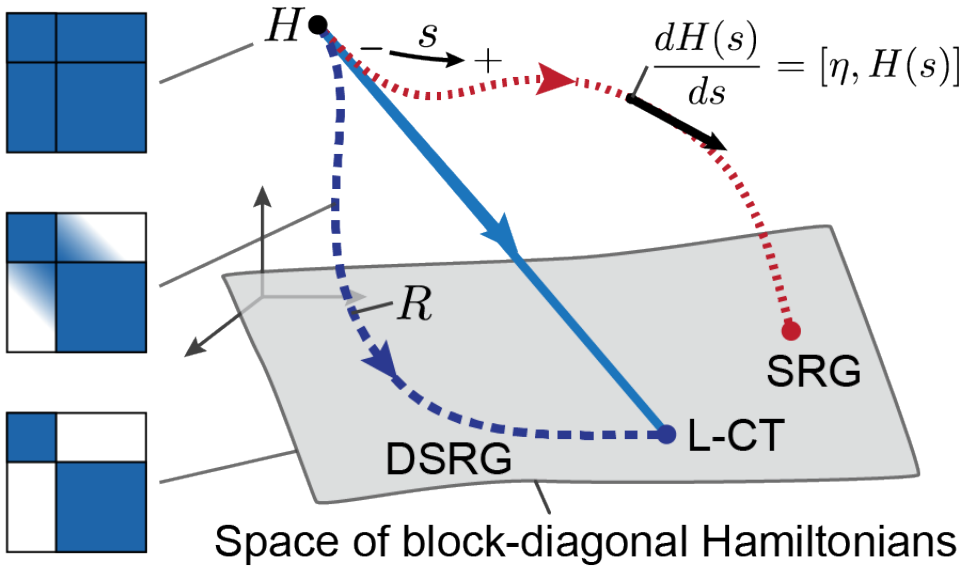
The similarity renormalization group in quantum chemistry



ESNT Workshop, Saclay, France, 2015

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Acknowledgments

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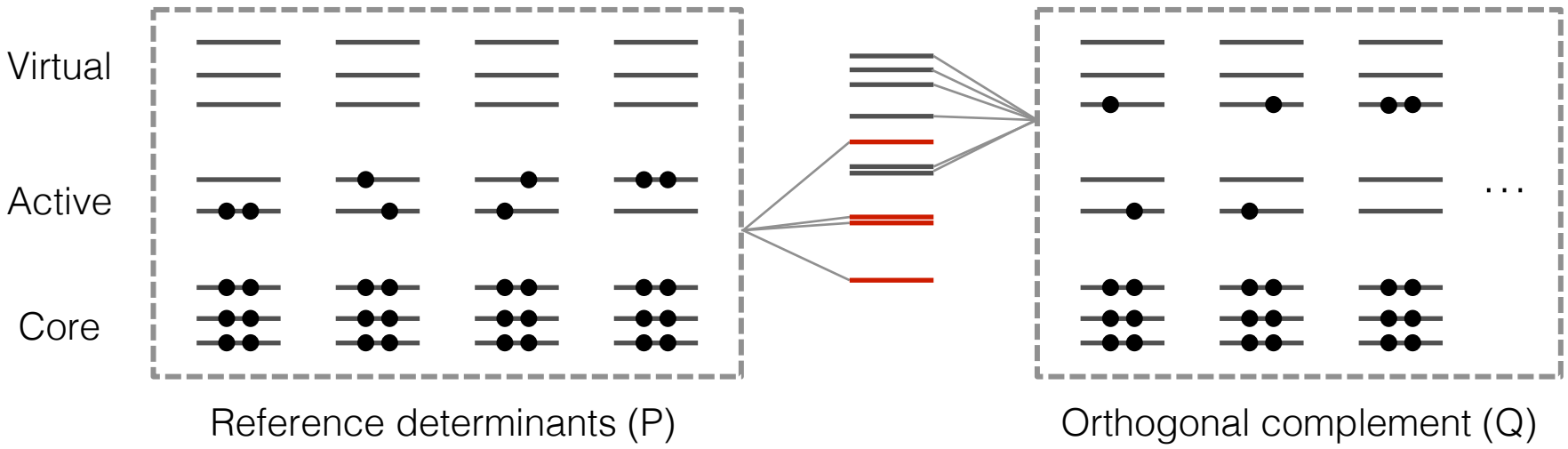
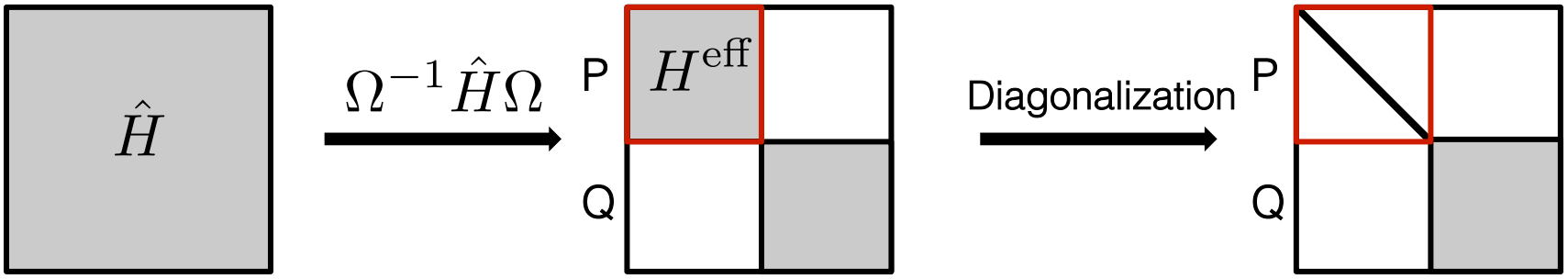
Psi4
OPEN-SOURCE QUANTUM CHEMISTRY

Multireference Effective Hamiltonian Theories





Difficulties with this strategy:

1. Intruder state problem $E_P - E_Q \to 0$
2. Redundancy problem (balance the number of parameters and conditions)

EXAMPLE: THE INTRUDER STATE PROBLEM IN QDPT2

Quasi-degenerate perturbation theory (Brandow, Lindgren, Freed, …)

$$H_{PP'}^{\mathrm{eff},(2)} = \langle \Phi_P | \hat{H} | \Phi_{P'} \rangle + \frac{1}{2} \sum_q \frac{\langle \Phi_P | \hat{V} | \Phi_Q \rangle \langle \Phi_Q | \hat{V} | \Phi_{P'} \rangle}{E_P^{(0)} - E_Q^{(0)}} + \mathrm{H.c.}$$

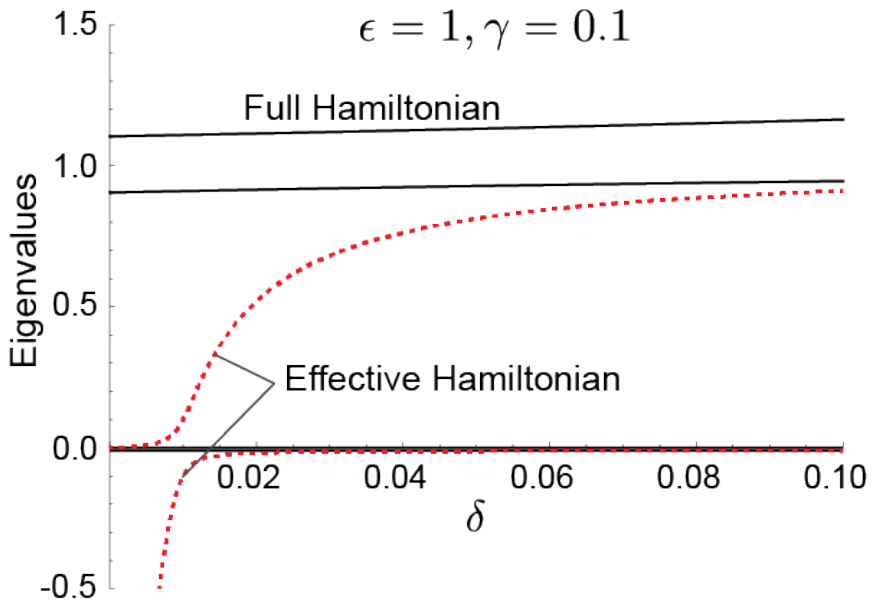
A model for intruder states in QDPT2

$$\mathbf{H} = \left(\begin{array}{cc|c} 0 & \gamma & 0 \\ \gamma & \epsilon & \gamma \\ \hline 0 & \gamma & \epsilon + \delta \end{array}\right)$$

δ

ϵ

$$\mathbf{H}^{\mathrm{eff},(2)} = \begin{pmatrix} 0 & \gamma \\ \gamma & \epsilon - \frac{\gamma^2}{\delta} \end{pmatrix}$$



Example: The intruder state problem in QDPT2

Quasi-degenerate perturbation theory (Brandow, Lindgren, Freed, …)

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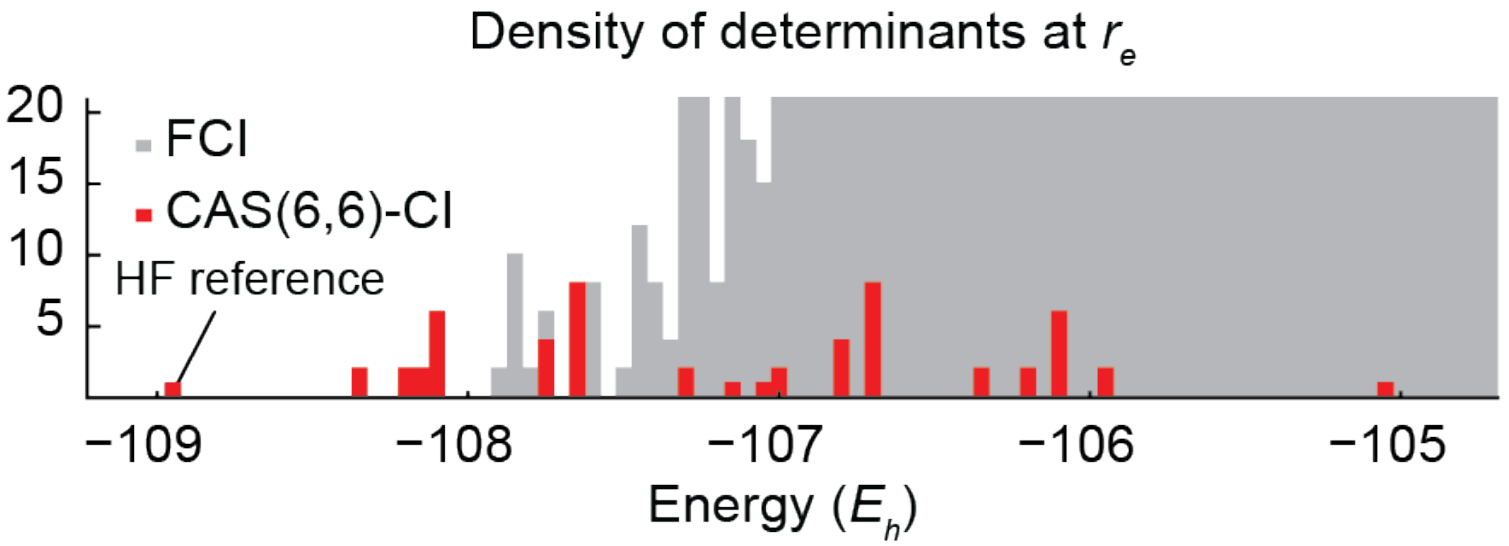
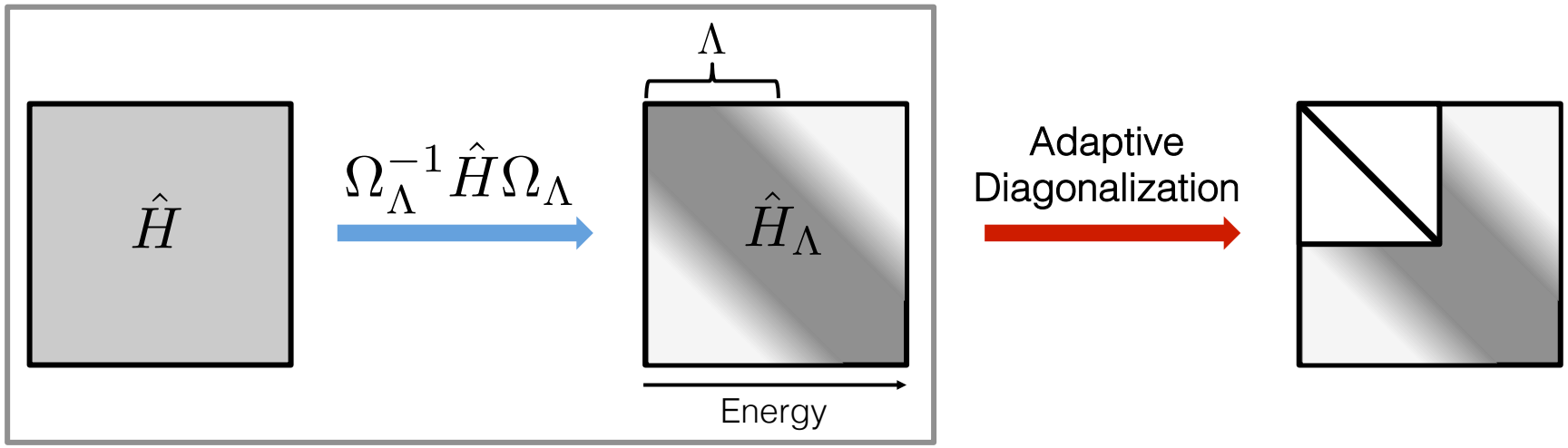


An Adaptive Strategy to Multireference Problems

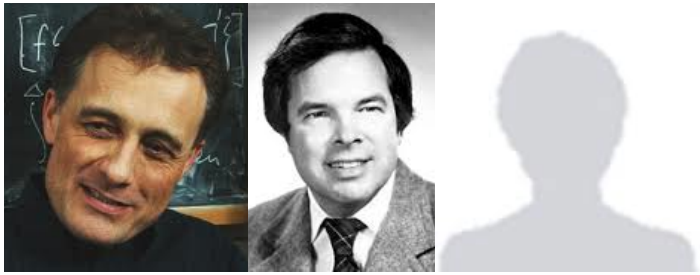


We are developing:

(1) **Renormalization Group (RG) approaches** for dynamical electron correlation.

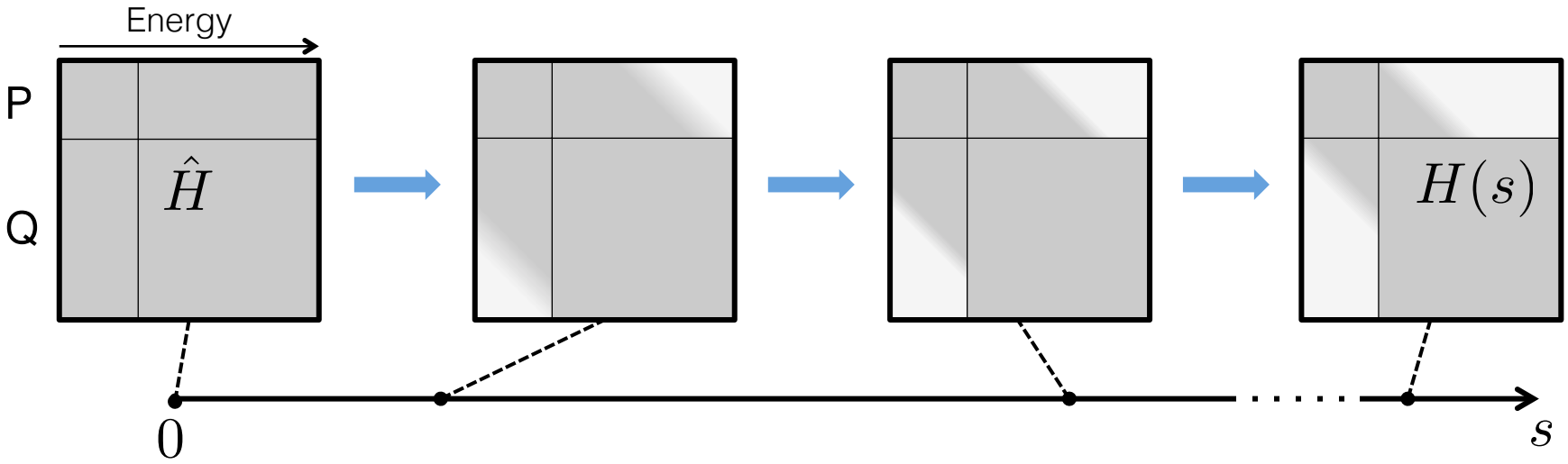
(2) **Adaptive diagonalization methods** to address strong electron correlation (ground and excited states).

THE SIMILARITY RENORMALIZATION GROUP (OR FLOW RG)



Stanisław Głazek, Kenneth Wilson, Franz Wegner

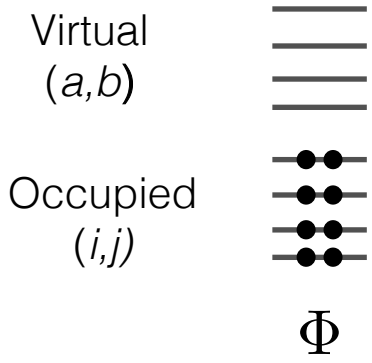
The basic idea behind the SRG approach:



Glazek, S. D.; Wilson, K. G. *Phys. Rev. D* (1994). Wegner, F. *Ann. Phys.* (1994), White, S. R. *J. Chem. Phys.* (2002).

THE SIMILARITY RENORMALIZATION GROUP FORMALISM

The bare Hamiltonian



$$H = E_0 + \sum_p \epsilon_p \{\hat{a}^p_q\} + \frac{1}{4}\sum_{pqrs} \langle pq||rs\rangle \{\hat{a}^{pq}_{rs}\}$$

Normal ordered[1] with respect to Φ

Unitary flow of the Hamiltonian

$$H(s) = U(s)HU^\dagger(s) \quad U(0) = 1$$

← *s* is a time-like parameter

The flow equation for the Hamiltonian

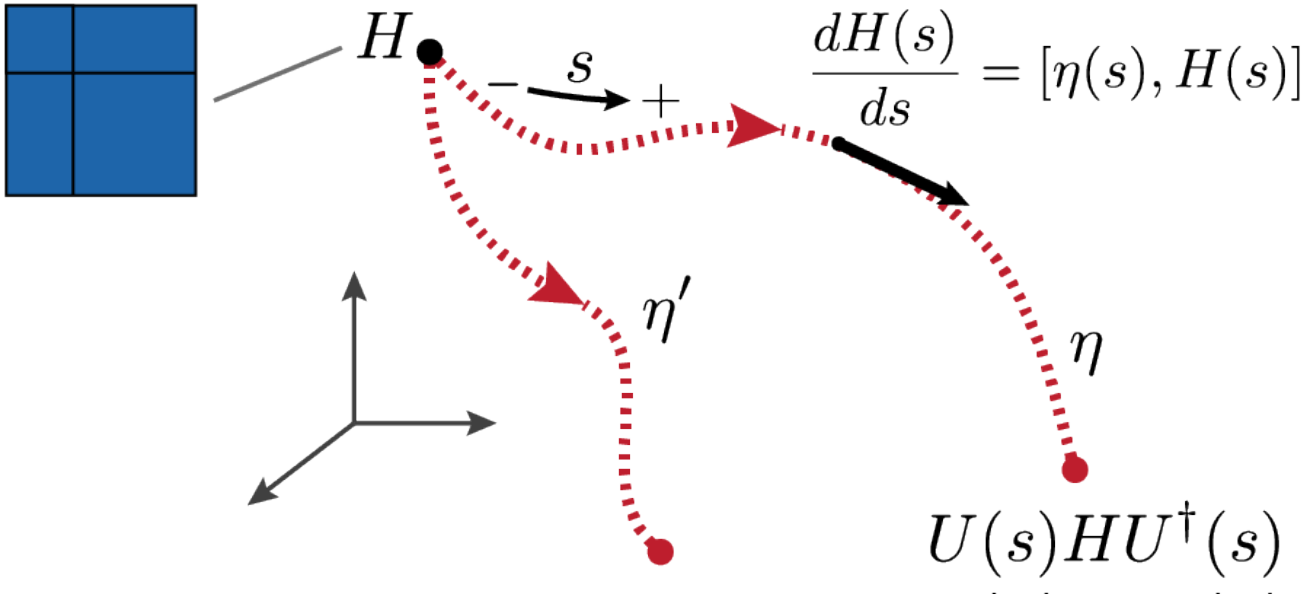
$$\frac{dH(s)}{ds} = [\eta(s), H(s)] \qquad \eta(s) = \frac{dU(s)}{ds}U(s)^\dagger = -\eta^\dagger(s)$$

The derivative of the Hamiltonian depends on the *flow generator η*(*s*)

1) Tsukiyama, K.; Bogner, S. K.; Schwenk, A. *Phys. Rev. C* (2012)

THE SRG FORMALISM

The SRG recipe: define a generator and *integrate* the RG flow equation



The transformed Hamiltonian

$$H(s) = E_0(s) + F(s) + V(s) + W(s) + \ldots$$

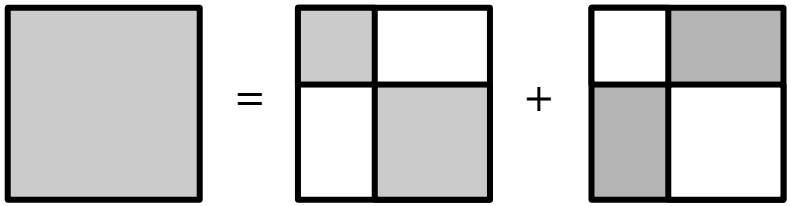
$$= E_0(s) + \sum_{pq} f_p^q(s)\{\hat{a}_q^p\} + \frac{1}{4}\sum_{pqrs} v_{pq}^{rs}(s)\{\hat{a}_{rs}^{pq}\} + \ldots$$

The SRG(2) keeps only these terms

CHOOSING THE GENERATOR $\eta(s)$

A certain class of flow generators brings the Hamiltonian to a band-diagonal form

$$H(s) = H^{\mathrm{d}}(s) + H^{\mathrm{od}}(s)$$



$$\eta(s) = [H^{\mathrm{d}}(s), H(s)] \quad \Rightarrow \quad \frac{d||H^{\mathrm{od}}(s)||_F^2}{ds} = -||\eta(s)||_F^2 \leq 0$$

Example: the *canonical generator of Wegner*

$$H^{\mathrm{od}}(s) = \sum_{ia} f_a^i(s)\{\hat{a}_i^a\} + \frac{1}{4}\sum_{ijab} v_{ab}^{ij}(s)\{\hat{a}_{ij}^{ab}\} + \mathrm{H.c.}$$

decouples a Slater determinant from the S + D space

$$\lim_{s\to\infty} v_{ab}^{ij}(s) = 0 \quad \Rightarrow \quad \lim_{s\to\infty} \left\langle \Phi_{ij}^{ab} \right| H(s) \left| \Phi \right\rangle = 0$$

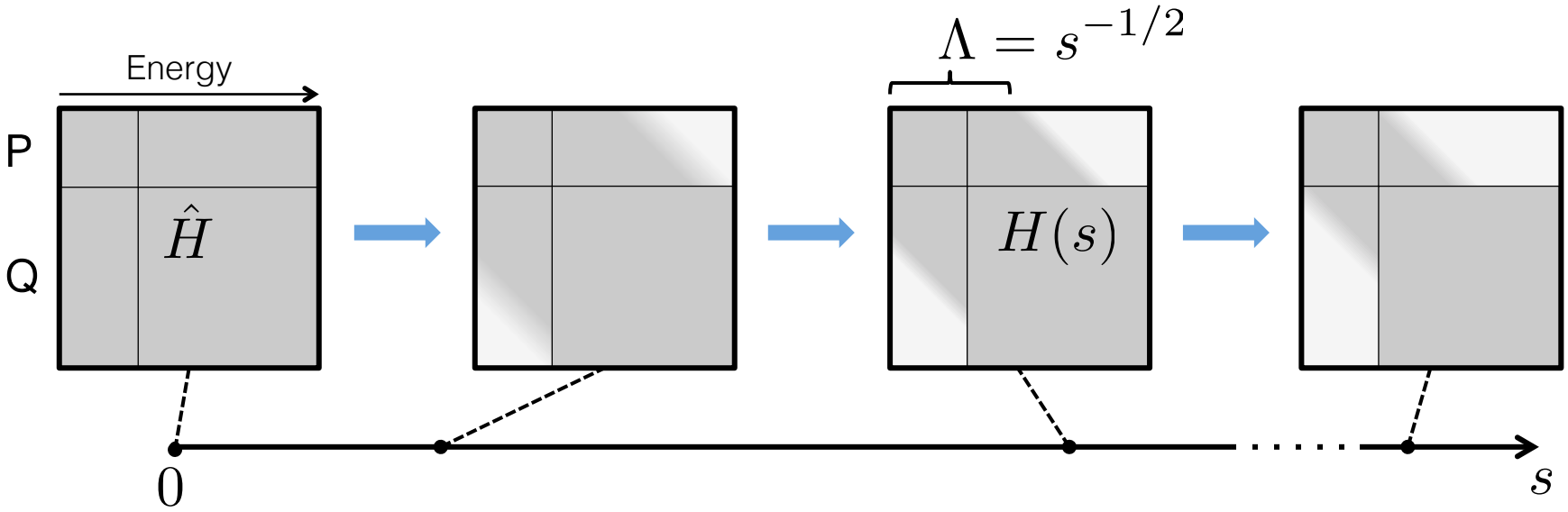
PERTURBATIVE ANALYSIS

How does the SRG avoid problems with small denominators?

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

Møller-Plessett denominator corresponding to Φ_{ij}^{ab}

$$|\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b| \gg s^{-1/2} \quad \Rightarrow \quad v_{ij}^{ab,(1)}(s) \approx 0$$

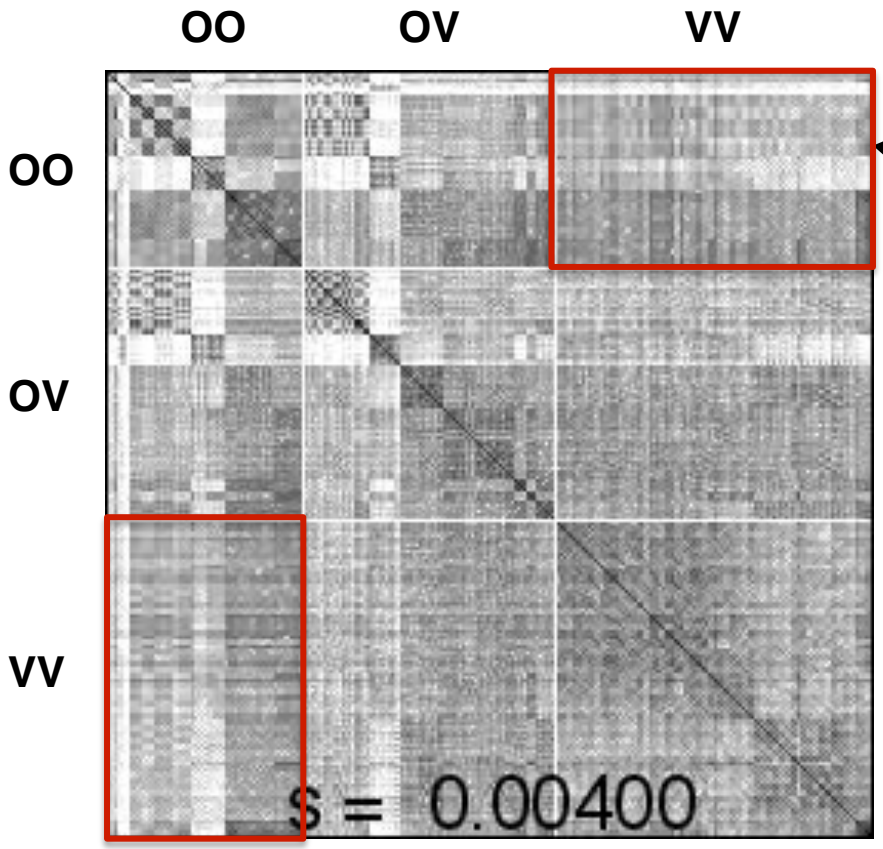


EXAMPLE: FLOW OF THE HAMILTONIAN

$$V(s) = \frac{1}{4} \sum_{pqrs} v_{pq}^{rs}(s) \{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\}$$

Sorted according to the value of

$$\epsilon_p + \epsilon_q$$



Off-diagonal part of the Hamiltonian

GOING BEYOND THE SRG: MOTIVATIONS

Eric Jurgenson's Ph.D. Thesis

> One difference between these procedures is that $V_{\mathrm{low}\,k}$ can be formulated as an integral transformation[13] while the SRG is currently only differential; here $V_{\mathrm{low}\,k}$ is implemented as a single transformation on the initial matrix, while the SRG flows to the desired amount of transformation. An integrated form of the SRG would be useful in understanding the exact correspondence between the two procedures, and to what extent $V_{\mathrm{low}\,k}$ is a subset of these block-diagonal SRG forms.

Limitations of the SRG:

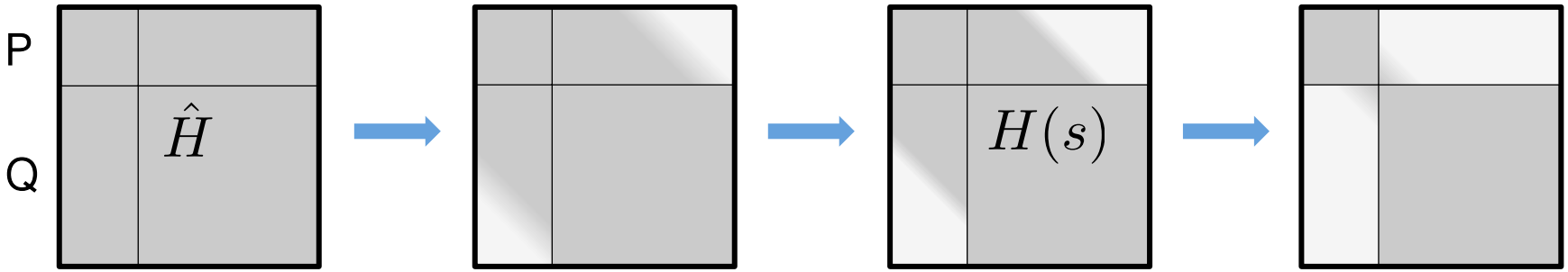
1. Requires solving a set of ODEs
2. Appears to work only with a unitary transformation

The proof of the trace condition relies on the unitarity of the transformation

$$\frac{d||H^{\mathrm{od}}(s)||_F^2}{ds} \leq 0$$

GOING BEYOND THE SRG: THE DRIVEN SRG[1]

The basic idea of the DSRG



Let the flow of $H(s)$ be defined by the (parameterized) evolution of its off-diagonal block. That is, given $R(s)$

$$\text{find } U(s) : [U(s)HU^{\dagger}(s)]^{\text{od}} = R(s)$$

1) Evangelista, F.A., *J. Chem. Phys.* (2014)

GOING BEYOND THE SRG: THE DRIVEN SRG

The DSRG ansatz and flow

$$\bar{H}(s) = e^{-S(s)} H e^{S(s)} \qquad [\bar{H}(s)]_{\mathrm{N}} = R(s)$$

Unitary or intermediate normalization (CC):

$$S(s) = \begin{cases} T(s) \\ A(s) = T(s) - T^{\dagger}(s) \end{cases}$$

The DSRG flow is driven by the *source* operator *R*(*s*)

N: *non-diagonal diagrams*

Boundary conditions on the source operator: $[\bar{H}(s)]_{\mathrm{N}} = R(s)$

$$[\bar{H}(0)]_{\mathrm{N}} = R(0) = H_{\mathrm{N}} \qquad [\bar{H}(\infty)]_{\mathrm{N}} = 0 \quad \text{if } \Delta \neq 0$$

The DSRG source operator used in this work (reproduces SRG-MBPT2 results)

$$r^{ij}_{ab}(s) = \left[\bar{H}^{ij}_{ab}(s) + t^{ij}_{ab}(s)\Delta^{ij}_{ab}\right] e^{-s(\Delta^{ij}_{ab})^2}$$

1) Yanai, T.; Chan, G. K.-L., *J. Chem. Phys.* (2006)

THE SINGLE-REFERENCE UNITARY DSRG(2)

The *unitary* DSRG(2) truncation scheme is defined by the following

$$S(s) \approx T_1(s) - T_1^\dagger(s) + T_2(s) - T_2^\dagger(s)$$

And the BCH expansion is truncated to one- and two-particle contributions[1]

$$\bar{H}_{1,2} = H + \sum_{k=1}^{\infty} \frac{1}{k!} \underbrace{[\cdots[[H,S]_{1,2},S]_{1,2},\cdots]_{1,2}}_{k\text{-fold commutator}}$$

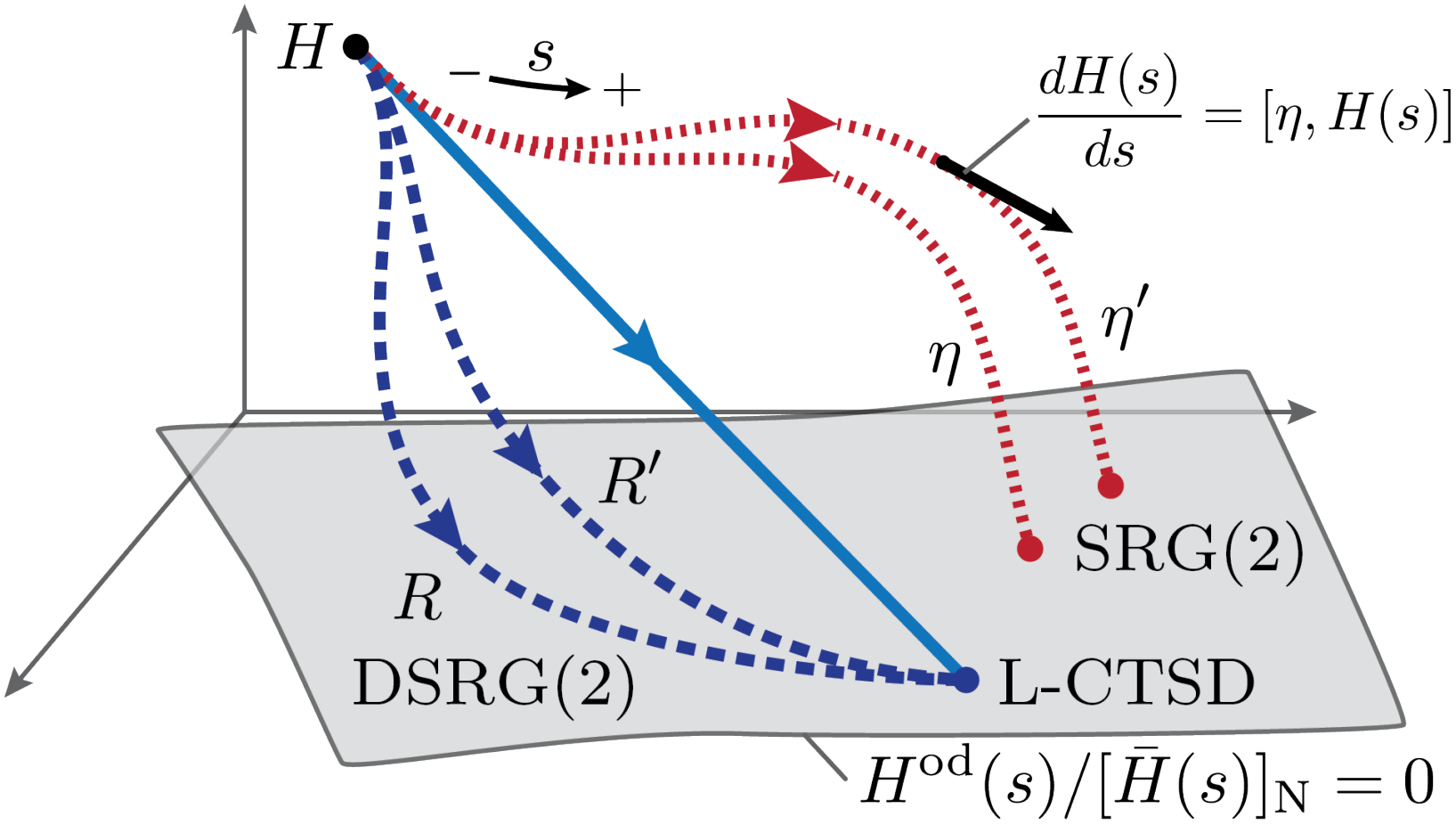
The DSRG conditions yields a set of *polynomial equations*

$$t_a^{i,\mathrm{new}}(s) = \left[\bar{H}_a^{i,\mathrm{old}}(s) + t_a^{i,\mathrm{old}}(s)\Delta_a^i\right] \frac{1 - e^{-s(\Delta_a^i)^2}}{\Delta_a^i},$$

$$t_{ab}^{ij,\mathrm{new}}(s) = \left[\bar{H}_{ab}^{ij,\mathrm{old}}(s) + t_{ab}^{ij,\mathrm{old}}(s)\Delta_{ab}^{ij}\right] \frac{1 - e^{-s(\Delta_{ab}^{ij})^2}}{\Delta_{ab}^{ij}},$$

1) Yanai, T.; Chan, G. K.-L., *J. Chem. Phys.* (2006)

Comparison with other methods



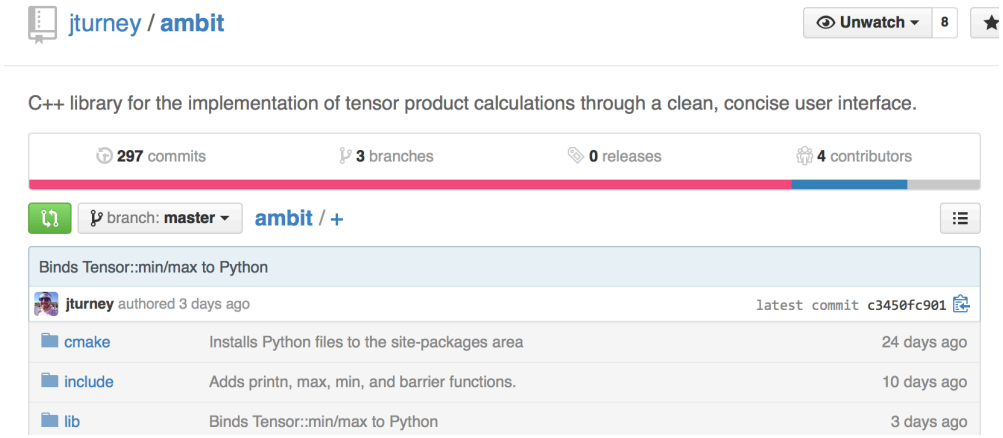
IMPLEMENTATION

Implementation based on an open-source tensor library[1]

$$[A_2, B_2]_p^q \leftarrow \frac{1}{2}\sum_{iab} A_{ip}^{ab} B_{ab}^{iq} - \frac{1}{2}\sum_{ija} A_{ij}^{aq} B_{ap}^{ij}$$

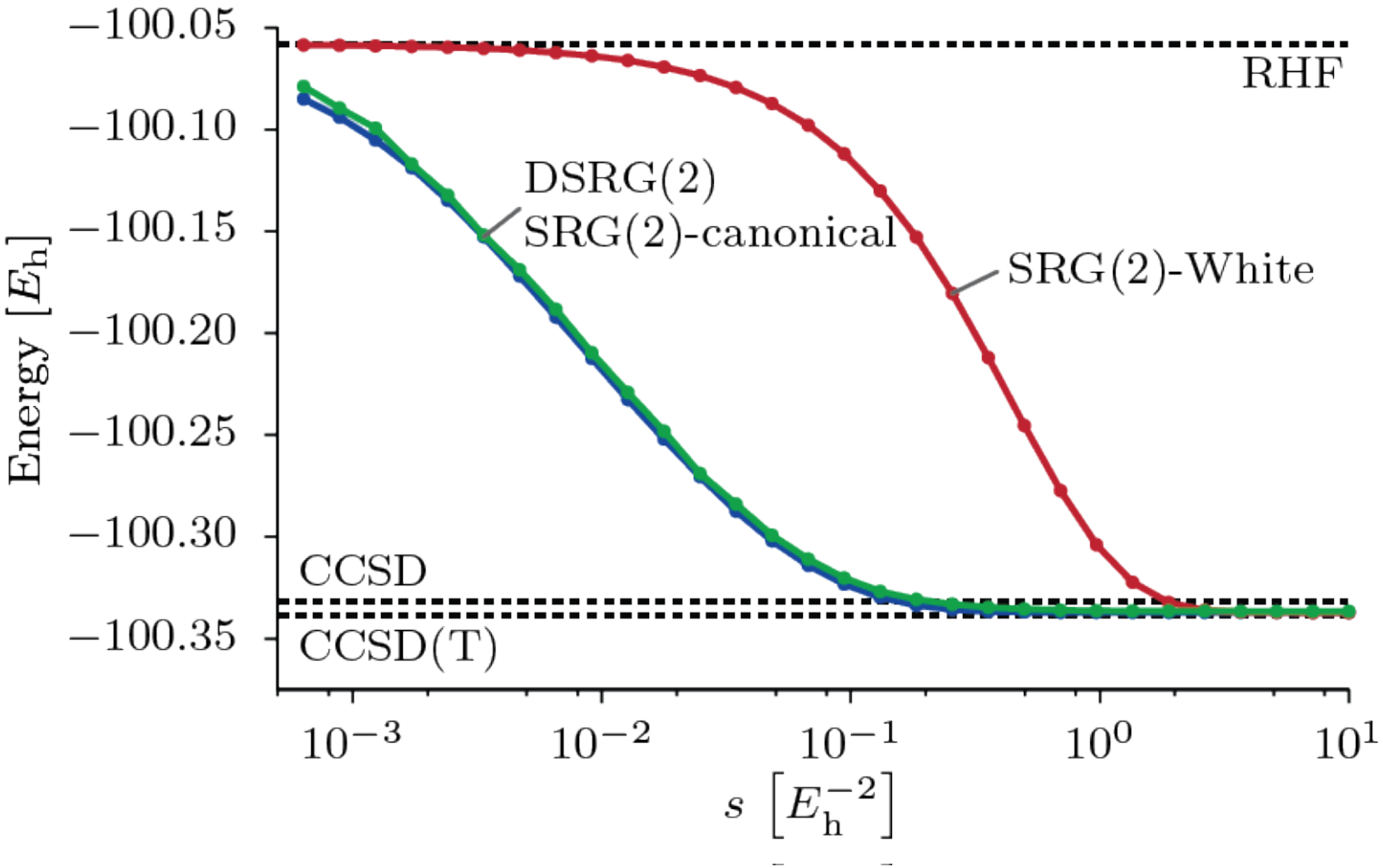
```
void TensorSRG::commutator_A2_B2_C1(BlockedTensor& A,BlockedTensor& B,BlockedTensor& C)
{
    C["qp"] += +0.5 * A["abip"] * B["iqab"];
    C["qp"] += +1.0 * A["aBpI"] * B["qIaB"];

    C["qp"] += -0.5 * A["aqij"] * B["ijap"];
    C["qp"] += -1.0 * A["qAiJ"] * B["iJpA"];

    C["QP"] += +0.5 * A["ABIP"] * B["IQAB"];
    C["QP"] += +1.0 * A["aBiP"] * B["iQaB"];

    C["QP"] += -0.5 * A["AQIJ"] * B["IJAP"];
    C["QP"] += -1.0 * A["aQiJ"] * B["iJaP"];
}
```

Users and developers are welcome!
See https://github.com/jturney/ambit

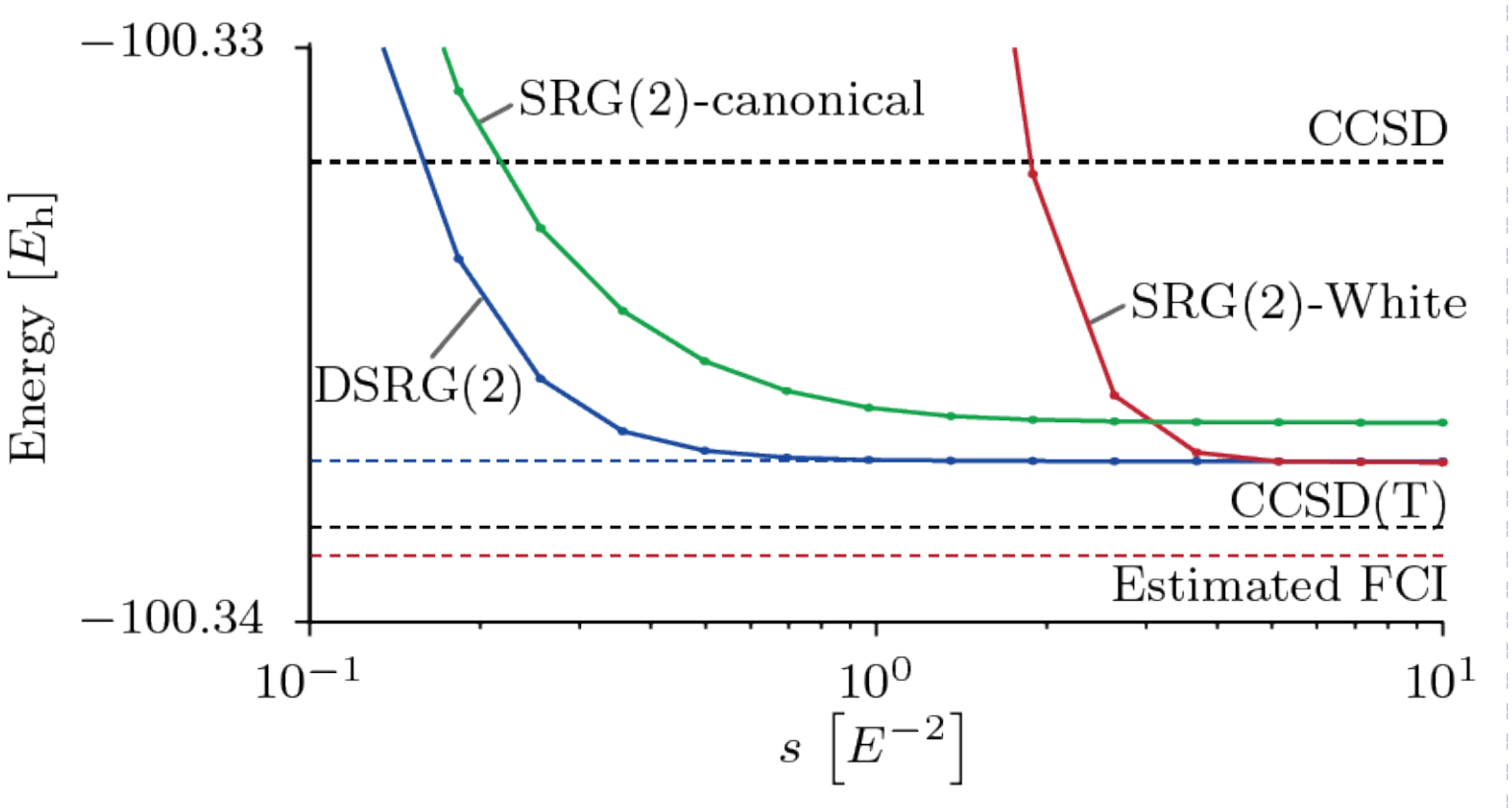


1) Turney, J.; Parrish, R.; Evangelista, F. A., *Ambit*

Comparison of the SRG and DSRG energy flow

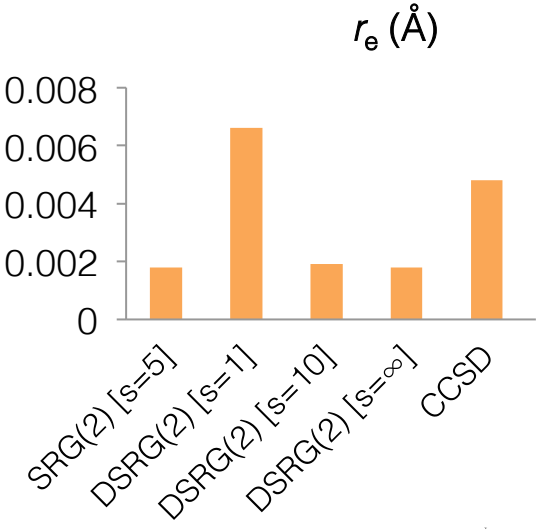


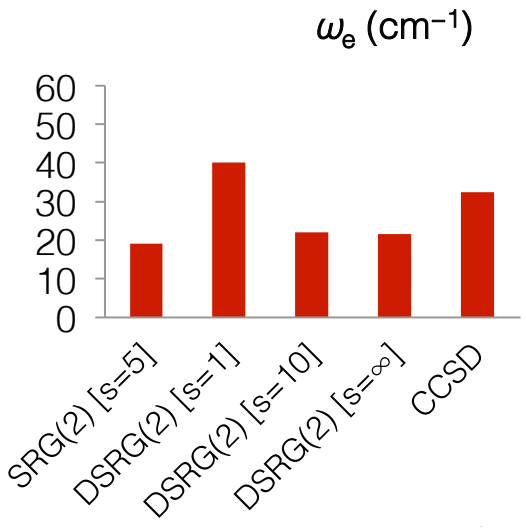
Comparison of the SRG and DSRG energy flow

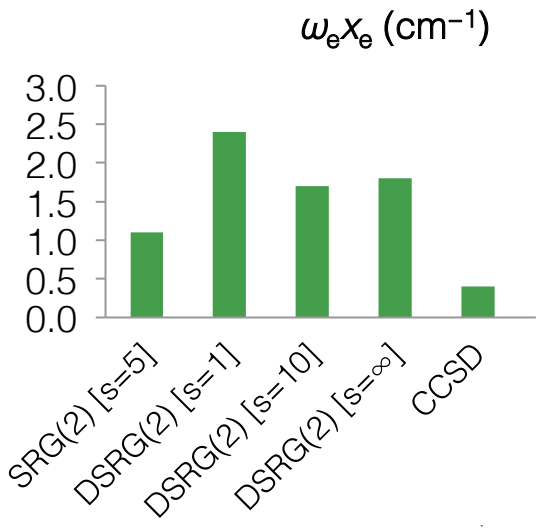


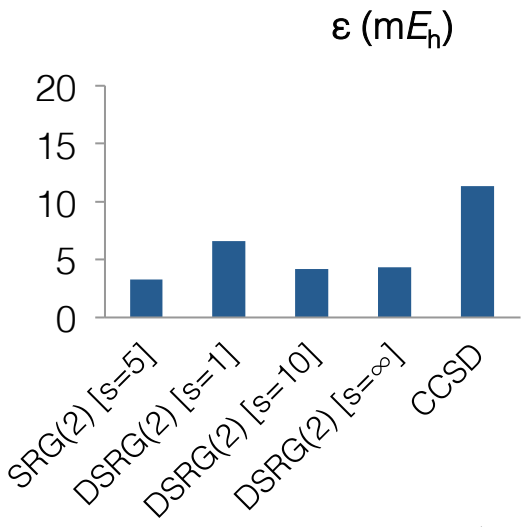
STATISTICS FOR ELEVEN DIATOMIC MOLECULES

Absolute Mean Deviations from CCSD(T) results







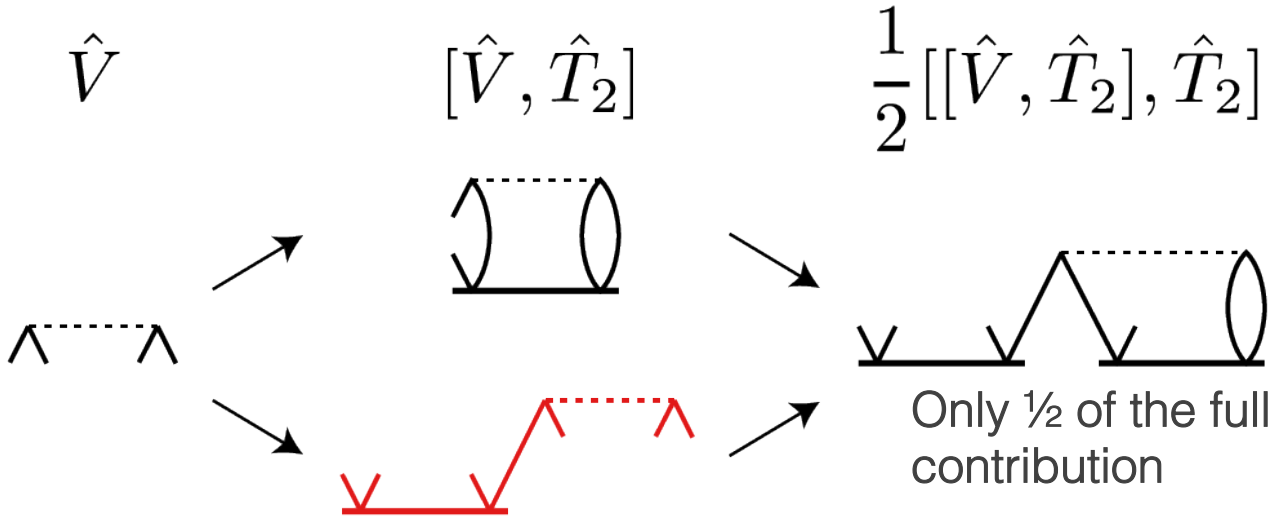


A MODIFIED BCH EXPANSION

The approximate BCH expansion contains incorrect prefactors.

$$\bar{H}_{1,2} = H + \sum_{k=1}^{\infty} \frac{1}{k!} \underbrace{[\cdots[[H,S]_{1,2},S]_{1,2},\cdots]_{1,2}}_{k\text{-fold commutator}}$$

In CCSD:

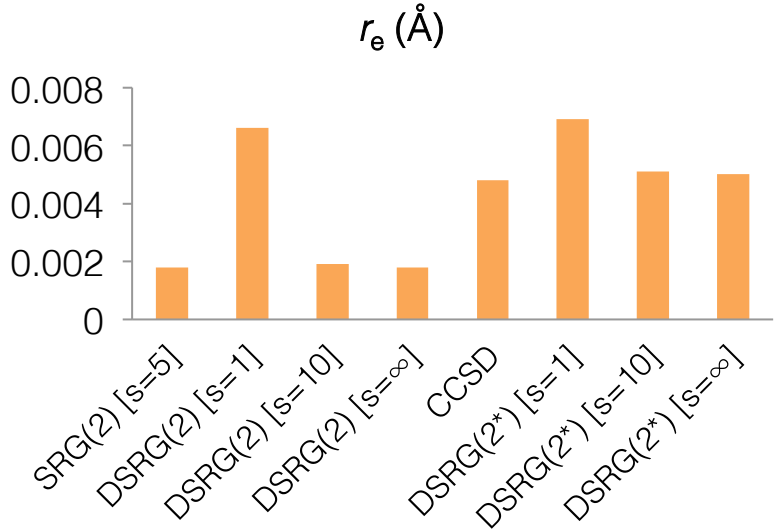


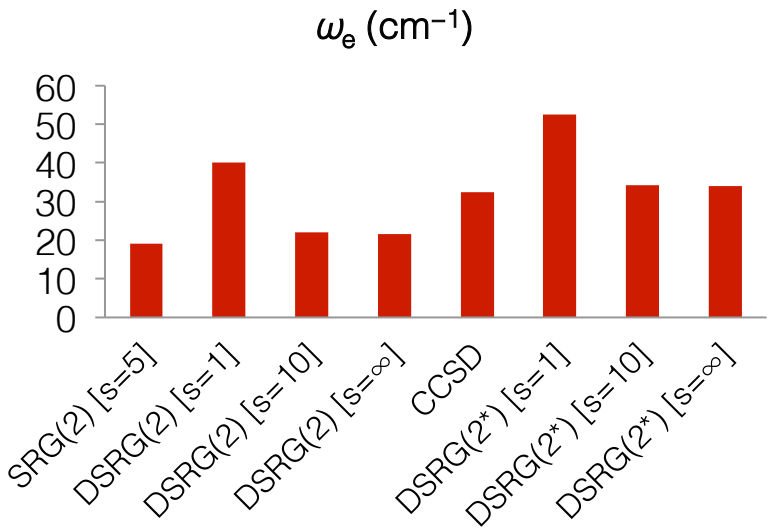
Observation: the following modification fixes leading order (3rd)

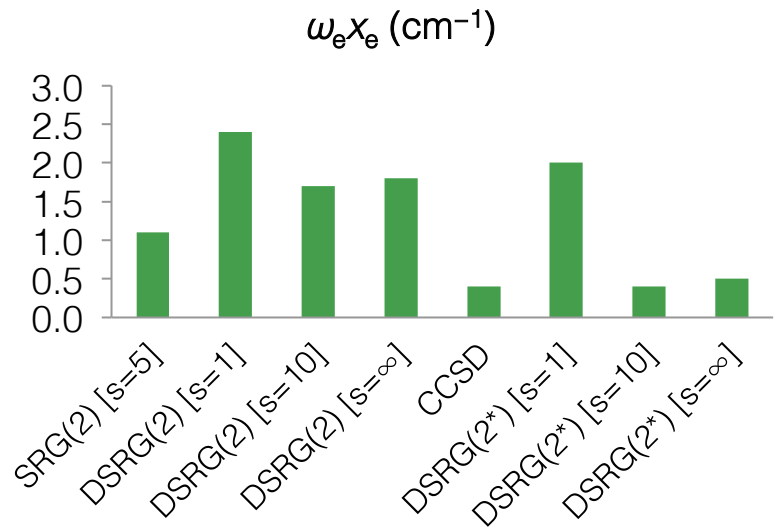
$$\bar{H}_1(s) \leftarrow 2[\hat{V},\hat{S}_2]$$ DSRG(2*)

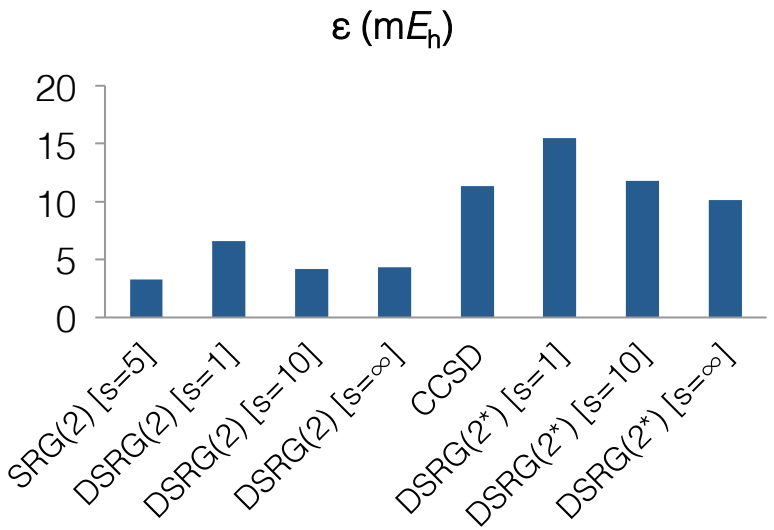
STATISTICS FOR ELEVEN DIATOMICS

Absolute Mean Deviations from CCSD(T) results

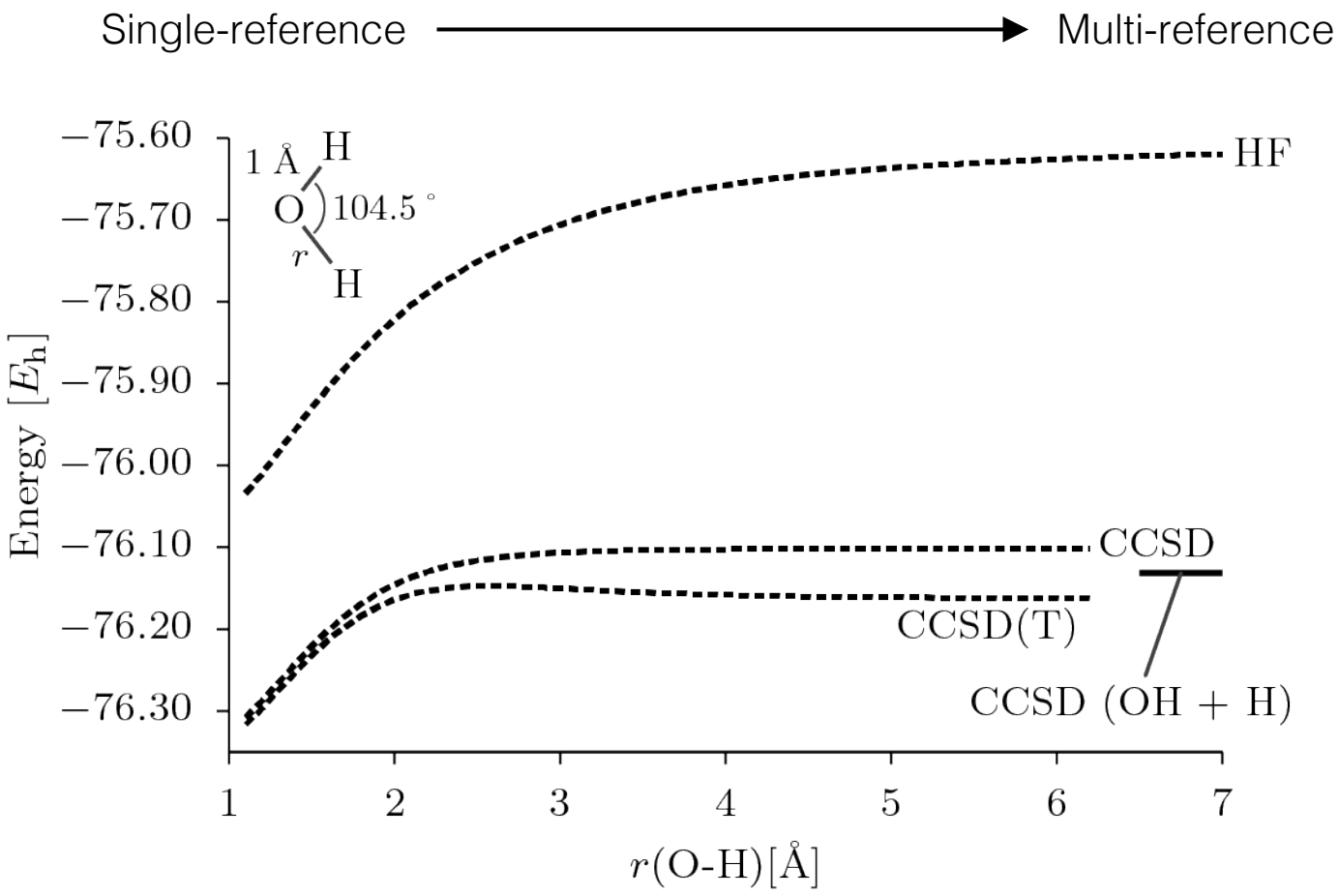




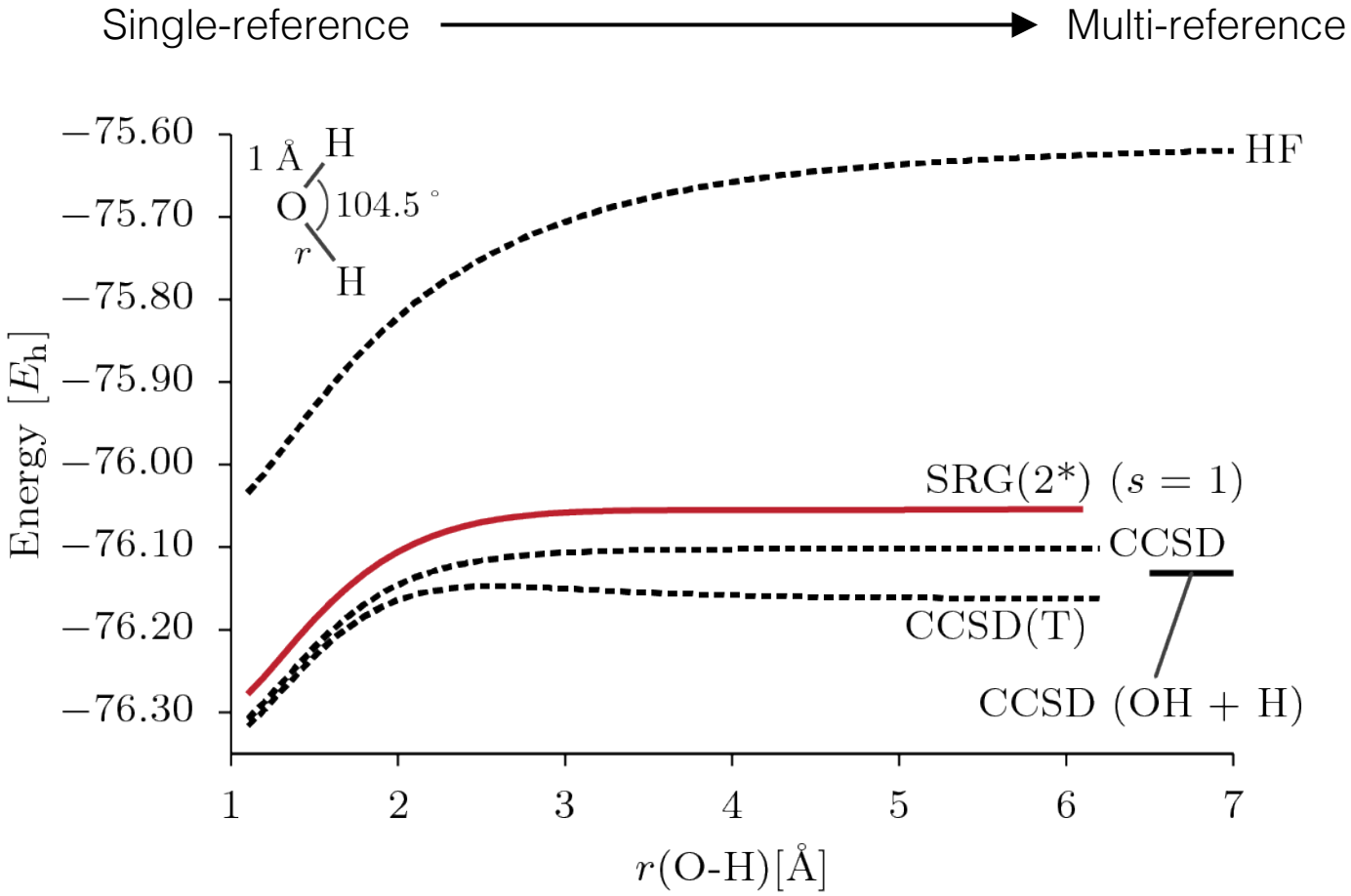




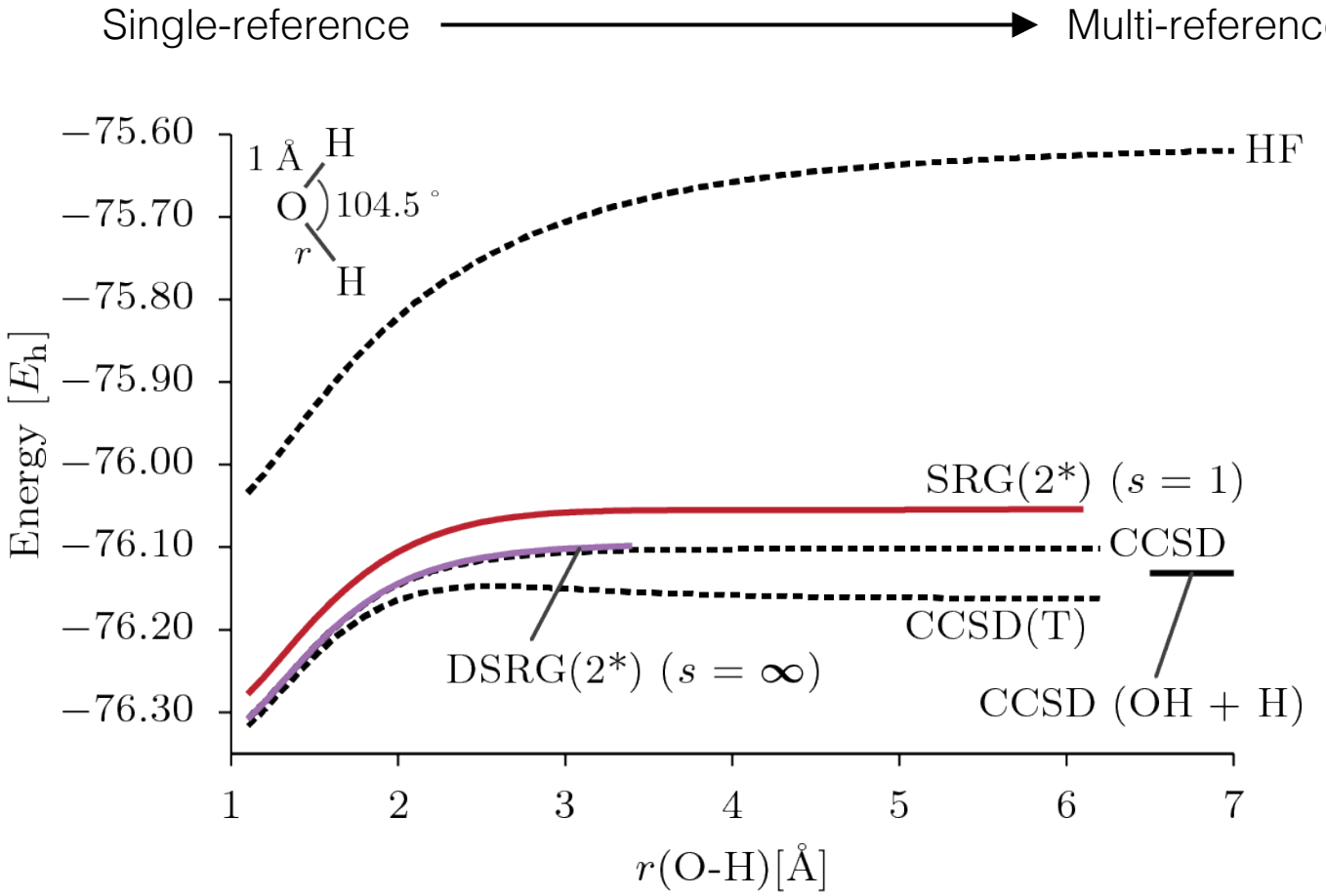
DISSOCIATING BONDS WITH THE SR-DSRG



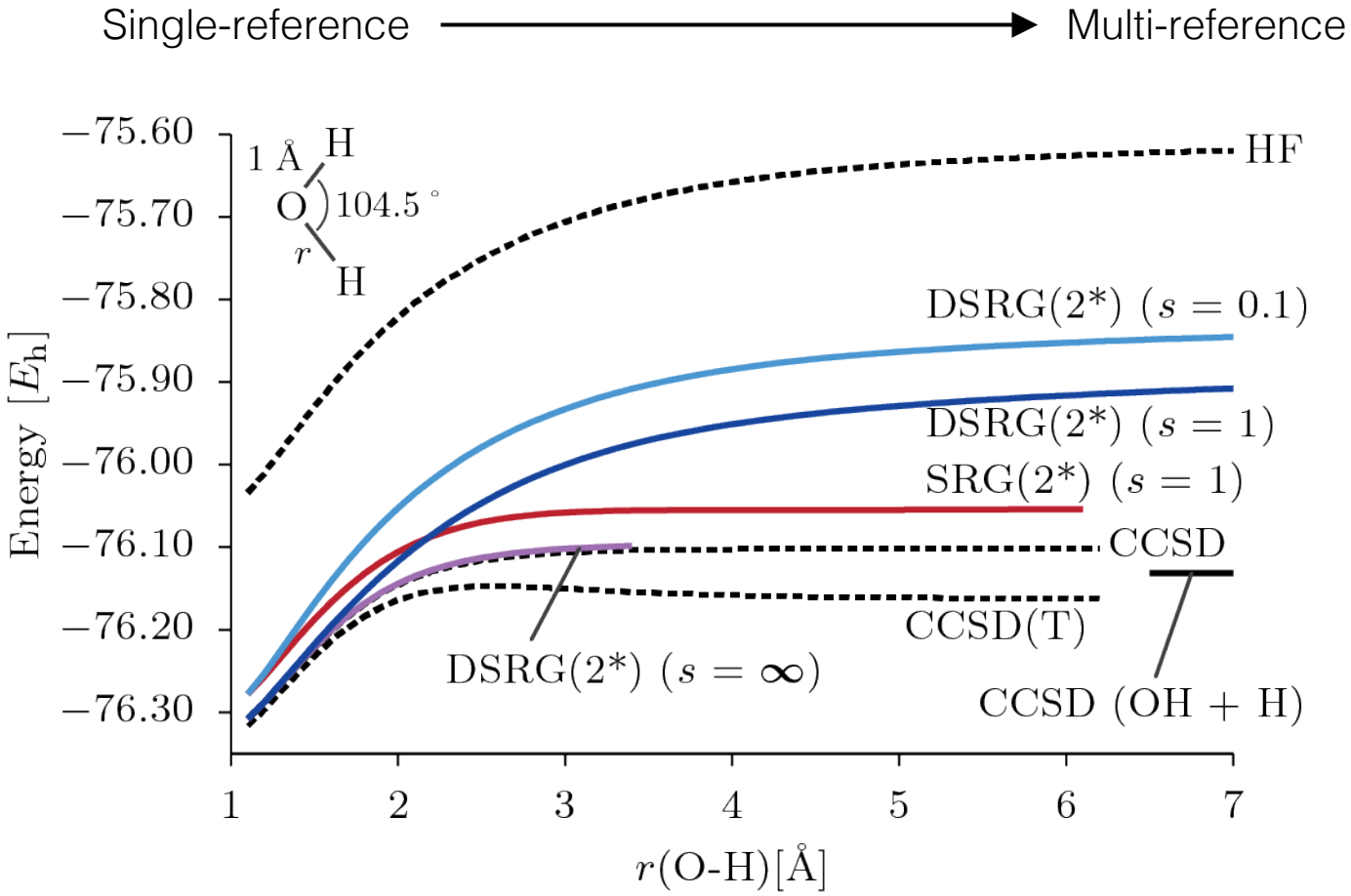
DISSOCIATING BONDS WITH THE SR-DSRG



DISSOCIATING BONDS WITH THE SR-DSRG

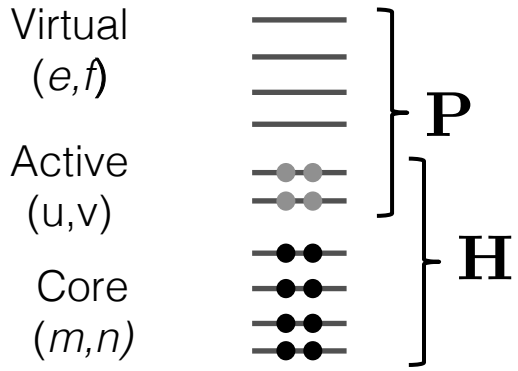


DISSOCIATING BONDS WITH THE SR-DSRG



EXTENSION TO THE MULTI-REFERENCE CASE: MR-DSRG[1]

Based on the generalized normal ordering formalism of Mukherjee and Kutzelnigg[2] (also see Hergert et al.[3])



$$|\Phi\rangle = \sum_{\mu}^{d} |\Phi_\mu\rangle c_\mu$$

$$|\Phi_\mu\rangle = \underbrace{\hat{a}_u^\dagger \hat{a}_v^\dagger \cdots}_{\text{active}} \prod_{i}^{\text{core}} |-\rangle$$

$$\hat{T}_k = \frac{1}{(k!)^2} \sum_{ij\cdots}^{\mathbf{H}} \sum_{ab\cdots}^{\mathbf{P}} t_{ij\cdots}^{ab\cdots} \underbrace{\{\hat{a}_{ij\cdots}^{ab\cdots}\}}_{k\text{-fold excitation}}$$

Normal ordered with respect to Φ

1) Li, C.; Evangelista, F.A., *J. Chem.. Theory Comput.* (2015)
2) Kutzelnigg, W.; Mukherjee, D. *J. Chem. Phys.* (1997)
3) Hergert, H.; Binder, S.; Calci, A.; Langhammer, J.; Roth, R., *Phys. Rev. Lett.* (2013)

SECOND-ORDER ANALYSIS OF THE MR-DSRG: DSRG-MRPT2

The zeroth-order Hamiltonian

$$\hat{F}^{(0)} = \sum_{mn}^{\mathbf{C}} f_m^n \{\hat{a}_n^m\} + \sum_{uv}^{\mathbf{A}} f_u^v \{\hat{a}_v^u\} + \sum_{ef}^{\mathbf{V}} f_e^f \{\hat{a}_f^e\} \rightarrow \sum_{p}^{\mathbf{C},\mathbf{A},\mathbf{V}} \epsilon_p \{\hat{a}_p^p\}$$

First-order amplitude equations

$$\hat{R}^{(1)}(s) = [\bar{H}^{(1)}(s)]_{\mathrm{N}} = \left(\hat{H}^{(1)} + [\hat{H}^{(0)}, \hat{A}^{(1)}(s)]\right)_{\mathrm{N}}$$

We use the single-reference source operator. This gives:

$$t_a^{i,(1)}(s) = \frac{\left[f_a^{i,(1)} + \sum_{ux}^{\mathbf{A}} \Delta_u^x t_{ax}^{iu,(1)}(s)\gamma_u^x\right]\left[1 - e^{-s(\Delta_a^i)^2}\right]}{\epsilon_i - \epsilon_a},$$

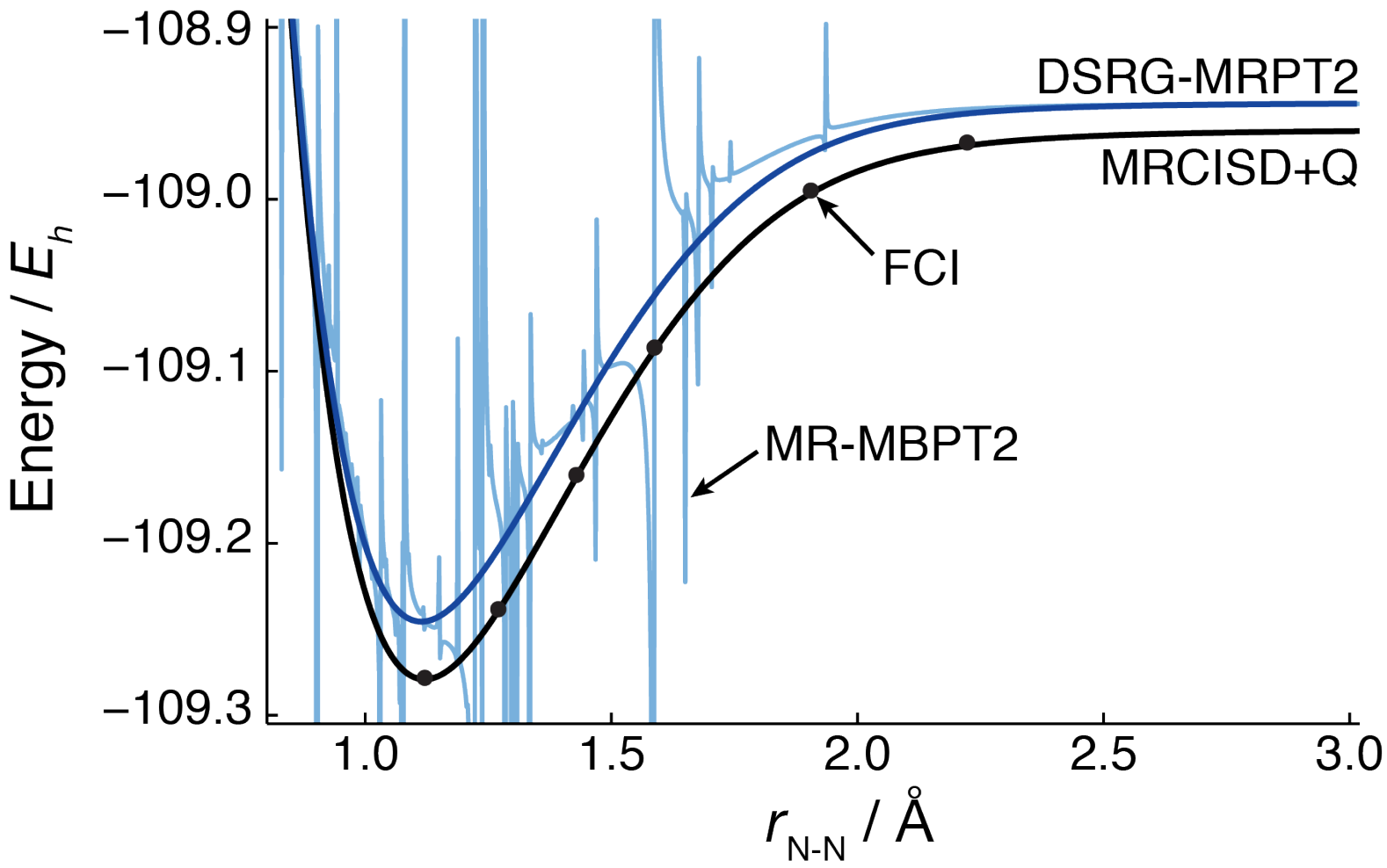
$$t_{ab}^{ij,(1)}(s) = \frac{v_{ab}^{ij,(1)}[1 - e^{-s(\Delta_{ab}^{ij})^2}]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

THE SECOND-ORDER ENERGY

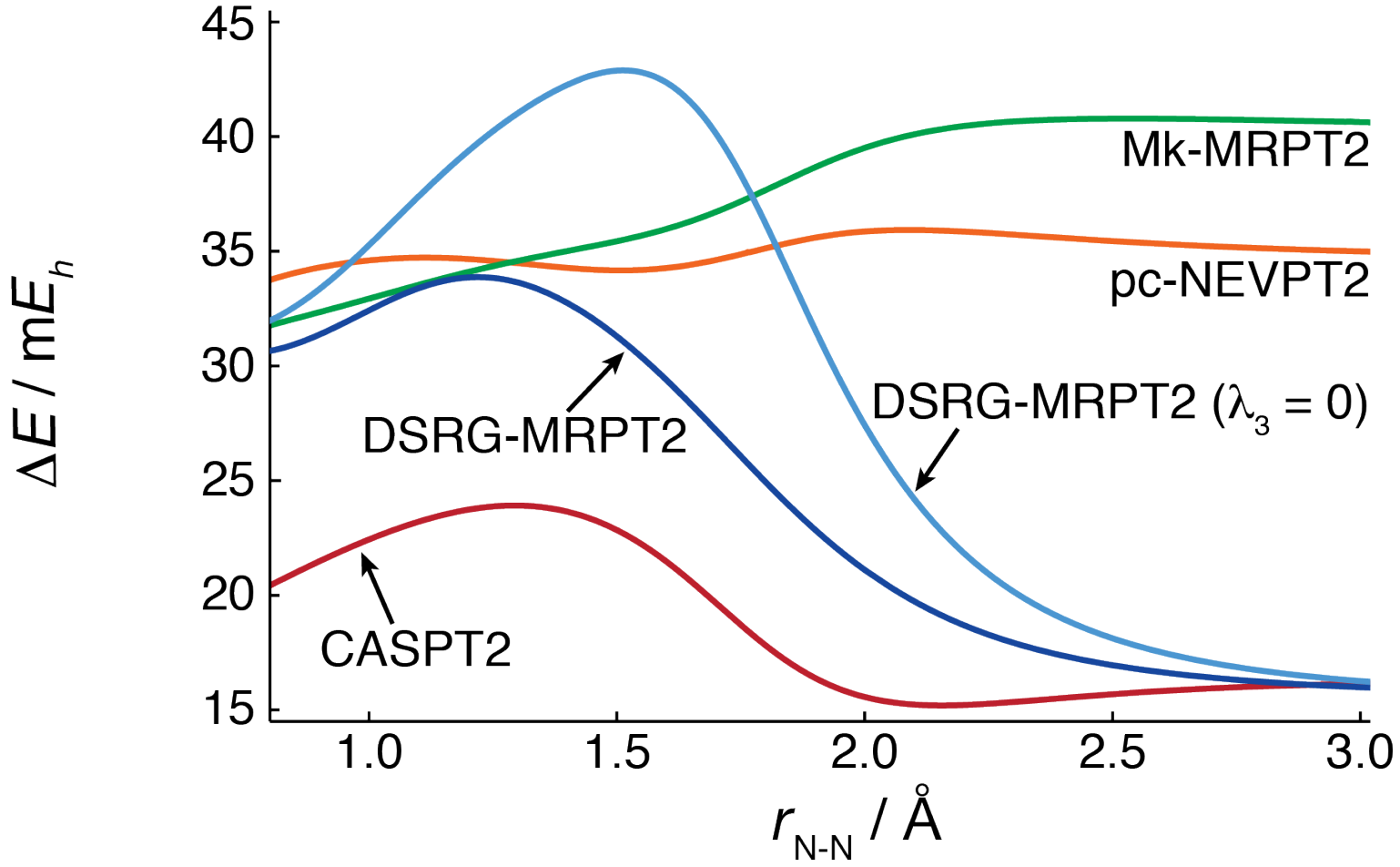
$$
\begin{aligned}
E^{(2)}(s) =& \langle\Phi|[\hat{H}^{(1)}, \hat{A}^{(1)}(s)]|\Phi\rangle \\
&+ \frac{1}{2}\langle\Phi|\big[[\hat{H}^{(0)}, \hat{A}^{(1)}(s)], \hat{A}^{(1)}(s)\big]|\Phi\rangle \\
=& \frac{1}{2}\langle\Phi|[\tilde{H}^{(1)}(s), \hat{A}^{(1)}(s)]|\Phi\rangle,
\end{aligned}
$$

$\frac{1}{2}\langle[\tilde{F}^{(1)}(s), \hat{A}_1^{(1)}(s)]\rangle$	$+\tilde{f}_j^{b,(1)}(s)t_a^{i,(1)}(s)\gamma_i^j\eta_b^a$
$\frac{1}{2}\langle[\tilde{V}^{(1)}(s), \hat{A}_1^{(1)}(s)]\rangle$	$+\frac{1}{2}\tilde{v}_{xy}^{ev,(1)}(s)t_e^{u,(1)}(s)\lambda_{uv}^{xy}$ $-\frac{1}{2}\tilde{v}_{my}^{uv,(1)}(s)t_x^{m,(1)}(s)\lambda_{uv}^{xy}$
$\frac{1}{2}\langle[\tilde{F}^{(1)}(s), \hat{A}_2^{(1)}(s)]\rangle$	$+\frac{1}{2}\tilde{f}_x^{e,(1)}(s)t_{ey}^{uv,(1)}(s)\lambda_{uv}^{xy}$ $-\frac{1}{2}\tilde{f}_m^{v,(1)}(s)t_{xy}^{um,(1)}(s)\lambda_{uv}^{xy}$
$\frac{1}{2}\langle[\tilde{V}^{(1)}(s), \hat{A}_2^{(1)}(s)]\rangle$	$+\frac{1}{4}\tilde{v}_{kl}^{cd,(1)}(s)t_{ab}^{ij,(1)}(s)\gamma_i^k\gamma_j^l\eta_c^a\eta_d^b$ $+\frac{1}{8}\tilde{v}_{xy}^{cd,(1)}(s)t_{ab}^{uv,(1)}(s)\eta_c^a\eta_d^b\lambda_{uv}^{xy}$ $+\frac{1}{8}\tilde{v}_{kl}^{uv,(1)}(s)t_{xy}^{ij,(1)}(s)\gamma_i^k\gamma_j^l\lambda_{uv}^{xy}$ $+\tilde{v}_{jx}^{vb,(1)}(s)t_{ay}^{iu,(1)}(s)\gamma_i^j\eta_b^a\lambda_{uv}^{xy}$

DSRG-MRPT2 EXAMPLES: N_2 DISSOCIATION CURVE

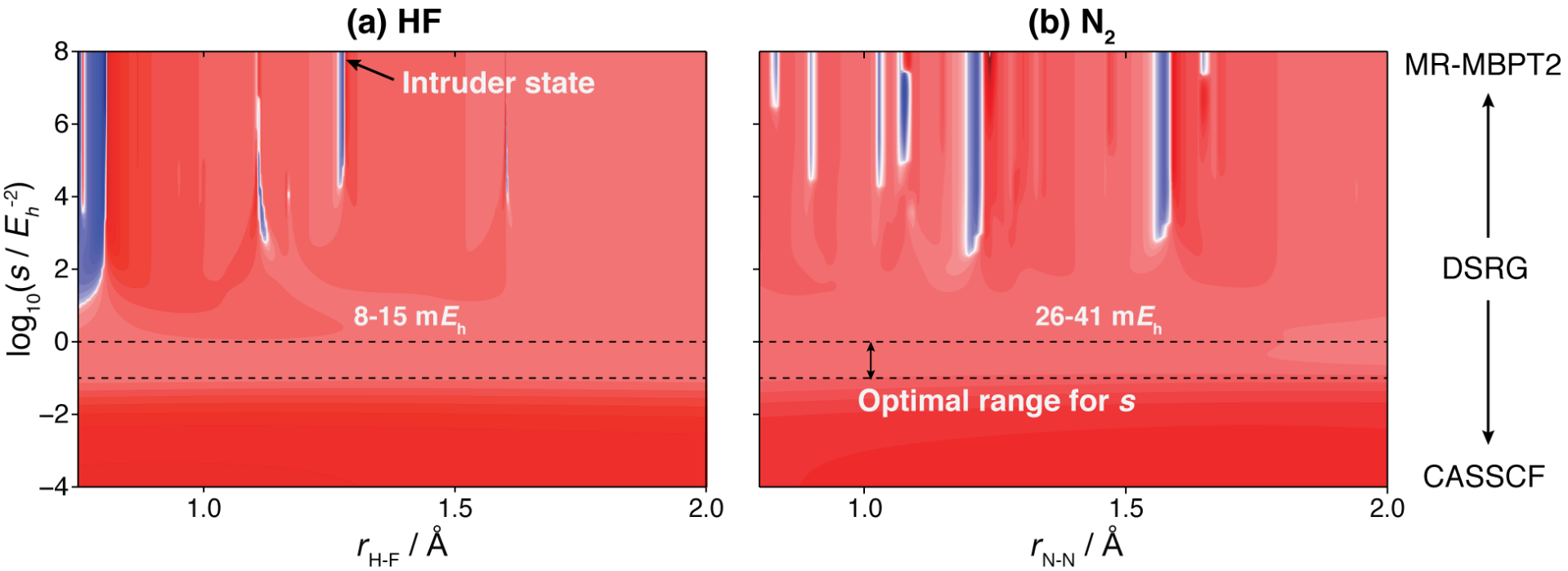


DSRG-MRPT2 EXAMPLES: N_2 DISSOCIATION CURVE



DSRG-MRPT2: Dependence of results on *s*

Error with respect to FCI (ED) as a function of *s*



Good News:

- It does not get worse than this.
- Can improve things: just keep many-body parts $\bar{H}(s)$

DSRG-MRPT2: Formal Aspects

Convergence:

- We are polishing a formal proof that for certain values of *s* the (MR-)DSRG equations are a contraction.

Orbital invariance:

- The single-reference DSRG can be made orbital invariant, expect the same to be true for the MR-DSRG.

CONCLUSIONS

The DSRG methods gives us:

- Control over the separation of static and dynamic correlation
- A numerically-robust approach to dynamic correlation
- A framework to develop adaptive theories for multireference ground states and excitation energies

Open problems:

- Can we find better ways to approximate the BCH series?
- Design of source operator, can we do better?
- Reduce the dependence of results on the value of *s* ?

What we are working on:

- Nonperturbative MR-DSRG
- Density-fitted implementation of the DSRG-MRPT2

$$\langle pq|rs\rangle = \sum_L (pr|L)(L|qs)$$