai, Z.-W. Li, H. Jiang, *Phys. Rev. Lett.* 135, 026502 (2025) .

Application: 4f-5d transitions in Ce complexes

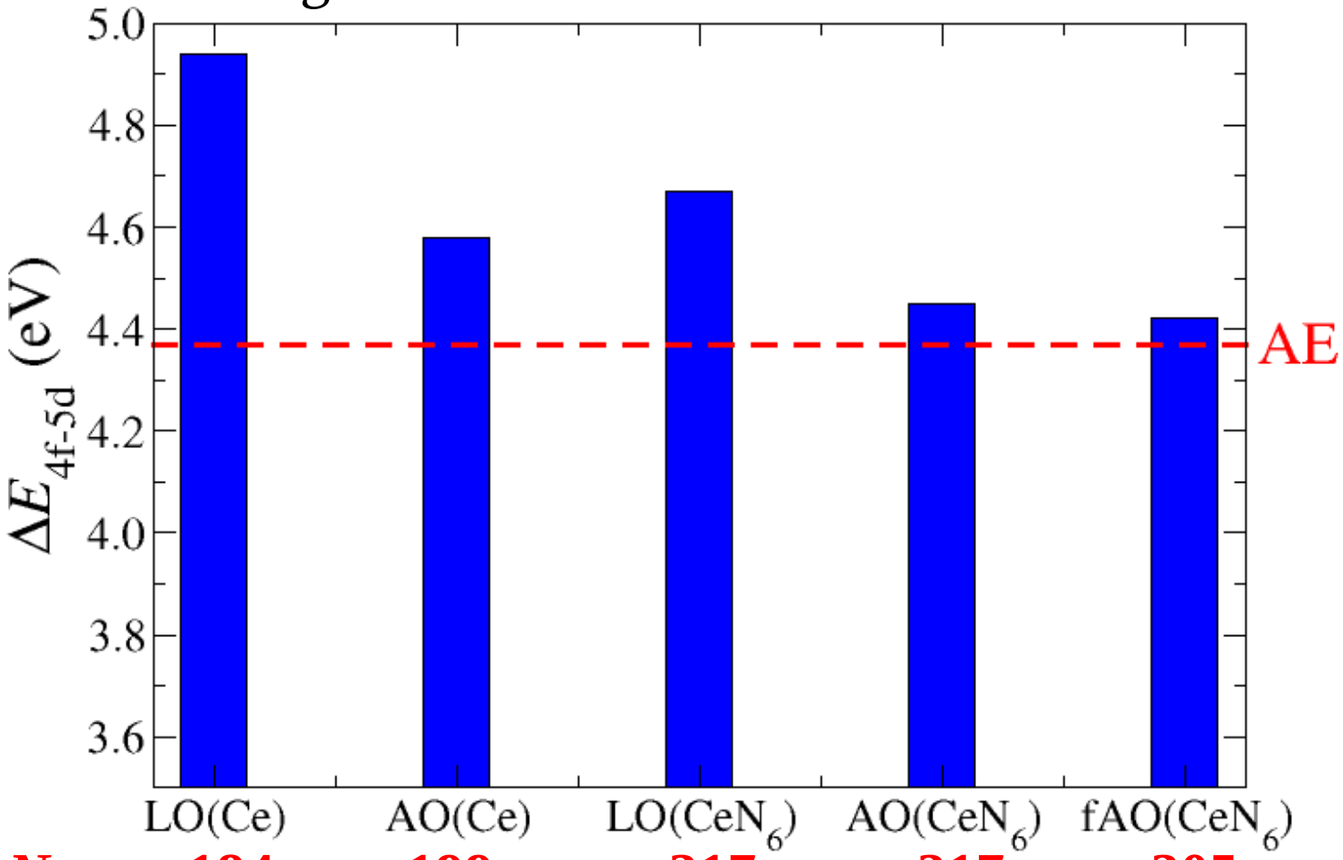
Ce-Bp



R. Guo et al. Inorg. Chem., **61**, 35, 14164 (2022).



High level solver: **CASSCF-SISO**



N_{ECO}= **184** **199** **317** **317** **305**

DMET methods

N_{ECO}: **number of embedded cluster orbitals**

Y. Ai, Z.-W. Li, H. Jiang, *Phys. Rev. Lett.* 135, 026502 (2025) .

State-averaged (SA)-DMET: SA-CASSCF/CAHF as low level solver

State-averaged CASSCF

$$E_{\mathrm{SA}} = \min_{\{C_{In}\},\{\psi_p\}} \sum_n^{N_s} w_n \langle \Psi_n | \hat{H} | \Psi_n \rangle$$

all states, equally averaged

$$|\Psi_n\rangle = \sum_I C_{In} |\Phi_I\rangle \equiv \sum_I C_{In} |\psi_{I_1} \ldots \psi_{I_N}\rangle$$

$$\overline{D}^{\mathcal{E}}_{\mu\nu} = \sum_I w_I \langle \Psi_I | \sum_\sigma c^\dagger_{\nu\sigma} c_{\mu\sigma} | \Psi_I \rangle, \quad (\mu, \nu \in \mathcal{E})$$

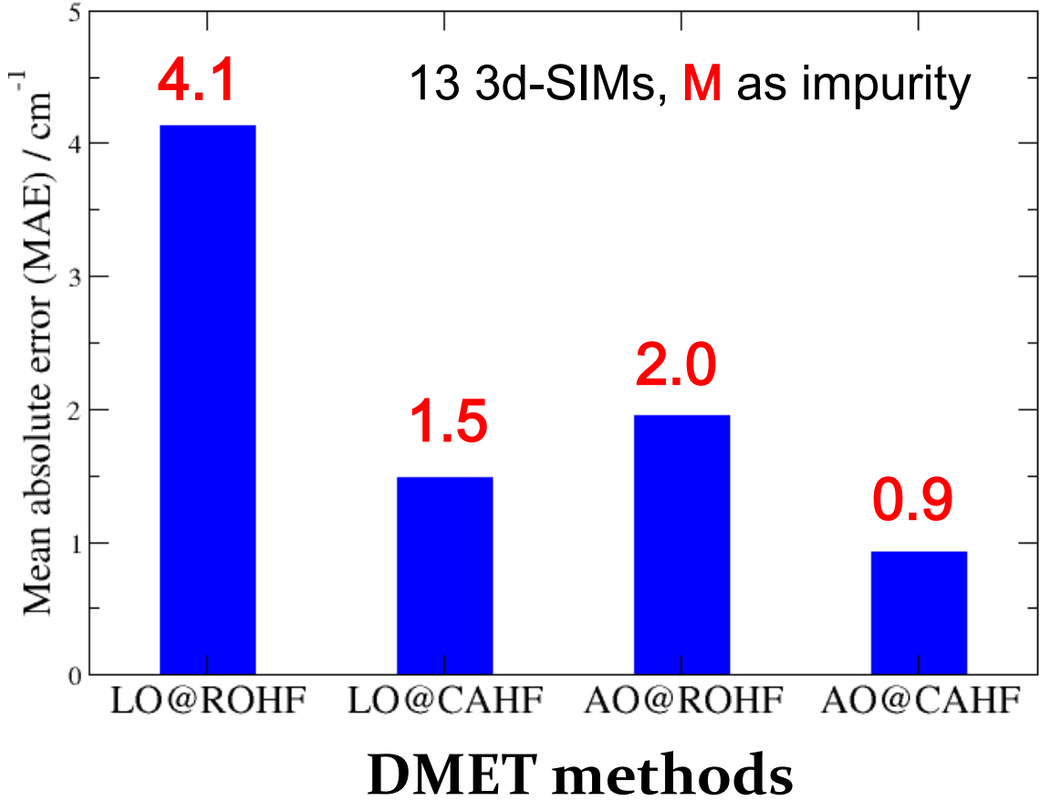
$$\bar{\mathbf{D}}^{(\mathrm{B})} \mathbf{c}^k = \zeta_k \mathbf{c}^k$$

bath orbitals : $\varepsilon_{\mathrm{bath}} < \zeta_k < 2\text{-}\varepsilon_{\mathrm{bath}}$

core orbitals: $\zeta_k > 2 - \varepsilon_{\mathrm{bath}}$

Configuration averaged HF (CAHF)

$$E^{\mathrm{CAHF}} = 2\sum_k h_k + \sum_{kl}(2J_{kl} - K_{kl})$$
$$+ f\left[2\sum_m h_m + f\sum_{mn}(2aJ_{mn} - bK_{mn}) + 2\sum_{km}(2J_{km} - K_{km})\right]$$

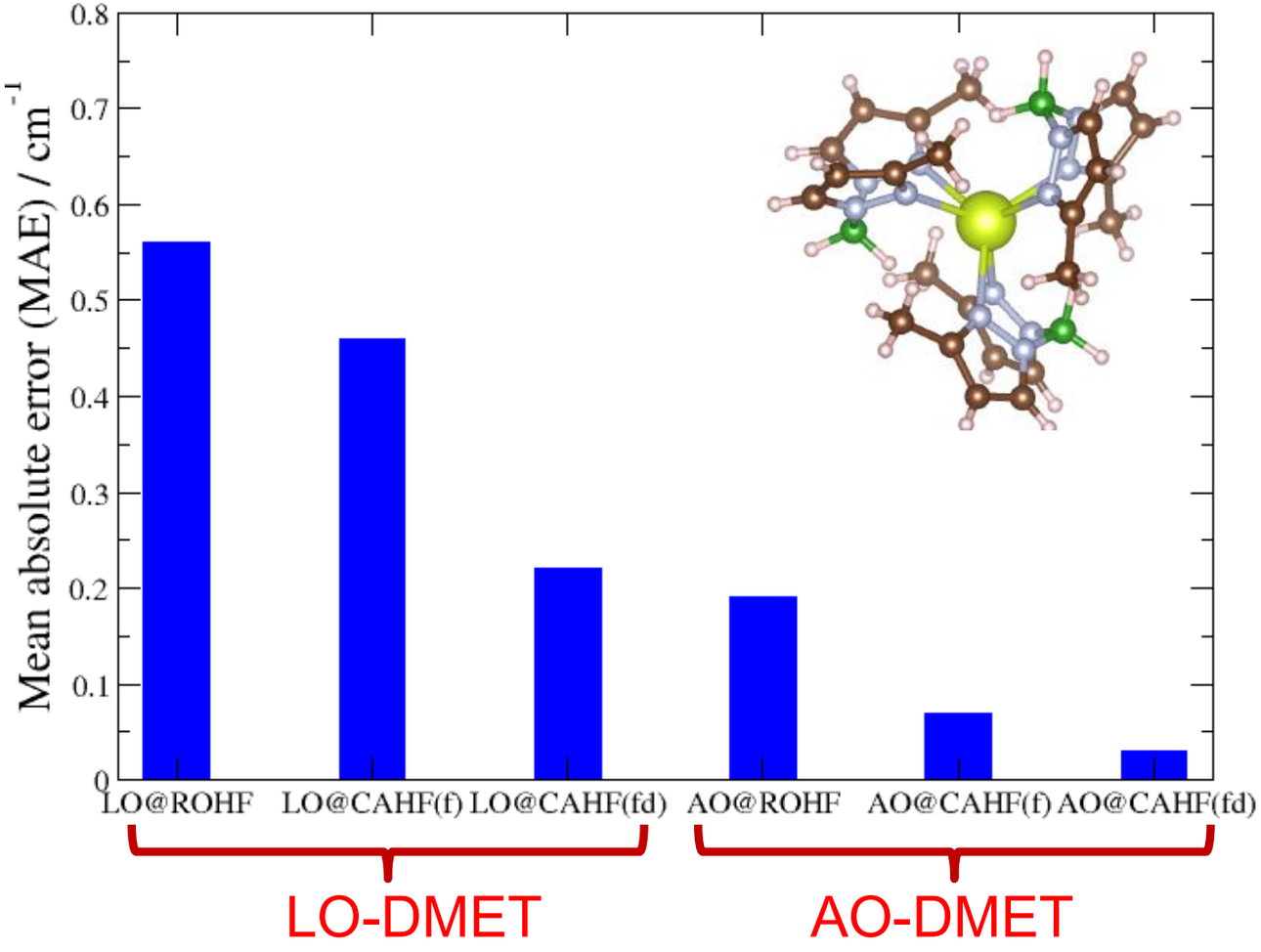


Z.-B. Guan and H. Jiang, *J. Chem. Theory Comput.* **22**, 9483 (2026).

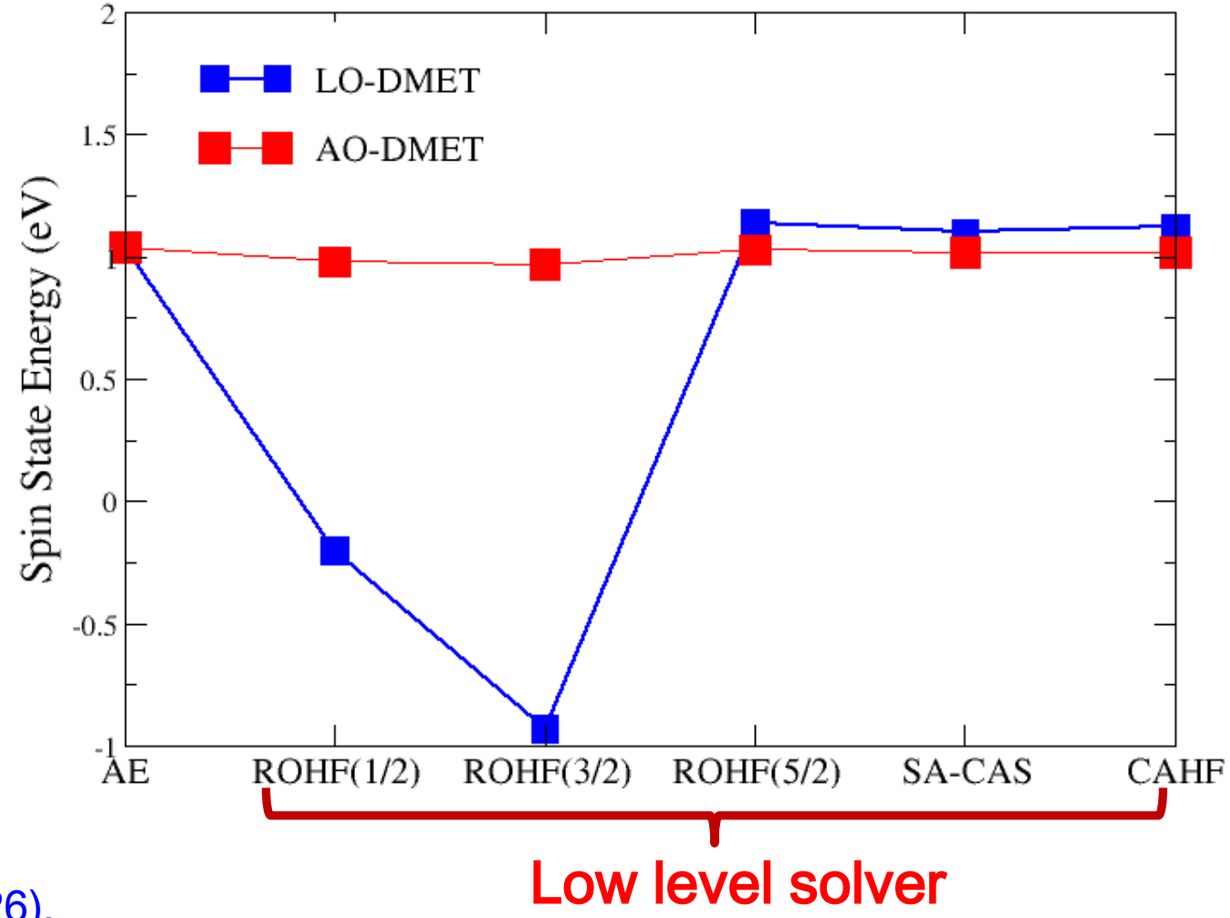
State-averaged (SA)-DMET: SA-CASSCF/CAHF as low level solver

4f-5d excitation energies in Ce-Bp

SA-CASSCF(1e, 120)-NEVPT2+SO, impurity: CeN_6



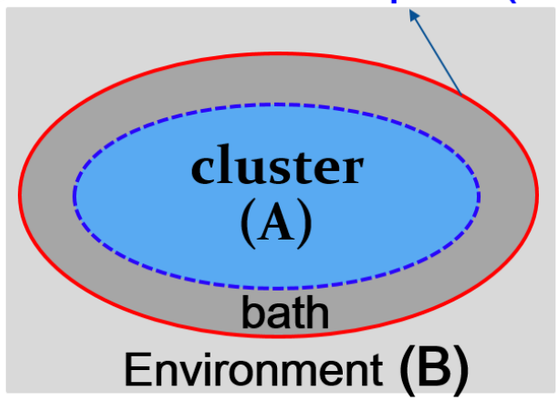
$Fe^{III}L_2OH$: Spin state energy difference (S=3/2 w.r.t. 5/2): SA-CASSCF(9e,7o)+NEVPT2 (State-averaging: 1 doublet+1 quartet+1 sextet; impurity: Fe



Z.-B. Guan and H. Jiang, *J. Chem. Theory Comput.* **22**, 9483 (2026).

Impurity preserved (IP) LO-DMET

Embedded cluster space ($\mathcal{A}$)

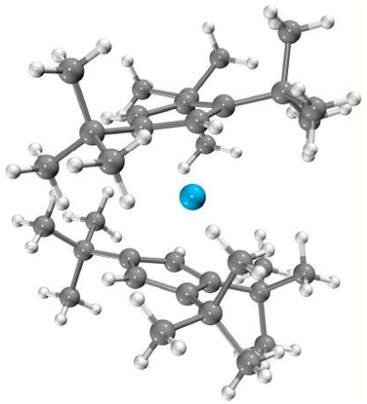


$$\{\phi_\alpha^A\} = \mathrm{orth}\left(\{\phi_{\alpha'}'^A\}\right)$$

$$\{|\phi_\beta^B\rangle\} = \mathrm{orth}\left(\{\hat{Q}_A\,|\phi_{\beta'}'^B\rangle\}\right)$$

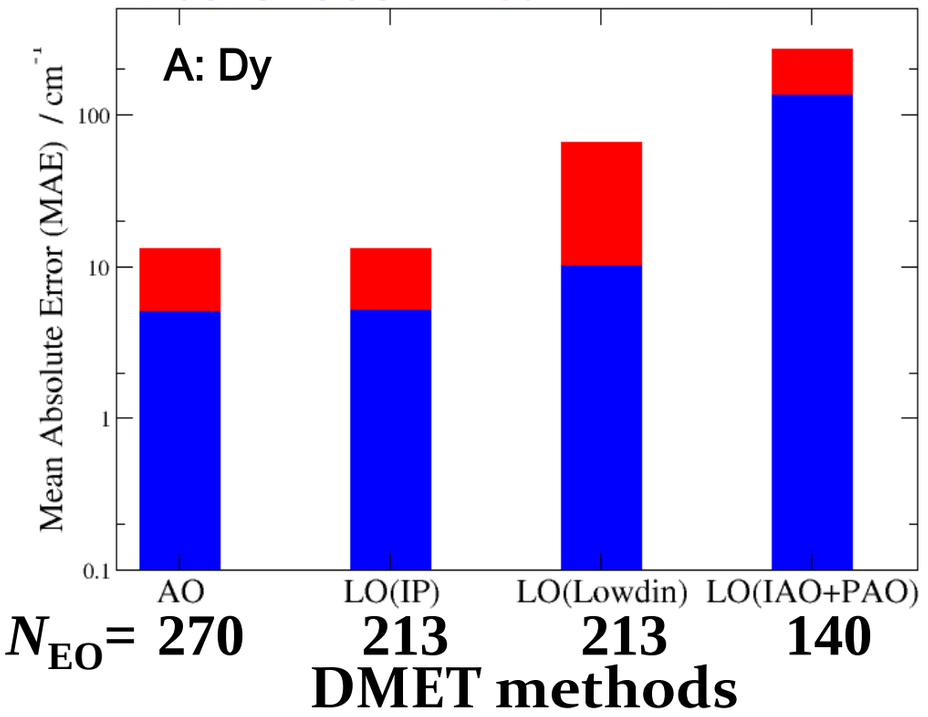
$$\hat{Q}_A = \hat{I} - \sum_\alpha |\phi_\alpha^A\rangle\langle\phi_\alpha^A|$$

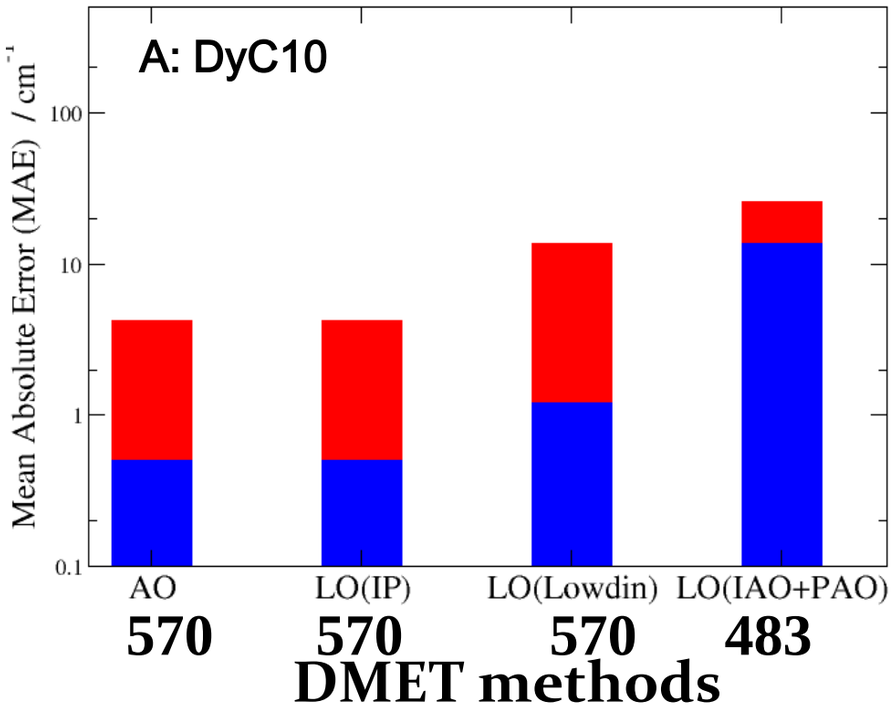
➔ ECO space in LO(IP)-DMET is exactly the subspace of the ECO space in AO-DMET with the same A-B partitioning.



Mean absolute errors (MAE) (in cm^{-1}) w. r. t. all-electron treatment (N_{AO}= 1030)

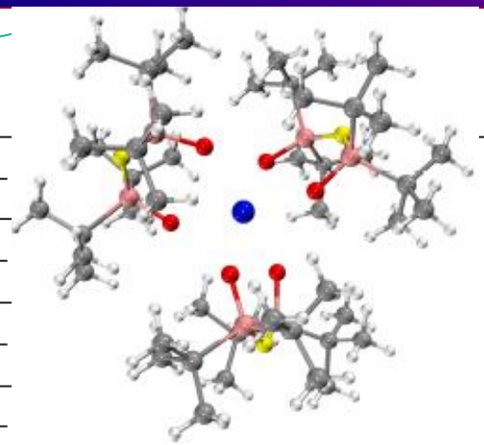
Blue: CASSCF Red: NEVPT2

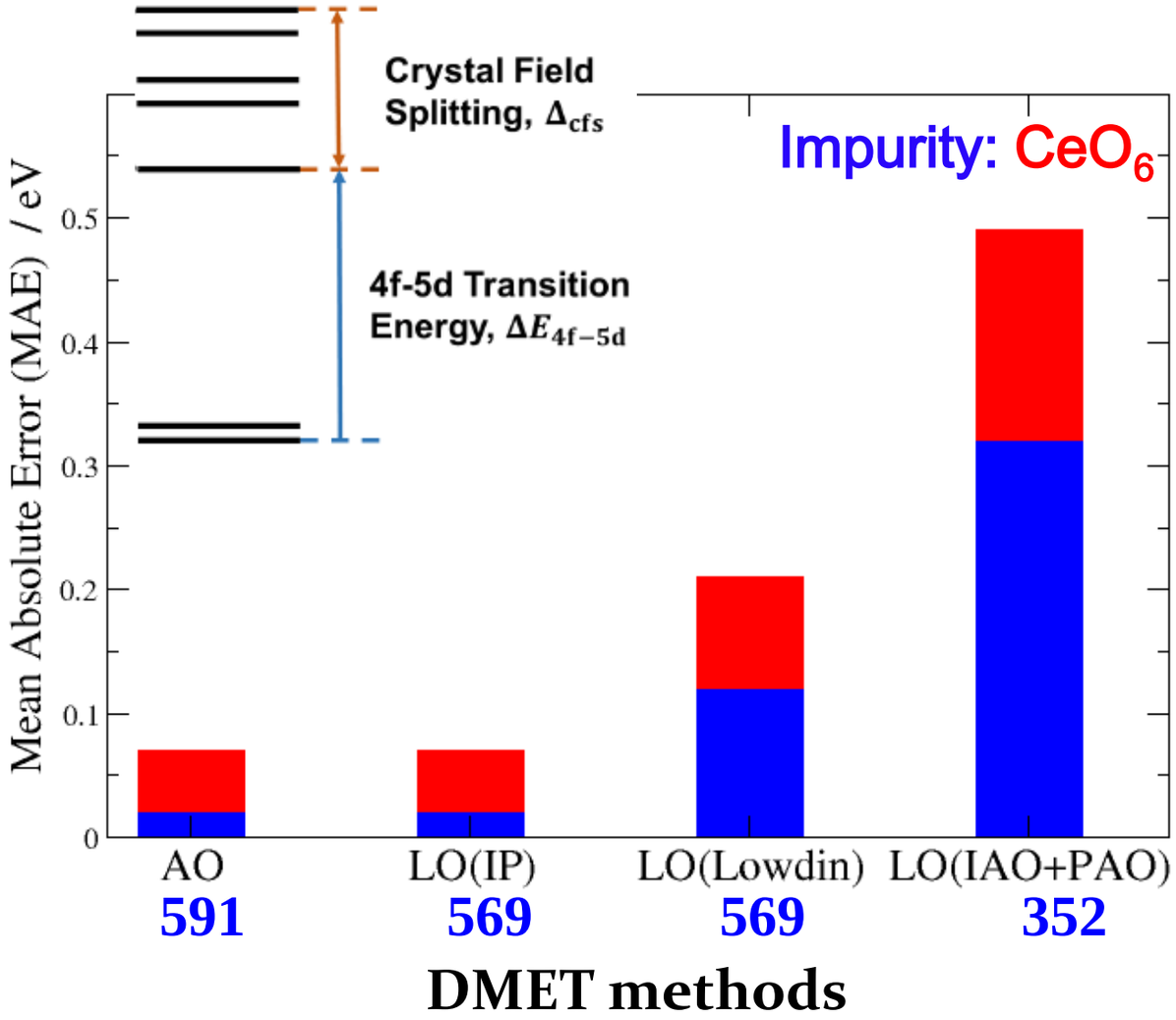




T. Zhang, Z.-W. Li, Z.-B. Guan and H. Jiang, *J. Chem. Theory Comput.* (in press) doi.org/10.1021/acs.jctc.6c01251 .

Impurity preserved (IP) LO-DMET





Mean absolute errors (MAE) (in eV) w. r. t. all-electron (N_{AO}= 878) treatment.

T. Zhang, Z.-W. Li, Z.-B. Guan and H. Jiang, *J. Chem. Theory Comput.* (in press) doi.org/10.1021/acs.jctc.6c01251 .

Conclusions

- **DMET+CASSCF(-PT2)-SISO**: **efficient** and highly **accurate** approach to **magnetic** properties of single-ion magnets, **promising** for lanthanide **luminescent** materials
- **Non-orthogonal decomposition of Slater determinant and AO-DMET**: significantly improved computational **efficiency** and **accuracy**, **new strategy for embedding and fragmentation**.
- **Further significant improvement** in accuracy achieved by using **new LOs + state-averaged low-level solvers** (CASSCF or CAHF).

