Current challenges in electronic structure theory for open-shell molecules and molecular clusters

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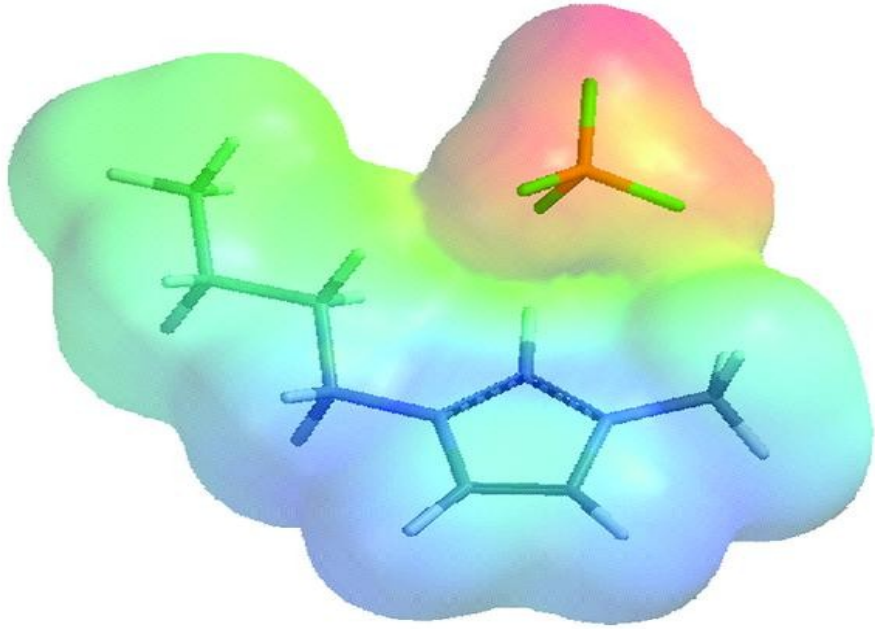
Formal computational problem

- Born-Oppenheimer system:

  (a) a set of M fixed nuclei;
  (b) N electrons;
  (c) external electro-magnetic fields;

  (d) non-relativistic Hamiltonian (not important for this talk).



$$i\hbar\frac{\partial}{\partial t}|\Psi_k\rangle=\hat{H}|\Psi_k\rangle\wedge(\text{Dirichlet}\,||\,\text{Periodic})\wedge_?\hat{S}^2|\Psi_k\rangle=s_k(s_k+1)|\Psi_k\rangle$$

$$\hat{H}|\Psi_k\rangle=E_k|\Psi_k\rangle\wedge(\text{Dirichlet}\,||\,\text{Periodic})\wedge_?\hat{S}^2|\Psi_k\rangle=s_k(s_k+1)|\Psi_k\rangle$$

Non-relativistic Hamiltonian:

$$\hat{H}=\sum_{k=1}^{N}\left(-\frac{1}{2}\hat{\nabla}_k^2+F(\hat{r}_k,t)+\sum_{\alpha=1}^{M}\frac{-Z_\alpha}{|\hat{r}_k-R_\alpha|}+\frac{1}{2}\sum_{j\neq k}^{N}\frac{1}{|\hat{r}_k-\hat{r}_j|}\right)+\frac{1}{2}\sum_{\alpha=1}^{M}\sum_{\beta\neq\alpha}^{M}\frac{Z_\alpha Z_\beta}{|R_\alpha-R_\beta|}$$

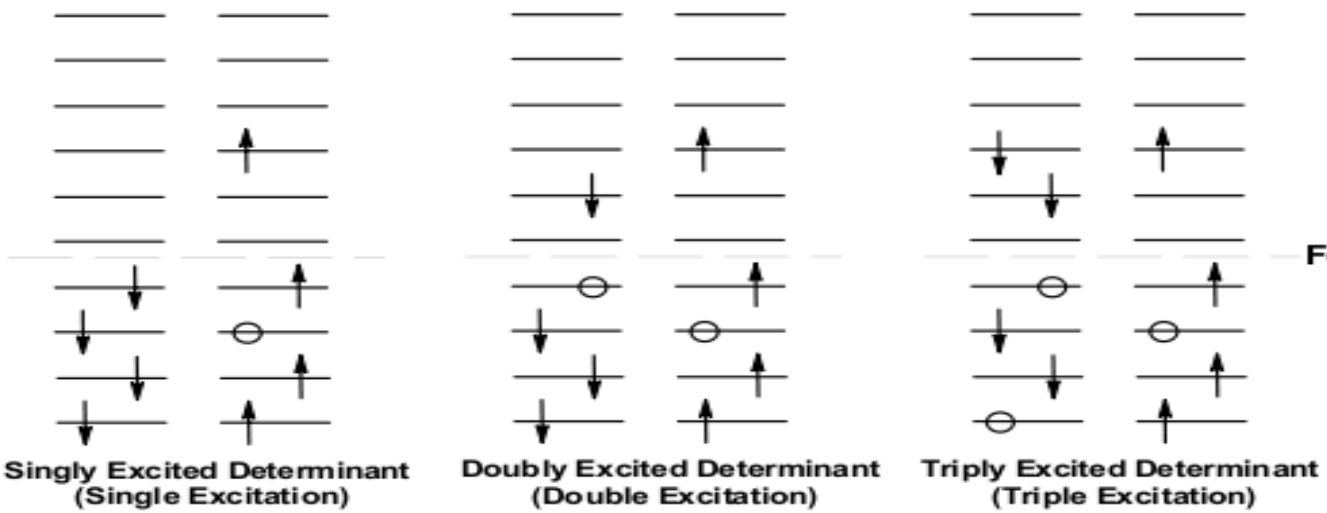
Many-particle Hilbert space

- 1-particle basis: $\{\phi_k(x,y,z,\sigma)\}_{k=1,n}: \mathbb{R}^3 \times \{\frac{-1}{2},\frac{+1}{2}\} \to \mathbb{C}$
- A tensor-product basis of antisymmetrized N-body functions (Slater determinants or independent particle states, IPS):

$$\forall\, i_1 i_2 .. i_N : \{\Phi^{i_1 i_2 .. i_N}(r_1 r_2 ... r_N)\} = \{\phi_{i_1}(r_1) \wedge \phi_{i_2}(r_2) \wedge ... \wedge \phi_{i_N}(r_N)\}$$

where $\wedge$ defines an *antisymmetrized tensor product*:

$$\phi_k(r_1) \wedge \phi_j(r_2) = 1/\sqrt{2!}\,(\phi_k(r_1)\phi_j(r_2) - \phi_j(r_1)\phi_k(r_2))$$



$$\left(\mathbb{R}^3 \times \{\frac{-1}{2},\frac{+1}{2}\}\right)^N \to \mathbb{C}$$

Tensor product structure

$$\Psi(r_1 r_2 ... r_N) = \sum_{i_1 < i_2 < .. < i_N} C_{i_1 i_2 .. i_N}\, \Phi^{i_1 i_2 .. i_N}(r_1 r_2 ... r_N) \to \text{Full CI limit}$$

Electron Correlation

- Effective 1-body problem: SCF eigenvectors (IPS):

$$|0\rangle = |\phi_1(r_1) \wedge \phi_2(r_2) \wedge \ldots \wedge \phi_N(r_N)\rangle \equiv |\phi_1 \phi_2 \ldots \phi_N\rangle$$

$$\hat{H} = \sum_{k=1}^{N} \hat{h}(k), \quad \rho(r_1 .. r_m) = \prod_{k=1}^{m \le N} \rho(r_k), \quad \hat{\rho}_1 = \sum_{k=1}^{N} |\phi_k\rangle\langle\phi_k| = \hat{\rho}_1^2$$

- 2-body (and higher) terms: Inter-particle ***Correlations***:

  Dynamic and ***Non-dynamic*** (spatial 2-body Coulomb term):

$$\sum_{i<j}^{N,N} |\hat{r}_i - \hat{r}_j|^{-1} \quad \text{or} \quad \sum_{i<j}^{N,N} |\hat{r}_i - \hat{r}_j|^{-1} - \sum_{i=1}^{N} v(\hat{r}_i)$$

  Static (proper spin-coupling, other symmetries):

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \sum_{i,j}^{N,N} \hat{s}_x(i)\hat{s}_x(j) + \sum_{i,j}^{N,N} \hat{s}_y(i)\hat{s}_y(j) + \sum_{i,j}^{N,N} \hat{s}_z(i)\hat{s}_z(j)$$

- In general, the *antisymmetry* requirement mixes both

Correlated wavefunction

- Non-separability of the N-body problem:

$$\forall \{\phi_{i_1}, \phi_{i_2}, \ldots, \phi_{i_N}\}: \; |\Psi\rangle \neq |\phi_{i_1}\phi_{i_2}\ldots\phi_{i_N}\rangle$$

$$\rho(r_1 \ldots r_m) \neq \prod_{k=1}^{2 \le m \le N} \rho(r_k), \qquad \hat{\rho}_1 \neq \hat{\rho}_1^2$$

$$\rho(r_1, r_2) = \rho(r_1)\rho(r_2) + \sigma(r_1, r_2) \; : \; \textit{2-body cumulant!}$$

- In the basis of arbitrary Slater determinants, a correlated wavefunction is always multicomponent:

$$|\Psi\rangle = |0\rangle + \sum_{m=1}^{N} \sum_{\substack{a_1<a_2<..<a_m \\ i_1<i_2<..<i_m}} C_{i_1 i_2 .. i_m}^{a_1 a_2 .. a_m} \left| {}^{i_1 i_2 .. i_m}_{a_1 a_2 .. a_m} \right\rangle =$$

$$= |0\rangle + \sum_{m=1}^{N} \sum_{\substack{a_1<a_2<..<a_m \\ i_1<i_2<..<i_m}} C_{i_1 i_2 .. i_m}^{a_1 a_2 .. a_m} \hat{\tau}_{a_1 a_2 .. a_m}^{i_1 i_2 .. i_m} |0\rangle$$

Hole-particle formalism

Hole-particle vacuum

$$\hat{\tau}_{a_1 a_2 .. a_N}^{i_1 i_2 .. i_N} \equiv \hat{a}_1^+ \hat{a}_2^+ .. \hat{a}_N^+ \hat{i}_N^- .. \hat{i}_2^- \hat{i}_1^-$$

Strength of the electron correlation

- 2x2 model: $span\{|0\rangle, |^{i_1 i_2}_{a_1 a_2}\rangle\}$: $|\Psi\rangle = C_0|0\rangle + C^{a_1 a_2}_{i_1 i_2}|^{i_1 i_2}_{a_1 a_2}\rangle$

$$\begin{bmatrix} H_{00} & H_{01} \\ H_{10} & H_{11} \end{bmatrix} \equiv \begin{bmatrix} \alpha & \beta \\ \beta & (\alpha+\Delta) \end{bmatrix}$$

Off-diagonal coupling due to 2-body terms

- State 0:

$$E = \alpha + \frac{\Delta}{2} - \sqrt{\left(\frac{\Delta}{2}\right)^2 + \beta^2} \approx \alpha + \frac{\Delta}{2} - \left(\frac{\Delta}{2} + \frac{\beta^2}{\Delta} - \frac{\beta^4}{\Delta^3}\right)$$

$$\frac{C^{a_1 a_2}_{i_1 i_2}}{C_0} \approx -\left(\frac{\beta}{\Delta}\right) + \left(\frac{\beta}{\Delta}\right)^3 \qquad \frac{C^{a_1 a_2}_{i_1 i_2}}{C_0} = \frac{1}{2}\left(\frac{\beta}{\Delta}\right)^{-1} - \sqrt{\frac{1}{4}\left(\frac{\beta}{\Delta}\right)^{-2} + 1}$$

- State 1:

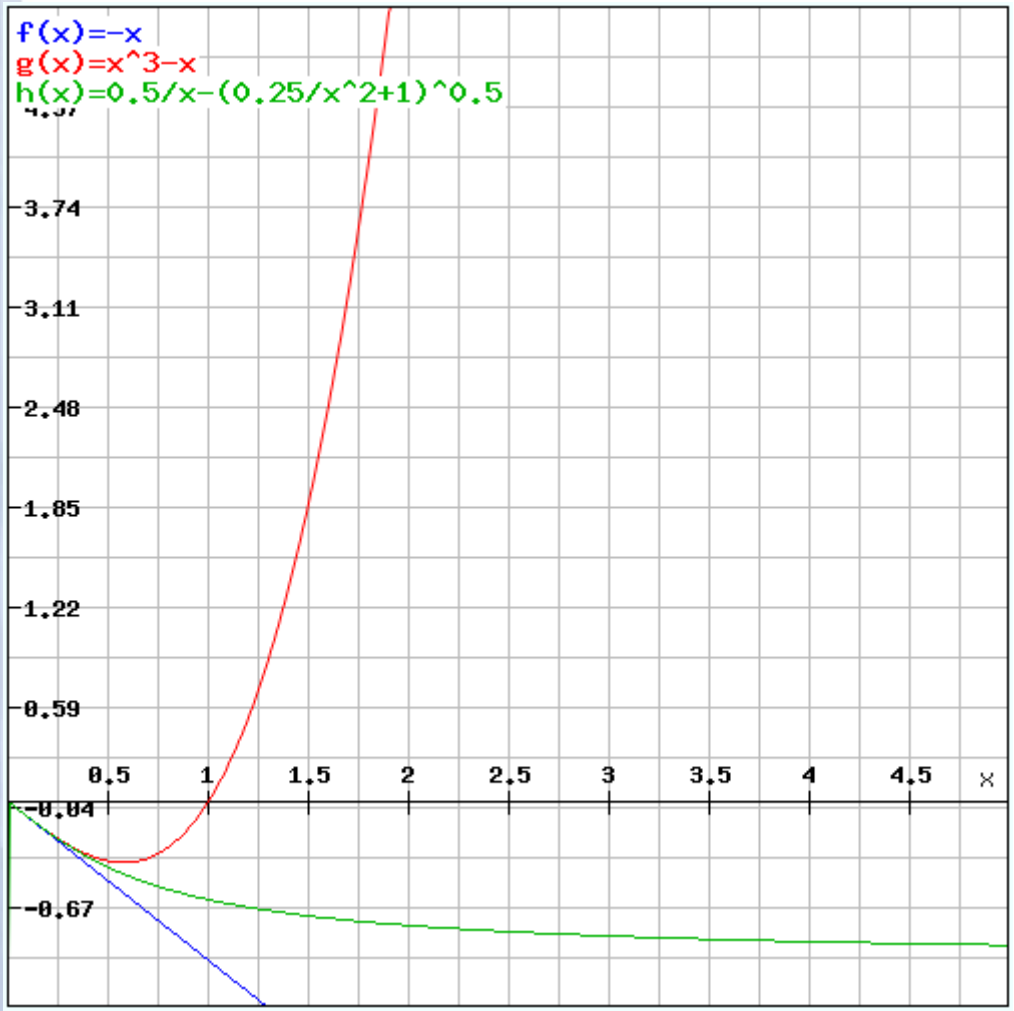
$$E = \alpha + \frac{\Delta}{2} + \sqrt{\left(\frac{\Delta}{2}\right)^2 + \beta^2} \approx \alpha + \frac{\Delta}{2} + \left(\frac{\Delta}{2} + \frac{\beta^2}{\Delta} - \frac{\beta^4}{\Delta^3}\right)$$

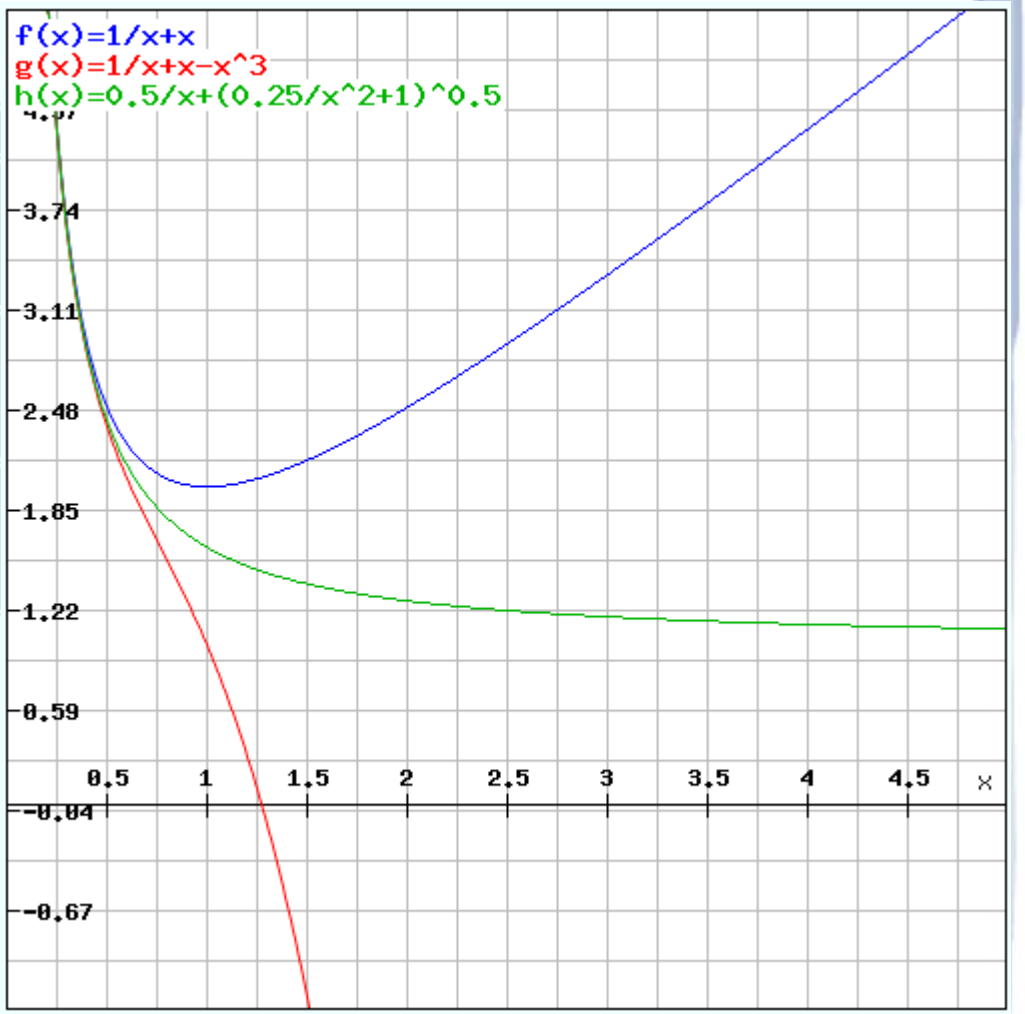
$$\frac{C^{a_1 a_2}_{i_1 i_2}}{C_0} \approx \left(\frac{\beta}{\Delta}\right)^{-1} + \left(\frac{\beta}{\Delta}\right) - \left(\frac{\beta}{\Delta}\right)^3 \qquad \frac{C^{a_1 a_2}_{i_1 i_2}}{C_0} = \frac{1}{2}\left(\frac{\beta}{\Delta}\right)^{-1} + \sqrt{\frac{1}{4}\left(\frac{\beta}{\Delta}\right)^{-2} + 1}$$

$Here\ \Delta \neq 0$

Strength of the electron correlation

- Parameter $\left(\frac{\beta}{\Delta}\right)$ regulates the strength of the electron correlation: $\frac{C_{i_1 i_2}^{a_1 a_2}}{C_0}$ as a function of $\left(\frac{\beta}{\Delta}\right)$:





Plotted on-line by http://rechneronline.de/function-graphs/

Structure of a correlated wavefunction

- ***Dynamic (weak):*** $|\beta/\Delta| \ll 1$

  The wavefunction is dominated by only ***one*** Slater determinant.

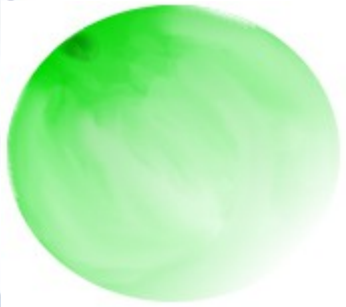
  Dispersion effects (fluctuations of the electron charge).

- ***Non-dynamic/static (moderate or strong):*** $|\beta/\Delta| \sim 1$

  The wavefunction is dominated by ***multiple/many*** Slater determinants with similarly large weights (***multireference***): <1000 → **moderate** (current focus), >1000 → strong.

  Localization of electrons during bond breaking, interaction among closely lying orbitals, spin-coupling. **Independent particle picture becomes qualitatively wrong!**

- Multireference wavefunctions spread more over the Hilbert space



Single-reference

(SR)

Multireference

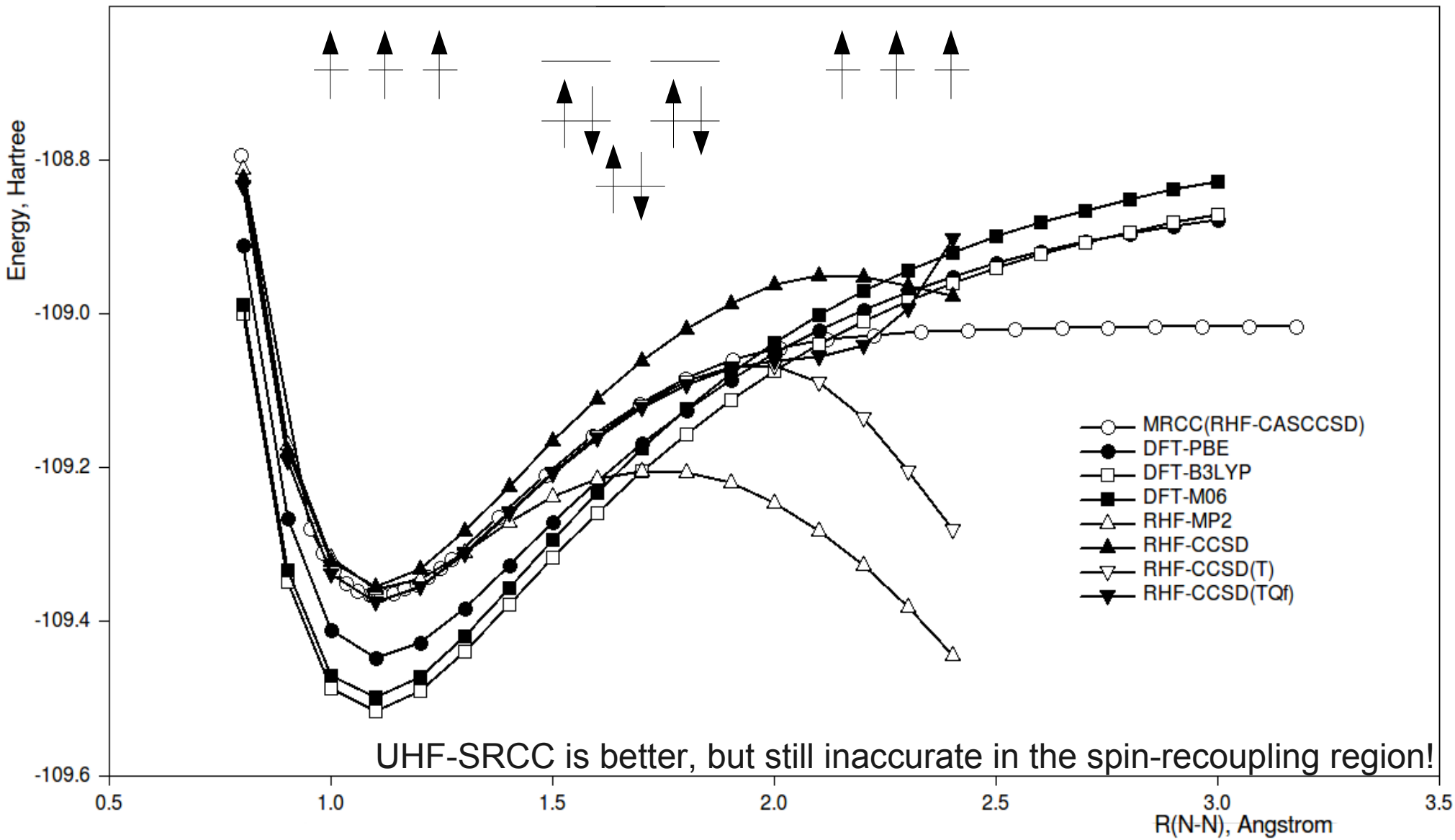
(MR)

Multireference problems

- Bond breaking/formation, especially for multiple bonds
- Molecules with open shells (radicals, biradicals)
- Excited electronic states, especially doubly-excited electronic states and charge-transfer excitations
- Molecular resonances
- Reaction dynamics involving multiple potential energy surfaces (conical intersections and avoided crossings)
- Conjugation in organic molecules and polymers
- Molecules, molecular complexes, and macromolecules containing d- and f-transition metals
- Any kind of orbital ***quasidegeneracy*** which leads to quasidegeneracy of many-particle basis functions (Slater determinants)

D.I.Lyakh, M.Musial, V.Lotrich, R.J.Bartlett, Chem. Rev. 112, 182 (2012).

N2 molecule triple-bond breaking (separation of two N atoms with 3 open-shell electrons on each: CAS(6,6)



D.I.Lyakh, V.V.Ivanov, L.Adamowicz, Mol. Phys. 105, 1335 (2007)

D.I.Lyakh, M.Musial, V.Lotrich, R.J.Bartlett, Chem. Rev. 112, 182 (2012)

Wavefunction complexity

- The best case: only one Slater determinant is present in the wavefunction (SR)
- The worst case: all Slater determinants have the same weights (strong MR)
- Let's use the Shannon entropy to characterize the complexity of the wavefunction (needs some additional normalization w.r.t. basis set size and N):

$$I_C = -\sum_k \frac{|C_k|^2}{Z} \log_2 \frac{|C_k|^2}{Z}, \quad Z = \sum_k |C_k|^2$$

V.V.Ivanov, D.I.Lyakh, L.Adamowicz, Mol. Phys. 103, 2131 (2005)

- The Shannon index is superior to other wavefunction diagnostics, like T1 (the latter mostly shows the orbital relaxation effects: Thouless theorem)
- The Shannon entropy is also routinely used for the 1-body density

Wavefunction *VS* Density entropy

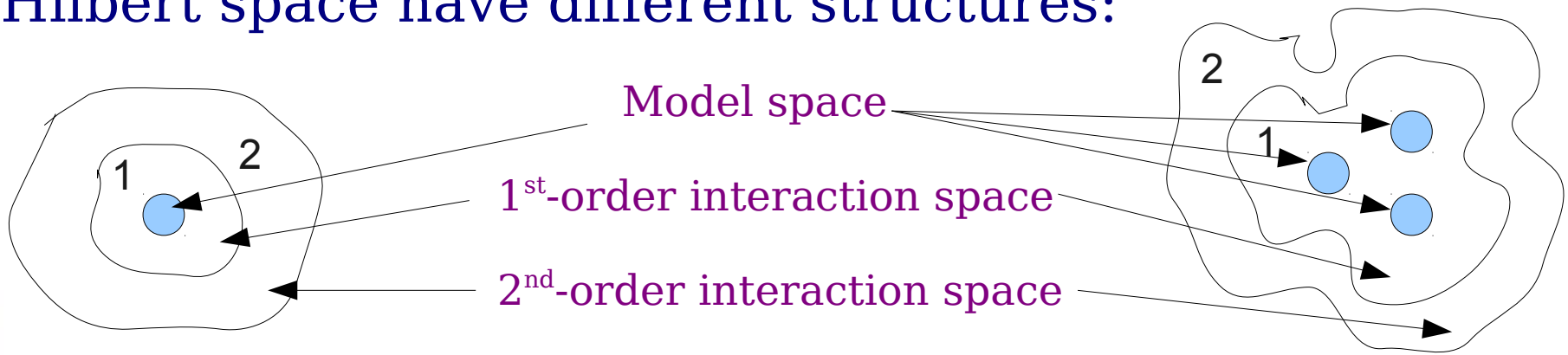
- The ***density entropy*** characterizes the complexity of the ***physical*** problem (its Full CI value is invariant w.r.t. arbitrary orbital rotations)
- The ***wavefunction entropy*** characterizes the complexity of the ***computational*** problem in a given many-particle basis set (its Full CI value is *not* invariant w.r.t. orbital rotations):

$$|\phi\rangle=\left(|\chi_1\rangle+|\chi_2\rangle\right) \quad \rightarrow \quad |\phi^\alpha\phi^\beta\rangle=|\chi_1^\alpha\chi_1^\beta\rangle+|\chi_2^\alpha\chi_2^\beta\rangle+|\chi_1^\alpha\chi_2^\beta\rangle+|\chi_2^\alpha\chi_1^\beta\rangle$$

- The preliminary SCF ”compression” (capturing all mean-field effects) is mandatory in order to focus solely on the complexity of the correlated problem (also Brueckner).
- Separable *N*-body problem: HF vs Full CI: $|\mathrm{HF}\rangle=\eta\, e^{\hat{T}_1}|0\rangle$
- The wavefunction complexity does depend on the Fermi vacuum chosen

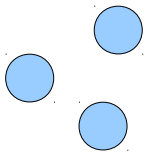
SR/MR excitation rank hierarchies

- Supports of SR and MR wavefunctions in the many-particle Hilbert space have different structures:



- The minimal number of Slater determinants, required for a ***qualitatively*** correct description of the many-particle state, spans the ***model space*** of the problem:

$$|\Theta\rangle = \sum_{\alpha=1}^{D} C^{\alpha} |\Phi_{\alpha}\rangle, \qquad \hat{P} = \sum_{\alpha=1}^{D} |\Phi_{\alpha}\rangle\langle\Phi_{\alpha}|$$



- The essence of any MR method is a ***quantitatively*** correct construction of the wavefunction in the model and MR 1st-order interaction spaces (chemical accuracy, 1 kcal/mol):

$$|\Psi\rangle = \hat{\Omega}|\Theta\rangle: \qquad \text{(MR) CI/CC/MBPT}$$

D.I.Lyakh, M.Musial, V.Lotrich, R.J.Bartlett, Chem. Rev. 112, 182 (2012).

The beauty of an exponential

- The structure of the exponential wave operator (coupled cluster) reflects the direct product structure of the Hilbert space spanned by Slater determinants:

$$\left|{}^{i_1}_{a_1}\right\rangle=\hat{\tau}^{i_1}_{a_1}|0\rangle,\qquad \left|{}^{i_1 i_2}_{a_1 a_2}\right\rangle=\left|{}^{i_1}_{a_1}\right\rangle\times\left|{}^{i_2}_{a_2}\right\rangle=\hat{\tau}^{i_1}_{a_1}\times\hat{\tau}^{i_2}_{a_2}|0\rangle=\hat{\tau}^{i_1 i_2}_{a_1 a_2}|0\rangle$$

$$|\Psi\rangle=e^{\hat{T}_1+\hat{T}_2+\ldots+\hat{T}_N}|0\rangle=\left(1+\hat{T}_1+\hat{T}_2+\frac{1}{2!}\hat{T}_1\hat{T}_1+\ldots\right)|0\rangle,\quad \hat{T}_m=\frac{1}{m!^2}\sum_{\substack{a_1..a_m\\ i_1..i_m}} t^{a_1..a_m}_{i_1..i_m}\hat{\tau}^{i_1..i_m}_{a_1..a_m}$$

- Hole-particle structure of the wavefunction is expressed in terms of ***connected*** and ***dicsconnected*** contributions:

$$\left\langle{}^{a_1 a_2}_{i_1 i_2}\right|e^{\hat{T}_1+\hat{T}_2+\ldots+\hat{T}_N}|0\rangle=\left\langle{}^{a_1 a_2}_{i_1 i_2}\right|\left(\hat{T}_2+\frac{1}{2!}\hat{T}_1\hat{T}_1\right)|0\rangle=t^{a_1 a_2}_{i_1 i_2}+\frac{1}{2!}t^{a_1}_{i_1}\wedge t^{a_2}_{i_2}$$

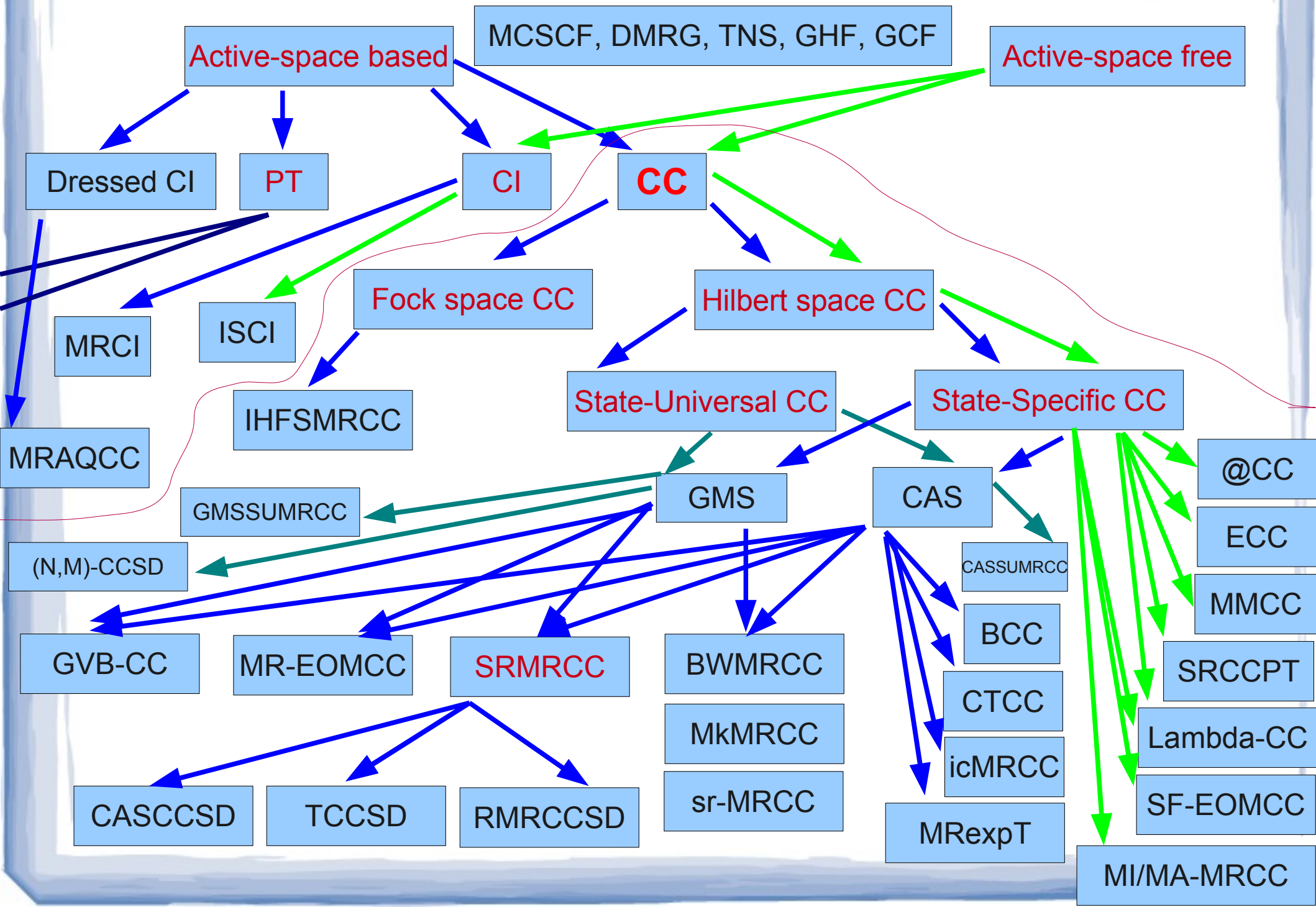
Collective (cumulative) double excitation (correlation)

Two independent single excitations

- The larger the cluster amplitude, the stronger the correlation (coupling) between the corresponding holes and particles (in contrast, CI coefficients do not necessarily reflect the correlations!)
- Size-extensivity of the energy, fast convergence!

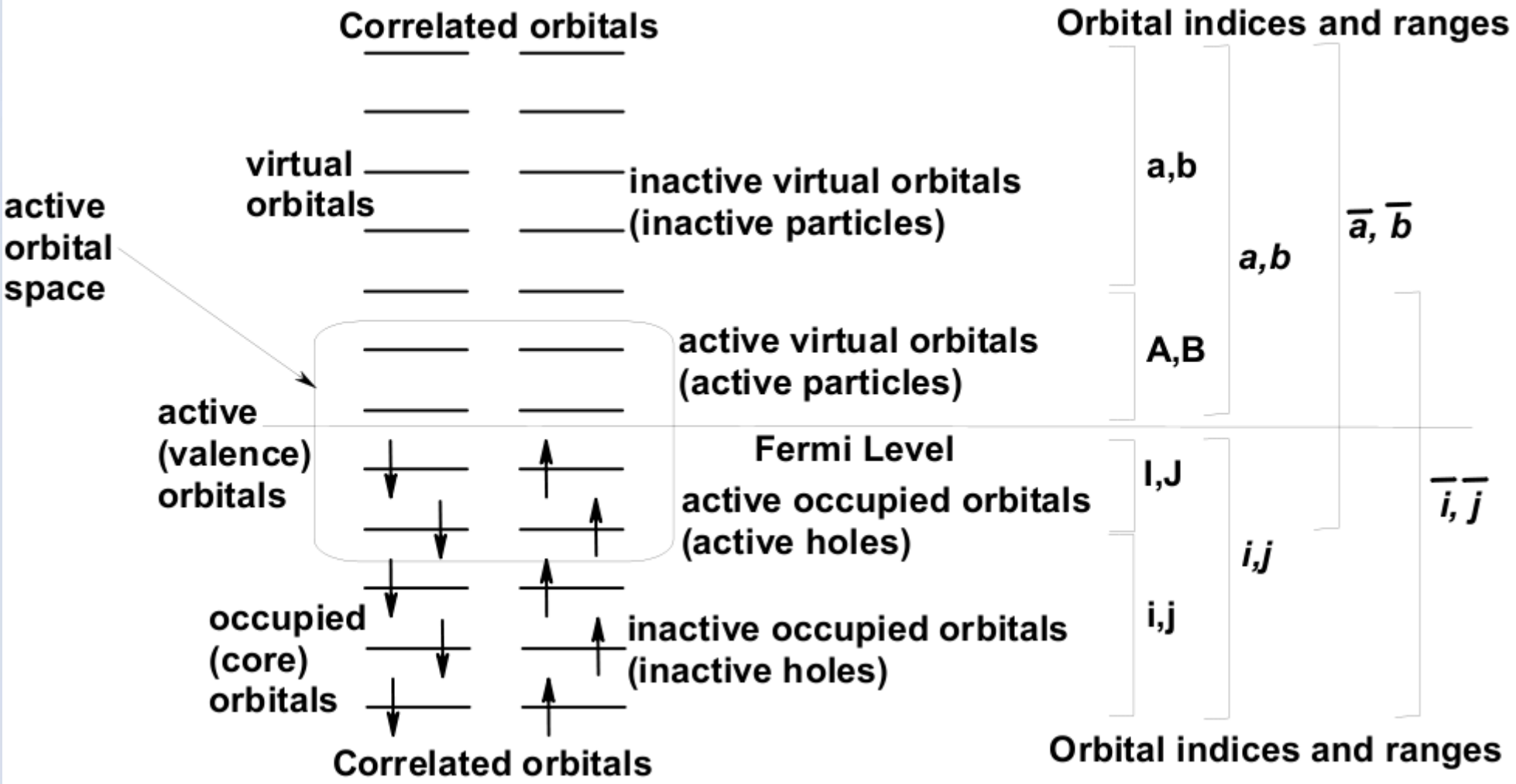
Totally exponential EST: D.I.Lyakh,R.J.Bartlett, Mol. Phys. (under review).

Multireference methods



Active orbital space

- Strongly coupled orbitals, which are essential for reproducing the principal character of the calculated state, form the ***Active Orbital Space*** (AOS).



All distributions of *n* active electrons on *m* active orbitals: CAS(n,m)

MR diagnostics & selection of the active space

- SR ***normal-ordered*** Hamiltonian (SCF energy shifted):

$$\hat{H}_N = \hat{H} - \langle 0|\hat{H}|0\rangle = \sum_{\substack{p_1 \\ q_1}} H_{q_1}^{p_1}\{\hat{p}_1^+ \hat{q}_1^-\} + \sum_{\substack{p_1 p_2 \\ q_1 q_2}} H_{q_1 q_2}^{p_1 p_2}\{\hat{p}_1^+ \hat{p}_2^+ \hat{q}_2^- \hat{q}_1^-\}$$

- Run a preliminary SR calculation of SD level (CISD/CCSD), then analyze the ***complexity*** of the wavefunction obtained:

$$I_C = -\sum_{m=1}^{2} \sum_{\substack{a_1 \dots a_m \\ i_1 \dots i_m}} \frac{\left|C_{i_1 \dots i_m}^{a_1 \dots a_m}\right|^2}{Z} \log_2 \frac{\left|C_{i_1 \dots i_m}^{a_1 \dots a_m}\right|^2}{Z}, \quad Z = \sum_{m=1}^{2} \sum_{\substack{a_1 \dots a_m \\ i_1 \dots i_m}} \left|C_{i_1 \dots i_m}^{a_1 \dots a_m}\right|^2$$

- If the Shannon index exceeds some threshold, determine the ***active orbital space***:

1) The importance of the orbital $p1$ in the CISD wavefunction:

$$\xi(p_1) = \sum_{m=1}^{2} \sum_{p_1 \in \left\{\substack{a_1 \dots a_m \\ i_1 \dots i_m}\right\}} |C_{i_1 \dots i_m}^{a_1 \dots a_m}|^2$$

2) OR Compute and diagonalize the 1-RDM: Occupation Numbers

CAS state-universal HS-MRCC

- N-electron reference wavefunction (0^{th} order):

$$|\Theta_k\rangle = \sum_{\alpha=1}^{D} C_k^{\alpha} |\Phi_\alpha\rangle, \quad P_\alpha = |\Phi_\alpha\rangle\langle\Phi_\alpha|, \quad P = \sum_{\alpha=1}^{D} P_\alpha, \quad \hat{I} = \hat{P} + \hat{Q} + \hat{Q}'$$

- Jeziorski-Monkhorst wave operator:

$$\hat{\Omega} = \sum_{\alpha} \exp\left(\hat{T}_1^{(\alpha)} + \hat{T}_2^{(\alpha)}\right) \hat{P}_\alpha \qquad \hat{T}_m = \frac{1}{m!^2} \sum_{\substack{a_1 \dots a_m \\ i_1 \dots i_m}} t_{i_1 \dots i_m}^{a_1 \dots a_m} \hat{a}_1^+ \dots \hat{a}_m^+ \hat{i}_m^- \dots \hat{i}_1^-$$

$$|\Psi_k\rangle = \hat{\Omega}|\Theta_k\rangle = \sum_{\alpha} C_k^{\alpha} \exp\left(\hat{T}_1^{(\alpha)} + \hat{T}_2^{(\alpha)}\right)|\Phi_\alpha\rangle$$

$$\hat{H}\,\hat{\Omega} = \hat{\Omega}\,\hat{H}\,\hat{\Omega}, \qquad \tilde{H}_{\alpha\beta} = \langle \Phi_\alpha | \left(\hat{H}\,\hat{\Omega}\right)_C | \Phi_\beta \rangle$$

- D N-electron states are obtained simultaneously
- The WF does not satisfy the projected SE: $\hat{Q}\left(\hat{H} - E_k\right)|\Psi_k\rangle \neq 0$
- ***Intruder*** state problem: severe convergence problems
- Not invariant to active orbital rotations
- Does not naturally reduce to an SR method

Solutions to the Intruder State Problem

- Incomplete and general model spaces: Mukherjee, Pal, Meissner, Kucharski, Bartlett, Paldus: different GMS-SU-MRCC: the issue of size-consistency
- State-specific approaches: one state at a time:

$$|\Psi\rangle = \sum_{\alpha} C^{\alpha} \exp(\hat{T}_1^{(\alpha)} + \hat{T}_2^{(\alpha)}) |\Phi_{\alpha}\rangle$$

- Underdefined problem: ***Sufficiency conditions*** (Mukherjee): Different ways of resolving redundancy:

  1) BW-MRCC: only moderate MR, not size-extensive;

  2) Mk-MRCC: only moderate MR, poor for excited states;

  3) sr-MRCC: only moderate MR, poor for excited states;

  4) MRexpT (Hanrath): accurate, but only core-extensive.

- All, except MRexpT, do not satisfy the projected SE: triples become essential → higher cost.
- Yet, all do not naturally reduce to an SR case.

Internally-contracted MRCC

- A single exponential acts on the entire MR reference function as a whole:

$$|\Psi\rangle = \exp(\hat{T}_1 + \hat{T}_2)|\Theta\rangle, \quad \hat{T}_m = \frac{1}{m!^2} \sum_{\substack{\bar{a}_1 \ldots \bar{a}_m \\ \bar{i}_1 \ldots \bar{i}_m}} t^{\bar{a}_1 \ldots \bar{a}_m}_{\bar{i}_1 \ldots \bar{i}_m} \hat{\bar{a}}^+_1 \ldots \hat{\bar{a}}^+_m \hat{\bar{i}}_m \ldots \hat{\bar{i}}_1$$

- Invariance w.r.t. active orbital rotations.
- SE is satisfied in $P+Q$.
- Non-commuting cluster operators: longer BCH expansion: much more diagrams.
- Overparameterized ansatz → SVD.
- The working equations make use of the GWT.
- Mukherjee/Koehn: **ic-MRCC**: chemically accurate, possible SVD dependence and convergence issues.
- Chan, Yanai: **CTCC** (anti-hermitian cluster operator): $\hat{T}_m = -\hat{T}_m$ much larger active spaces are accesible via DMRG; necessary BCH truncation and density cumulant use; possible SVD dependence and convergence issues.

Fock-space MRCC

- FS = Union of HS with different numbers of particles (sectors of the FS): ionization, attachment, excited states...
- Valence-universal wave operator: $\hat{\Omega} = \{\exp(\hat{T}_1 + \hat{T}_2 + \hat{S})\}$

$$|\Psi^{(k,l)}\rangle = \hat{\Omega}|\Phi^{(k,l)}\rangle = \{\exp(\hat{T}_1 + \hat{T}_2 + \hat{S})\}|\Theta^{(k,l)}\rangle$$

$$|\Theta^{(0,1)}\rangle = \sum_I C_I |^I\rangle, \quad |\Theta^{(1,0)}\rangle = \sum_A C^A |_A\rangle, \quad |\Theta^{(1,1)}\rangle = \sum_{I,A} C_I^A |_A^I\rangle$$

Active space

$$\hat{I}^{(k,l)} = \hat{P}^{(k,l)} + \hat{Q}^{(k,l)} + \hat{Q}'^{(k,l)}$$

- Full separability (inter-sector) of the FSMRCC wave operator
- Different components of *S* do not commute → impose ***normal ordering*** w.r.t. to some Slater determinant (Lindgren)
- SEC and valence-universal hierarchical solver: difficulty in getting to higher sectors: Rapidly growing number of diagrams:

$$\hat{Q}^{(k,l)}\left(\hat{H}\, e^{\hat{T}_1+\hat{T}_2}\right)_C e^{\hat{S}}\, \hat{P}^{(k,l)} = \hat{Q}^{(k,l)}\, e^{\hat{S}}\left(\hat{H}\, e^{\hat{T}_1+\hat{T}_2}\right)_C \hat{P}^{(k,l)}$$

Each subsequent (*k*+*l*) must have all preceding solved!

- *T* captures global correlations; *S* delivers local corrections
- Invariant to active orbital rotations
- Orbital relaxation effects become important for higher sectors

Systematic decoupling in the Hamiltonian

- Stolarzcyk & Monkhorst: consecutive SU-FSMRCC ***similarity transformations*** (a generalization of SRCC):

	$\vert 0\rangle$	$\vert {}^{I_1}_{A_1}\rangle$	$\vert {}^{I_1 I_2}_{A_1 A_2}\rangle$	$\vert {}^{i_1}_{a_1}\rangle$	$\vert {}^{i_1 i_2}_{a_1 a_2}\rangle$	Q'
$\langle 0\vert$	E_0					
$\langle {}^{A_1}_{I_1}\vert$	0	S				
$\langle {}^{A_1 A_2}_{I_1 I_2}\vert$	0	0	D			
$\langle {}^{a_1}_{i_1}\vert$	0	0	0			
$\langle {}^{a_1 a_2}_{i_1 i_2}\vert$	0	0	0			
Q'						

Intermediate Hamiltonian FSMRCC

- FSMRCC Bloch equation is also plagued by intruders!
- Malrieu → Mukherjee | Kaldor, Eliav | Meissner, Musial, Bartlett: three Intermediate Hamiltonian formalisms.
- The elegant Meissner's scheme (Musial, Bartlett):

$$\tilde{\bar{\hat{H}}}^{(k,l)} = \bar{\hat{H}}^{(k,l)} + \left(\bar{\hat{H}}\, \hat{Q}'\, e^{\hat{S}} \right)$$

Dressing

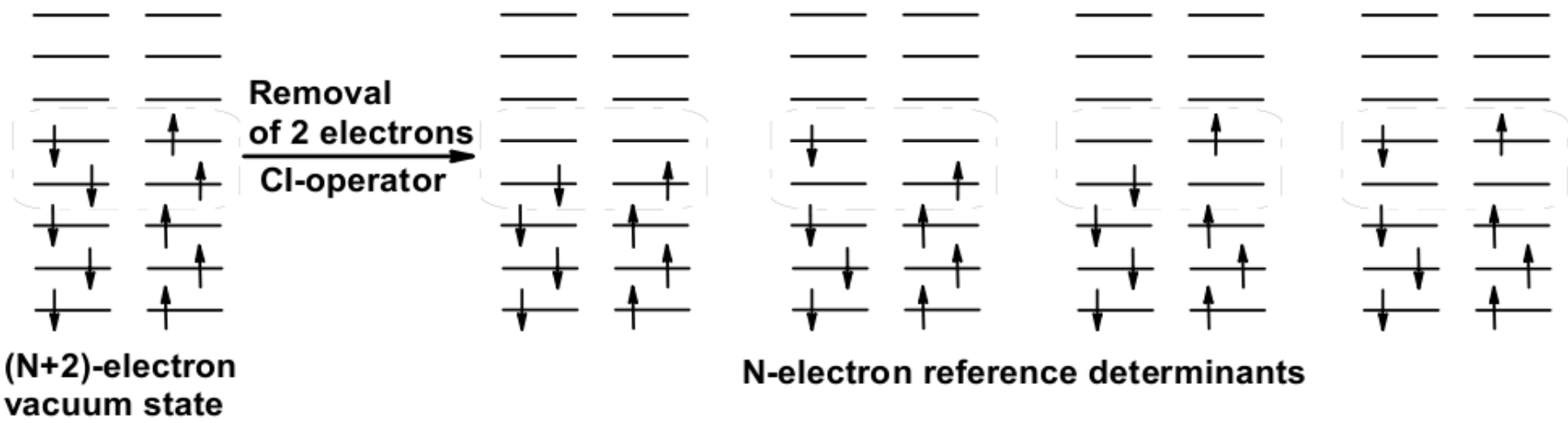
EOMCC similarity transformed Hamiltonian:

$$\bar{\hat{H}}^{(k,l)} \equiv (P+Q)^{(k,l)} \left(e^{-\hat{T}}\, \hat{H}\, e^{\hat{T}} \right) (P+Q)^{(k,l)} = (P+Q)^{(k,l)} \left(\hat{H}\, e^{\hat{T}} \right)_C (P+Q)^{(k,l)}$$

- Meissner's IHFSMRCC is ***equivalent*** to FSMRCC, but without convergence problems (non-linear solver → diagonalization)!
- The IHFSMRCC Hamiltonian is the EOMCC Hamiltonian + specific ***Dressing*** term which depends on the FSMRCC cluster amplitudes from preceding sectors.
- Also EOMCCx (Musial, Bartlett); STEOM (Nooijen, Bartlett).

EOM based MRCC

- MR-MI/MA-EOMCC scheme of Bartlett & Musial: $|\Psi\rangle = \hat{R}\, e^{\hat{T}} |0\rangle$



Higher excitations can be required in the EOM CI operator.

- Also SF-EOMCC scheme of Krylov et al.
- pIC-MR-EOMCC scheme of Nooijen et al: $|\Psi\rangle = \hat{R}\, e^{\hat{T}} |\Theta\rangle$
- All above: assumption on the transferability of the electron correlation. Orbital relaxtion effects (similar to FSMRCC).
- Multiple electronic states can be accessed simultaneously.

Alternative CAS/GMS MRCC schemes

- Single-reference based MRCC (SRMRCC):

$$|\Psi\rangle = \hat{\Omega}|\Theta_{MR}\rangle = \exp(\hat{T}_1 + \hat{T}_2 + \tilde{\hat{T}}_3 + \ldots + \tilde{\hat{T}}_m)|0\rangle$$

Constructing the same MR wavefunction, but starting from a single Slater determinant (Oliphant & Adamowicz)

- CASCCSD (Ivanov, Lyakh, Adamowicz): all singles and doubles from a multidimensional reference function $|\Theta_{MR}\rangle$:

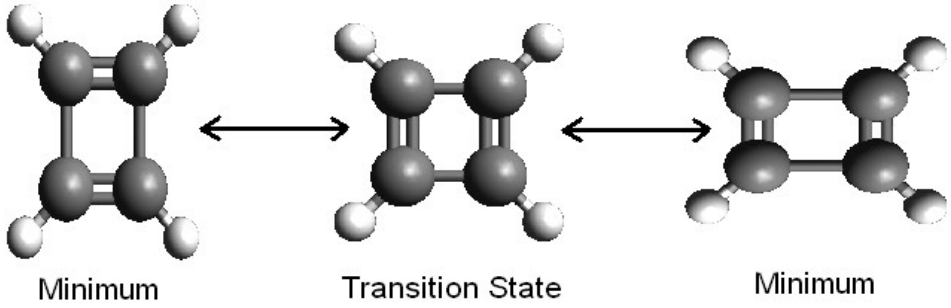
$$|\Psi\rangle = \hat{\Omega}|\Theta_{MR}\rangle = \exp\left(\hat{T}'_1 + \hat{T}'_2 + \tilde{\hat{T}}'_3 + \ldots + \tilde{\hat{T}}'_m\right)\left(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \ldots + \hat{C}_m\right)|0\rangle$$

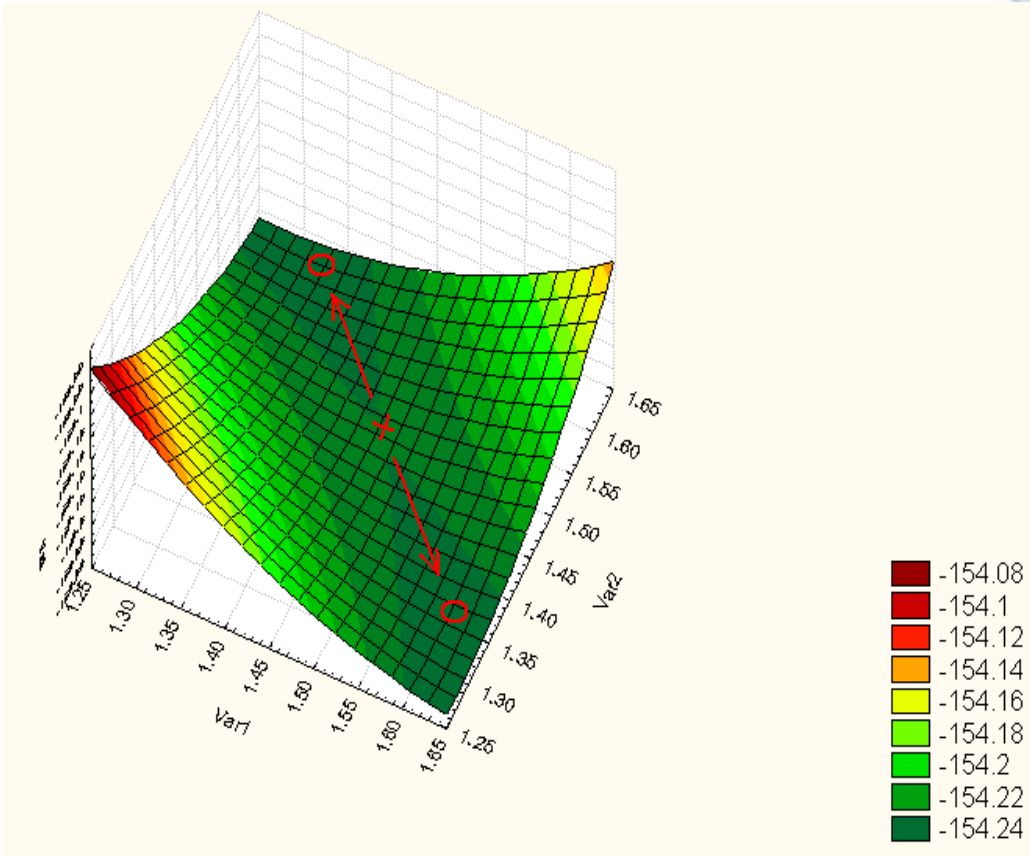
- Chemical accuracy in many severe cases (N2, C2)
- Much more diagrams; much larger scaling prefactor due to the inclusion of ***selected*** higher excitations (still $O(N\text{^}6)$)
- Not invariant w.r.t. the choice of the reference determinant (a symmetry distortion can occur, discontinuity)
- Related methods: RMRCCSD (Paldus) uses MRCI; TCCSD (Kinoshita, Bartlett, et al) lacks *P*-*Q* coupling.

D.I. Lyakh, V.V.Ivanov, L. Adamowicz, J. Chem. Phys. 122, 024108 (2005)
D.I. Lyakh, V.V.Ivanov, L. Adamowicz, J. Chem. Phys. 128, 074101 (2008)

Automerization of cyclobutadiene

Method	Barrier
CCSD	23.2
CCSD(T)	18.3
Mk-MRCCSD(T)	8.9
SU-MRCCSD(T)	5.9
TCCSD(T)	7.0
Experiment	1.6-10.0





D.I.Lyakh, V.Lotrich, R.J.Bartlett, Chem. Phys. Lett. 501, 166 (2011)

Problems with SRCC/MRCC ansaetze

- **Chemical reactions**: the structure of the active space can easily change along the PES: SR regions, MR regions → necessity of maintaining the largest active space (expensive); the lack of natural reduction to an SR problem.
- The size of the active space affects the computational cost **exponentially**! (CASSCF → DMRG, TNS, GCF, GHF).
- Not ”black box” enough → Lambda-CCSD(T) (Kucharski, Taube, Bartlett), CCSD(TQ) (Bartlett), perturbative CRCC & MMCC (Piecuch et al) methods: except the (2,2) cases, one has an ***unbalanced*** and ***incomplete*** treatment of the MR 1st order interaction space; divergence of the perturbation theory (e.g., in N2); **UHF** behaves much better.
- Standard (SRCC/MRCC) methods have a ***fixed*** form of the correlated ansatz: the complexity of the CC ansatz used often ***does not match*** the complexity of the electronic state!
- Poor error control.

Adaptive CC: @CC

- Let us further exploit the flexibility of the exponential ansatz, following the ideas from the importance-selected CI:

  @CC ansatz: $|\Psi\rangle = e^{\tilde{\hat{T}}_1 + \tilde{\hat{T}}_2 + \ldots \tilde{\hat{T}}_m}|0\rangle$: No restrictions on m and $\tilde{\hat{T}}_k$ structure!

- Once all important cluster amplitudes are included in the @CC ansatz, all important correlations are accounted for, the problem is solved (SR or MR).
- **Adaptivity**: New (important) amplitudes are gradually added into the @CC ansatz until the convergence of the size-intensive quantity of interest is achieved (complexity matching): naturally reduces to SR when the MR character is lost.
- Given a good discriminatory function (DF), a fast convergence to the Full CI answer can be achieved: proper topological properties of DF.
- No need in active space.
- Each $\tilde{\hat{T}}_k$ operator becomes **sparse** when using ***localized*** orbitals (ACCSD of Auer and Nooijen).
- For any desired ***relative accuracy*** in the correlation energy, the number of @CC amplitudes will grow ***linearly*** with the system size (in a local basis). In contrast, the number of CI coefficients will grow at least ***quadratically***!
- Still, @CC can be computationally expensive for some problems.
- Requires a good initial guess for excited states.
- Can have spin contaminations (though controlable).

D.I.Lyakh, R.J. Bartlett, J. Chem. Phys. 133, 244112 (2010)

MRCC problems yet to be addressed

- ***Very large*** model spaces (CASSCF → DMRG, TNS, GHF): GWT.
- ***Orbital relaxation*** for FS-MRCC/MR-EOMCC.
- ***Adaptivity***: reasonable error control in the method (+basis).
- ***Locality*** exploitation.
- ***Iteration convergence*** control.
- ***Non-adiabatic*** extensions (conical intersections, avoided crossings).
- ***Push a button***: Advanced internal logic built-in into an MRCC method which will tune all the internal parameters of the method with respect to the calculated system.
- ***Heterogeneity*** of the working equations: Usually, the MRCC equations have much more terms (diagrams), each of which may have very different scaling.
- Efficient (and usable) ***parallel*** implementation, including the analytical energy ***gradients*** and molecular properties.

Automated symbolic algebra

- Working equations of advanced quantum many-body methods (e.g., MRCC) can consist of thousands of tensor expressions of significantly varying computational costs.
- Fully automated approach: Formal model → Working equations (tensor expressions) → factorized equations → cost-optimized sequence of elementary tensor operations to perform → parallel code written either in a domain specific language (like SIAL in ACESIII) or regular language (Fortran, C), or direct interpretation (in progress now at UF/OSU: hybrid parallelization, optimized data distribution and data processing).
- **DIAGEN** (D.I.L.): (a) arbitrary rank/structure tensors; (b) enhanced support of MR methods, active/inactive indices; (c) non-commutative exponentials; (d) massive parallelism via data locality (in progress).

V.V.Ivanov, D.I.Lyakh, Kharkiv University Bulletin: Chemistry 549, 15 (2002)
D.I.Lyakh, V.V.Ivanov, L.Adamowicz, J. Chem. Phys 122, 024108 (2005)
D.I.Lyakh, R.J.Bartlett, 50th Sanibel Symposium, Feb 2010.

DIAGEN input

```
<domain name="DIP-EOMCC: active space">
set H12=ham(1)+ham(2)
set P0=P()
set Q0=P(2i+;2J+)
set Q1=P(3i+;1a-;2J+)
set Q2=P(4i+;2a-;2J+)
set R0=C(2i-;2J-)
set R1=C(3i-;1a+;2J-)
set R2=C(4i-;2a+;2J-)
set R012=C(2i-;2J-)+C(3i-;1a+;2J-)+C(4i-;2a+;2J-)
set T12=S(1i-;1a+)+S(2i-;2a+)

product Q0*H12*expn(T12,4,8)*R012*P0
 connect(2,3)(2,4)

product Q1*H12*expn(T12,4,8)*R012*P0
 connect(2,3)(2,4)

product Q2*H12*expn(T12,4,8)*R012*P0
 connect(2,3)(2,4)

input H(1i+;1i-)
input H(1i+;1a-)
input H(1a+;1i-)
input H(1a+;1a-)
input H(2i+;2i-)
input H(2i+;1i-;1a-)
input H(2i+;2a-)
input H(1i+;1a+;2i-)
input H(1i+;1a+;1i-;1a-)
input H(1i+;1a+;2a-)
```

DIAGEN output

$$(285)\quad 192.3.896 : Z^{A^b_1}_{I^a_1 I^a_2 I^b_1} += H^{l^a_1 K^a_1}_{d^a_1,d^a_2} S^{d^a_1}_{I^a_1} S^{d^a_2}_{I^a_2} C^{A^b_1}_{I^b_1,l^a_1 K^a_1} \cdot +1/2$$

$$(286)\quad 198.1.932 : Z^{A^b_1}_{I^a_1 I^a_2 I^b_1} += H^{l^b_1,l^b_2}_{d^b_1,d^b_2} S^{d^b_1}_{I^b_1} S^{d^b_2}_{l^b_1} C^{A^b_1}_{I^a_1 I^a_2,l^b_2}$$

$$(287)\quad 198.2.933 : Z^{A^b_1}_{I^a_1 I^a_2 I^b_1} += H^{l^b_1,l^a_1}_{d^a_1,d^b_1} S^{d^a_1}_{I^a_1} S^{d^b_1}_{l^b_1} C^{A^b_1}_{I^a_2 I^b_1,l^a_1}$$

$$(288)\quad 198.4.935 : Z^{A^b_1}_{I^a_1 I^a_2 I^b_1} += H^{l^a_1,l^b_1}_{d^b_1,d^a_1} S^{d^b_1}_{I^b_1} S^{d^a_1}_{l^a_1} C^{A^b_1}_{I^a_1 I^a_2,l^b_1}$$

$$(289)\quad 198.5.936 : Z^{A^b_1}_{I^a_1 I^a_2 I^b_1} += H^{l^a_1,l^a_2}_{d^a_1,d^a_2} S^{d^a_1}_{I^a_1} S^{d^a_2}_{l^a_1} C^{A^b_1}_{I^a_2 I^b_1,l^a_2}$$

$$(290)\quad 202.1.946 : Z^{A^b_1}_{I^a_1 I^a_2 I^b_1} += H^{l^b_1,K^a_1}_{d^a_1 d^b_1} S^{A^b_1}_{l^b_1} S^{d^a_1 d^b_1}_{I^a_1 I^b_1} C_{I^a_2,K^a_1}$$

$$(447)\quad 324.85.1.1.3.1.0.20333376.09 : Z^{l^b_1}_{I^a_1 I^a_2 i^b_1} += H^{l^b_1,l^b_2}_{i^b_1,d^b_1} C^{d^b_1}_{I^a_1 I^a_2,l^b_2} \cdot -1.$$

$$(448)\quad 331.86.1.1.2.1.0.10042704.09 : Z^{l^b_1}_{I^a_1 I^a_2 i^b_1} += H^{l^b_1,K^a_1}_{I^a_1,d^b_1} C^{d^b_1}_{I^a_2 i^b_1,K^a_1} \cdot -1.$$

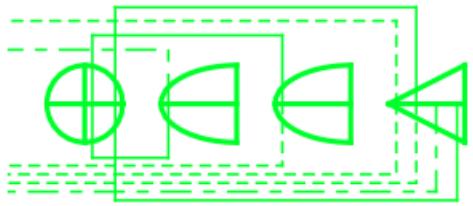
$$(449)\quad 325.85.1.1.3.1.0.20333376.09 : Z^{l^b_1}_{I^a_1 I^a_2 i^b_1} += H^{l^b_1,l^a_1}_{i^b_1,d^a_1} C^{d^a_1}_{I^a_1 I^a_2,l^a_1} \cdot -1.$$

$$(450)\quad 821.177.2.1.2.1.0.49593600.07 : Z^{l^b_1}_{I^a_1 I^a_2 i^b_1} += S^{d^b_1}_{i^b_1} R^{l^b_1}_{I^a_1 I^a_2,d^b_1} \cdot -1.$$

$$(451)\quad 938.199.1.2.2.2.0.11716488.10 : R^{l^b_1,K^a_1}_{I^a_1 i^b_1} += H^{l^b_1,K^a_1}_{d^a_1 d^b_1} S^{d^a_1 d^b_1}_{I^a_1 i^b_1}$$

```
##ORMO        847; Diagram     182; Scaling  1/ 1/ 0.12553380D+08
#Z50(A1b|I1aI2aI1b)+=C44(d1b|I1aI2a,l1b)*R481(A1b,l1b|I1b,d1b)
 PARDO I1b,I1a,I2a,A1b
  WHERE I1a<=I2a
  pref=1.0
  lpref=1.0
  npref=1.0
  A50(I1b,I1a,I2a,A1b)=0.0
  DO d1b
   DO l1b
    get C44(I1a,I2a,l1b,d1b)
    get R481(I1b,A1b,d1b,l1b)
    T50(I1b,I1a,I2a,A1b)=C44(I1a,I2a,l1b,d1b)*R481(I1b,A1b,d1b,l1b)
    A50(I1b,I1a,I2a,A1b)+=T50(I1b,I1a,I2a,A1b)
   ENDDO l1b
  ENDDO d1b
  put Z50(I1b,I1a,I2a,A1b)+=A50(I1b,I1a,I2a,A1b)
 ENDPARDO I1b,I1a,I2a,A1b
```

960



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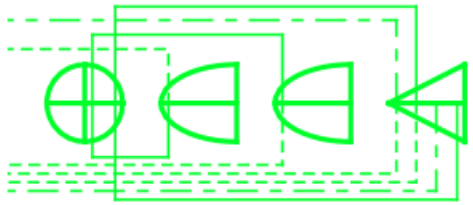

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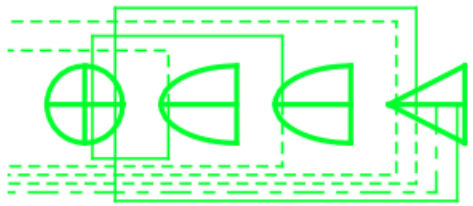

Epoch of massive parallelism

- An increase in computational power is governed by the increasing level of parallelism
- Many new computer architectures include accelerators (GPU, Intel MIC) => non-trivial task-scheduling problem due to heterogeneity of the computer architecture => maximization of the communication/computation overlap (data prefetching)
- For massively parallel computers, a global minimization of MPI communications is vital => exploration of data locality
- For GPUs: not every tensor operation can take advantage
- In progress: Automated parallel MPI/OMP/GPU framework for tensor algebra (Florida UF, Columbus OSU)

Conclusions: Complexity requires complexity

- Many open-shell systems are already accessible by existing MRCC methods (~10 open-shell particles)
- Efficient treatment of large active spaces
- Efficient analytical gradients and properties
- Reasonable approximations to reduce the cost
- Locality exploitation
- Adaptivity
- Iteration convergence control
- Efficient parallelization

THANK YOU!