A two-pronged approach to electron correlation in RDMFT

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New Challenges in RDMFT
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Outline

1. Static and dynamic correlation
2. ΔNO method
3. Bond dissociation
4. Conclusions and Future Work

The correlation problem

Correlation Energy

$$E_c = \mathcal{E} - E_{\text{RHF}} \quad \text{(Löwdin, 1959)}^{1}$$

- Error due to approximation of Ψ by a Slater determinant of MOs.
- Generally required for chemically accurate calculations.

The correlation problem

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- Generally required for chemically accurate calculations.

A useful decomposition

$$E_c = E_{\text{stat}} + E_{\text{dyn}}$$

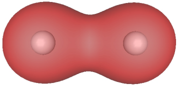
- Characterize significantly different failures of Ψ_{RHF}.
- Methods vary in their ability to capture both.

(1) P-O Löwdin *Adv. Chem. Phys.* **1959**, *2*, 207-322.
(2) DKW Mok, R Neumann and NC Handy *J. Chem. Phys.* **1996**, *100*, 6225-6230.

The static correlation problem

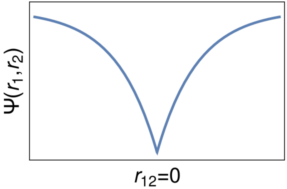
Static correlation, E_{stat}

- *Cause:* near-degeneracy of Slater determinant configurations.
- *Effect:* different spatial distribution of e⁻s.
- *Example:* H_2 at large internuclear separation.
- *Remedy:* Multi-configurational (reference) wavefunction (MCSCF).



(1) DKW Mok, R Neumann and NC Handy *J. Chem. Phys.* **1996**, *100*, 6225-6230.
(2) JW Hollett and PMW Gill *J. Chem. Phys.* **2011**, *134*, 114111.

The dynamic correlation problem



Dynamic correlation, E_{dyn}

- *Cause:* Inability of Slater determinant to describe relative e⁻ motion.
- *Includes:* e⁻-e⁻ cusp and dispersion
- *Example:* He atom
- *Remedy:* CCSD(T)-F12

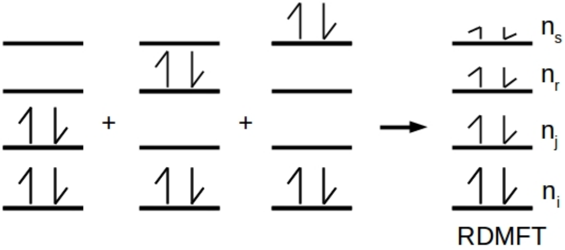
(1) W Klöpper and W Kutzelnigg *J. Phys. Chem.* **1990**, *94*, 5625-5630.
(2) J Noga and W Kutzelnigg *J. Chem. Phys.* **1994**, *101*, 7738.

Two prongs

Static correlation prong

Key aspects:

- Relatively few configurations
- Optimized orbitals
- All configs. within active space?

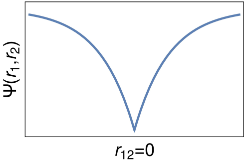


Two prongs

Dynamic correlation prong

Key aspects:

- *Universal*, present in single or multi-reference
- WF-like approach converges slowly with 1e-basis.



$\Longrightarrow \quad \Gamma[\boldsymbol{R},\boldsymbol{R}] \quad \Longrightarrow$ density functional

The ΔNO energy expression

A “hybrid” cumulant functional

$$E_{\Delta\text{NO}} = E^{0}_{\text{1-RDM}} + E^{\Delta\text{NO}}_{\text{pair}} + E^{\Delta\text{NO}}_{\text{stat}} + E^{\Delta\text{NO}}_{\text{dyn}}$$

The ΔNO energy expression

A "hybrid" cumulant functional

$$E_{\Delta\text{NO}} = E^0_{\text{1-RDM}} + E^{\Delta\text{NO}}_{\text{pair}} + E^{\Delta\text{NO}}_{\text{stat}} + E^{\Delta\text{NO}}_{\text{dyn}}$$

cumulant

$$E^{\Delta\text{NO}}_q = E^{\Delta\text{NO}}_{\text{pair}} + E^{\Delta\text{NO}}_{\text{stat}} + E^{\Delta\text{NO}}_{\text{dyn}}$$

- *static* $\implies$ RDMFT
- *dynamic* $\implies$ (on-top) density functional

JWH, H Hosseini and C Menzies *J. Chem. Phys* **2016**, *145*, 084106.

The RDMs

1-RDM

$$\gamma(\mathbf{x}, \mathbf{x}') = N \int \Psi(\mathbf{x}', \mathbf{x}_2, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N) d\mathbf{x}_2 \ldots \mathbf{x}_N$$

- spin coordinates: $\mathbf{x} = (\boldsymbol{r}, \omega)$
- one-electron density: $\rho(\boldsymbol{r}) = \int \gamma(\mathbf{x}, \mathbf{x}) d\omega$
- ONs and NOs: $\int \gamma(\mathbf{x}, \mathbf{x}')\phi_a(\mathbf{x}')d\mathbf{x}' = n_i \phi_a(\mathbf{x})$

2-RDM

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2') = \frac{N(N-1)}{2} \int \Psi(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_3, \ldots, \mathbf{x}_N) \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N) d\mathbf{x}_3 \ldots \mathbf{x}_N$$

- 1-RDM: $\gamma(\mathbf{x}, \mathbf{x}') = \frac{2}{N-1} \int \Gamma(\mathbf{x}, \mathbf{x}_2, \mathbf{x}', \mathbf{x}_2) d\mathbf{x}_2$

Zeroth-order 1-RDM energy

$$E_{\text{1-RDM}}[\gamma] = \int \left[\left(-\frac{1}{2}\nabla_{\boldsymbol{r}}^2 - \sum_{A=1}^{M} \frac{Z}{|\boldsymbol{r} - \boldsymbol{R}_A|} \right) \gamma(\mathbf{x}, \mathbf{x}') \right]_{\mathbf{x}'=\mathbf{x}} d\mathbf{x} + \frac{1}{2} \int \frac{\gamma(\mathbf{x}_1, \mathbf{x}_1)\gamma(\mathbf{x}_2, \mathbf{x}_2) - \gamma(\mathbf{x}_1, \mathbf{x}_2)\gamma(\mathbf{x}_2, \mathbf{x}_1)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 + E_q[\gamma]$$

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Zeroth-order component expanded in a basis (open-shell):

$$E^0_{\text{1-RDM}} = \sum_a^{\text{cl}} 2n_a h_{aa} + \sum_a^{\text{op}} n_a h_{aa} + \sum_{ab}^{\text{cl}} n_a n_b \left(2J_{ab} - K_{ab}\right) + \sum_a^{\text{op}} \sum_b^{\text{cl}} n_a n_b \left(2J_{ab} - K_{ab}\right) + \sum_{ab}^{\text{op}} \frac{n_a n_b}{2} \left(J_{ab} - K_{ab}\right)$$

JWH and N Pegoretti *in prep.*

Zeroth-order 1-RDM energy

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$$+ \sum_a^{\text{op}} \sum_b^{\text{cl}} n_a n_b \left(2J_{ab} - K_{ab}\right) + \sum_{ab}^{\text{op}} \frac{n_a n_b}{2} \left(J_{ab} - K_{ab}\right)$$

Integrals over NOs:

$$h_{aa} = \int \phi_a^*(\boldsymbol{r}) \left(-\tfrac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{r_A}\right) \phi_a(\boldsymbol{r}) d\boldsymbol{r}$$

$$J_{ab} = \int \phi_a^*(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2) \frac{1}{r_{12}} \phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$K_{ab} = \int \phi_a^*(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2) \frac{1}{r_{12}} \phi_b(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

Transferring electrons

Extended Löwdin-Shull wave function (Restricted 2n-tuple MR-SCF)

$$\Psi_{\text{ELS}} = c_0 \Psi_{\text{HF}} + \sum_{ir} c_{ir} \Psi_{i\bar{i}}^{r\bar{r}} + \frac{1}{4} \sum_{ijrs} c_{ijrs} \Psi_{i\bar{i}j\bar{j}}^{r\bar{r}s\bar{s}} + \dots$$

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Occupation numbers (ONs)

$$n_i = 1 - \sum_r \left(c_{i\bar{i}}^{r\bar{r}}\right)^2 - \frac{1}{2} \sum_{jrs} \left(c_{i\bar{i}j\bar{j}}^{r\bar{r}s\bar{s}}\right)^2 - \ldots$$

$$n_r = \sum_i \left(c_{i\bar{i}}^{r\bar{r}}\right)^2 + \frac{1}{2} \sum_{ijs} \left(c_{i\bar{i}j\bar{j}}^{r\bar{r}s\bar{s}}\right)^2 + \ldots$$

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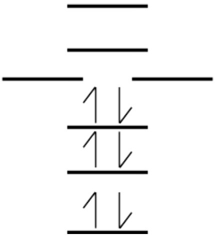
Electron transfer

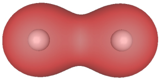
$$n_i = 1 - \sum_r \Delta_{ir}$$

$$n_r = \sum_i \Delta_{ir}$$

Electron transfer and near-degeneracy

Restricted $2n$-tuple excitations to near-degenerate orbitals.





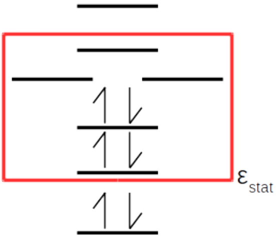
Near-degeneracy

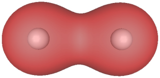
$$\epsilon_r - \epsilon_i < \epsilon_{\text{stat}}$$

ϵ_{stat} - system specific threshold

Electron transfer and near-degeneracy

Restricted 2n-tuple excitations to near-degenerate orbitals.





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ΔNO cost $\Longrightarrow N_{\text{act}} K^4$

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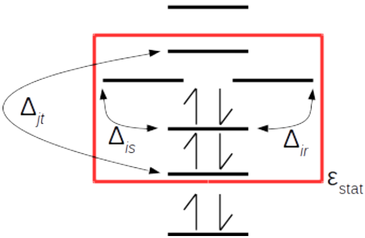

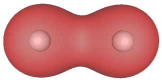

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Pair correction

For non-integer ONs the number of electron pairs is incorrect.

$$\int \Gamma^0_{\text{1RDM}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{N(N-1)}{2}, \quad \text{only if } n_i = 0, 1$$

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$$E^{\Delta\text{NO}}_{\text{pair}} = \sum_i n_i (1 - n_i) J_{ii} + \sum_{ir} \Delta_{ir} (n_r - n_i - \Delta_{ir}) (4J_{ir} - K_{ir}) - \sum_{a \neq b} \eta_{ab} (2J_{ab} - K_{ab})$$

$$\eta_{ab} = \begin{cases} \sum_r \Delta_{ir}\Delta_{jr}, & a, b \in \{i, j\} \\ \sum_i \Delta_{ir}\Delta_{is}, & a, b \in \{r, s\} \\ 0, & \text{otherwise} \end{cases}$$

Pair correction

$$E_{\text{pair}}^{\Delta\text{NO}} = \sum_i n_i \left(1 - n_i\right) J_{ii} + \sum_{ir} \Delta_{ir} \left(n_r - n_i - \Delta_{ir}\right) \left(4J_{ir} - K_{ir}\right) - \sum_{a \neq b} \eta_{ab} \left(2J_{ab} - K_{ab}\right)$$

$$\int \Gamma^0_{\text{1RDM}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_2) + \Gamma^{\Delta\text{NO}}_{\text{pair}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 = \frac{N(N-1)}{2}, \text{ for all } \Delta_{ir}$$

Static correlation

$$E = \langle \Psi_{\text{ELS}} | \hat{H} | \Psi_{\text{ELS}} \rangle$$

Static correlation

$$E_{\text{stat}}^{\Delta\text{NO}} = -\sum_{ir} \sqrt{n_i \Delta_{ir}} \left(L_{ir} + L_{ri} \right) + \sum_{\substack{ab \\ a \neq b}} \zeta_{ab} L_{ab}$$

Time-inversion-exchange integral

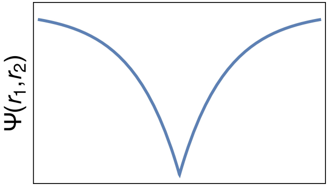
$$L_{ir} = \int \phi_i^*(\boldsymbol{r}_1) \phi_i^*(\boldsymbol{r}_2) r_{12}^{-1} \phi_r(\boldsymbol{r}_1) \phi_r(\boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

$$\int \Gamma_{\text{stat}}^{\Delta\text{NO}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_2) d\boldsymbol{r}_1 d\boldsymbol{r}_2 = 0, \quad \text{for all } \Delta_{ir}$$

Dynamic Correlation

$$E_{\text{dyn}}^{\Delta\text{NO}} = E_{\text{sr-dyn}}^{\Delta\text{NO}} + E_{d}^{\Delta\text{NO}}$$

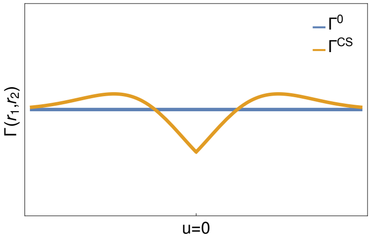
- Long-range dynamic correlation is dispersion, E_d
- Short-range dynamic correlation is modelled with on-top 2-RDM.



$$E_{\text{sr-dyn}}^{\Delta\text{NO}} = E_{\text{sr-dyn}}[\Gamma^{\Delta\text{NO}}(\boldsymbol{R}, \boldsymbol{R})]$$

Short-range dynamic correlation

Colle-Salvetti Functional



Cusp condition

$$\lim_{u \to 0} \Gamma(\boldsymbol{r}_1, \boldsymbol{r}_2) = \Gamma(\boldsymbol{R}, \boldsymbol{R})\,(1 + u + \dots)$$

$$\boldsymbol{u} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \quad \boldsymbol{R} = \frac{\boldsymbol{r}_1 + \boldsymbol{r}_2}{2}$$

Correlation length

$$e^{-\beta(\boldsymbol{R})^2 u^2}, \quad \beta(\boldsymbol{R}) = q\rho(\boldsymbol{R})^{1/3}$$

Short-range dynamic correlation

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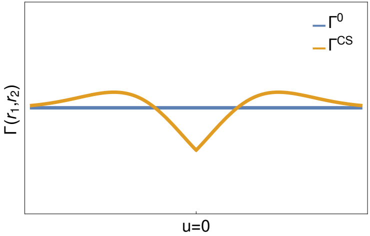

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Correlation length

$$e^{-\beta(\boldsymbol{R})^2 u^2}, \quad \beta(\boldsymbol{R}) = q\rho(\boldsymbol{R})^{1/3}$$

$$E_{\mathrm{CS}}\left[\Gamma^0(\boldsymbol{R},\boldsymbol{R})\right] = -4a\int \frac{\Gamma^0(\boldsymbol{R},\boldsymbol{R})}{\rho(\boldsymbol{R})}\left(\frac{1 + b\rho(\boldsymbol{R})^{-8/3}\, e^{-c\rho(\boldsymbol{R})^{-1/3}}\left[\nabla^2_{\boldsymbol{u}}\Gamma^0\left(\boldsymbol{R}+\frac{\boldsymbol{u}}{2}, \boldsymbol{R}-\frac{\boldsymbol{u}}{2}\right)\right]_{\boldsymbol{u}=0}}{1 + d\rho(\boldsymbol{R})^{-1/3}}\right) d\boldsymbol{R}$$

$a = 0.049, \quad b = 0.132, \quad c = 0.2533,$ and $d = 0.349$

R Colle and O Salvetti *Theor. Chim. Acta*, **1975**, *37*, 329.

A cumulant functional

$$E_q^{\Delta\text{NO}} = E_{\text{pair}}^{\Delta\text{NO}} + E_{\text{stat}}^{\Delta\text{NO}} + E_{\text{dyn}}^{\Delta\text{NO}}$$

- $E_{\text{pair}}^{\Delta\text{NO}}$ and $E_{\text{stat}}^{\Delta\text{NO}}$ are functionals of $\{\phi_a\}$ and $\{\Delta_{ir}\}$
- $E_{\text{sr-dyn}}^{\Delta\text{NO}}$ is a functional of $\Gamma^{\Delta\text{NO}}(\boldsymbol{R}, \boldsymbol{R})$
- No E_d yet.
- Requires simultaneous optimization of $\{\phi_a\}$ and $\{\Delta_{ir}\}$
- Scales as $N_{\text{act}} N^4$

A practical algorithm

1. Obtain guess ONs and NOs (*eg.* $\phi_a = \phi_a^{\text{ROHF}}$ and $n_a = n_a^{\text{ROHF}}$)
2. Optimize $\{\Delta_{ir}\}$ using a Newton-Raphson procedure.
   - $\Delta_{ir} = \cos^2\theta_{ir}$
3. Hermitize $\boldsymbol{\lambda}$

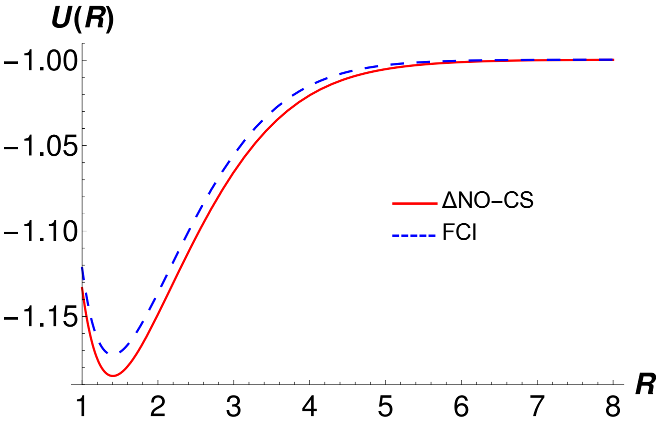
$$\lambda_{cd} = \int \frac{\delta E_{\Delta\text{NO}}}{\delta\phi_c(\boldsymbol{x})}\phi_d(\boldsymbol{x})d\boldsymbol{x}$$

   - orbital rotation (quick convergence)
   - iterative diagonalization (reliable minimum)
4. Check for convergence of ONs ($\{\Delta_{ir}\}$) and NOs ($\boldsymbol{\lambda}$), return to 2 if necessary.

M Piris and JM Ugalde *J. Comput. Chem.* **2009**, *30*, 2078.

H_2 bond dissociation

cc-pVTZ

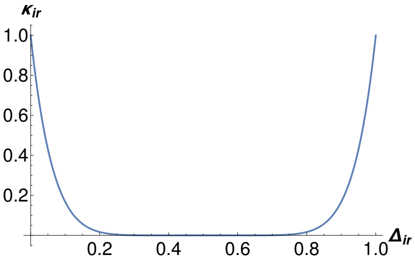


Reducing double-counting

$$L^{\kappa}_{ir} = (1 - \kappa_{ir})L_{ir} + \kappa_{ir}L^{\text{lr}}_{ir}$$

Long-range time-inversion-exchange integral:

$$L^{\text{lr}}_{ir} = \int \phi^*_i(\boldsymbol{r}_1)\phi_r(\boldsymbol{r}_1)\frac{\text{erf}(\omega r_{12})}{r_{12}}\phi^*_i(\boldsymbol{r}_2)\phi_r(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2$$



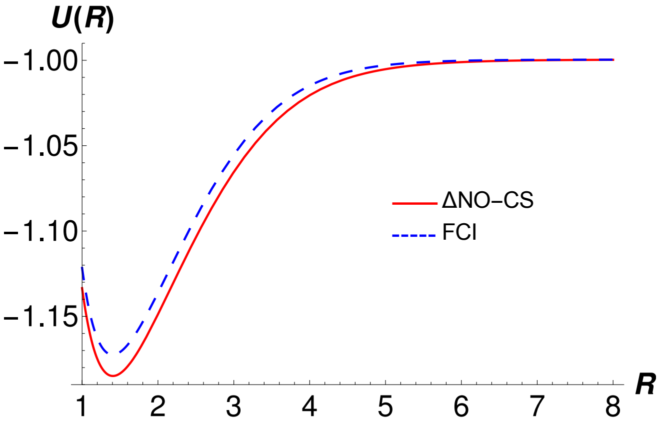
$$\kappa_{ir} = |1 - 2\Delta_{ir}|^{\alpha}$$

ΔNOκ-CS

$$L_{ir} \to L^{\kappa}_{ir}, \qquad \omega = 1 \text{ and } \alpha = 8$$

H_2 bond dissociation

cc-pVTZ



H_2 bond dissociation

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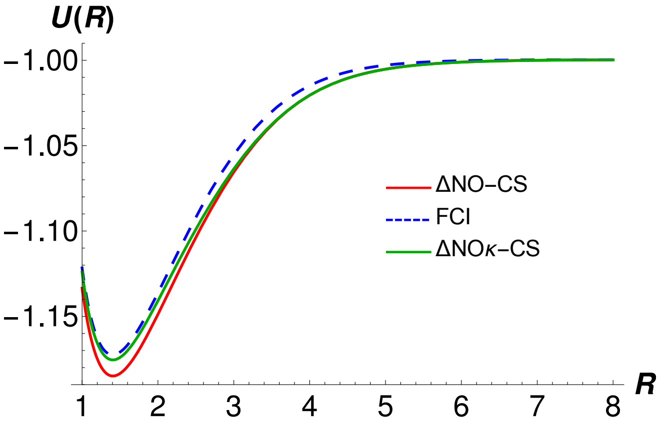

H_2 bond dissociation

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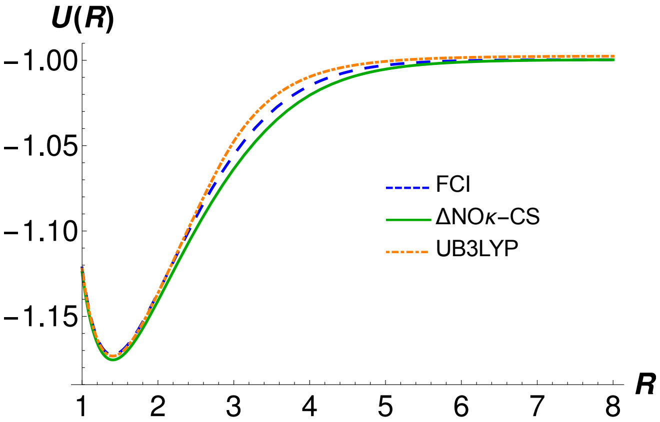
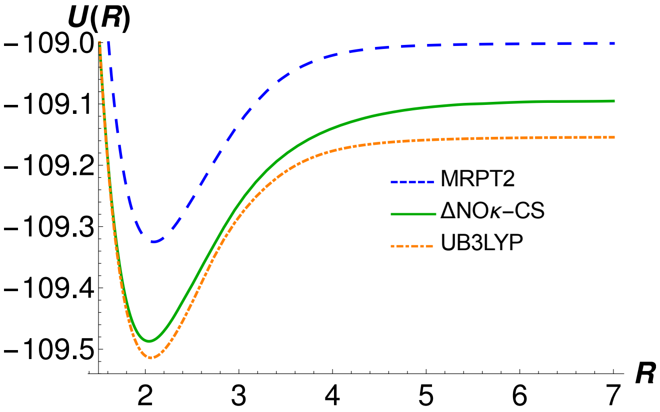


N_2 bond dissociation

cc-pVTZ



Diatomics

cc-pVTZ

Equilibrium bond lengths (Bohr)

Molecule	UB3LYP	FCI/MRPT2	PNOF6[a]	ΔNOκ-CS	Expt.[b]
H_2	1.405	1.404	1.427	1.406	1.401
LiH	3.014	3.027	3.090	3.027	3.014
HF	1.744	1.747	1.727	1.702	1.733
F_2	2.644	2.707	2.750	2.828	2.668
N_2	2.062	2.090	2.048	2.040	2.075

[a]M Piris *J. Chem. Phys.* **2014**, *141*, 044107.
[b]NIST Standard Reference Database No. 101, Release 16a (NIST, 2013) available at http://cccbdb.nist.gov/.

Diatomics

cc-pVTZ

Dissociation energies (kJ mol^{-1})

Molecule	UB3LYP	FCI/MRPT2	PNOF6[a]	ΔNOκ-CS	Expt.[b]
H_2	461	454	399	462	458
LiH	242	236	187	248	243
HF	574	574	498	526	590
F_2	158	162	92	88	164
N_2	944	850	930	1029	955

[a] M Piris *J. Chem. Phys.* **2014**, *141*, 044107.
[b] http://www.nist.gov/srd/monogr.cfm.

Conclusions and Future Work

Conclusions

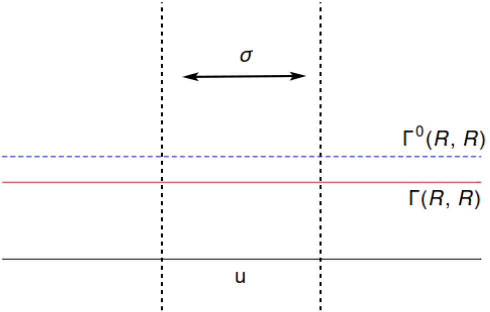
- ΔNO is a two-pronged approach to E_c.
  - CF for static
  - on-top DF for dynamic.
- Scales as $N_{\text{stat}} N^4$.
- Some double-counting removed by range-separation.

Current Efforts

- A universal ϵ_{stat}
- Double-counting correction...
- CS alternative
- Testing on thermochemical data sets

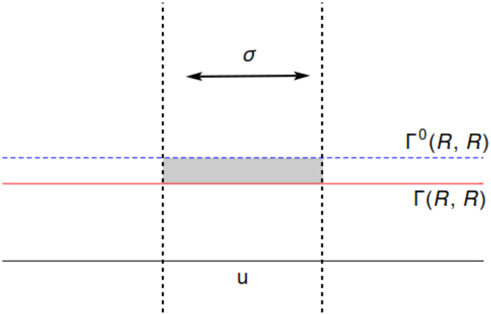
Improved double-counting correction

$$E_{DCC}^{\Delta \text{NO}} = c_{\text{DCC}} \pi \int \sum_i \left(\frac{\Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\Gamma^0_{ii}(\boldsymbol{R},\boldsymbol{R})} \right) \frac{\Gamma^0_{ii}(\boldsymbol{R},\boldsymbol{R}) - \Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\sigma(\boldsymbol{R})^2} d\boldsymbol{R}$$



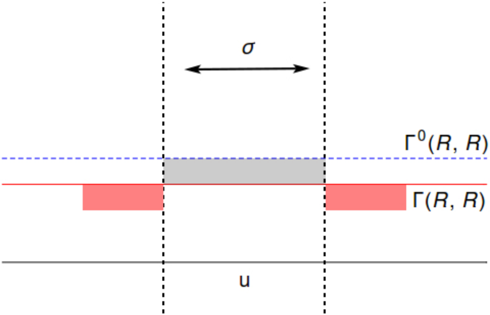
Improved double-counting correction

$$E_{DCC}^{\Delta\text{NO}} = c_{\text{DCC}}\pi \int \sum_i \left(\frac{\Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\Gamma_{ii}^0(\boldsymbol{R},\boldsymbol{R})} \right) \frac{\Gamma_{ii}^0(\boldsymbol{R},\boldsymbol{R}) - \Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\sigma(\boldsymbol{R})^2} d\boldsymbol{R}$$



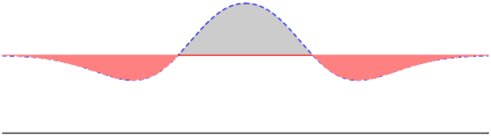
Improved double-counting correction

$$E_{DCC}^{\Delta\text{NO}} = c_{\text{DCC}}\pi \int \sum_i \left(\frac{\Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\Gamma_{ii}^0(\boldsymbol{R},\boldsymbol{R})} \right) \frac{\Gamma_{ii}^0(\boldsymbol{R},\boldsymbol{R}) - \Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\sigma(\boldsymbol{R})^2} d\boldsymbol{R}$$



Improved double-counting correction

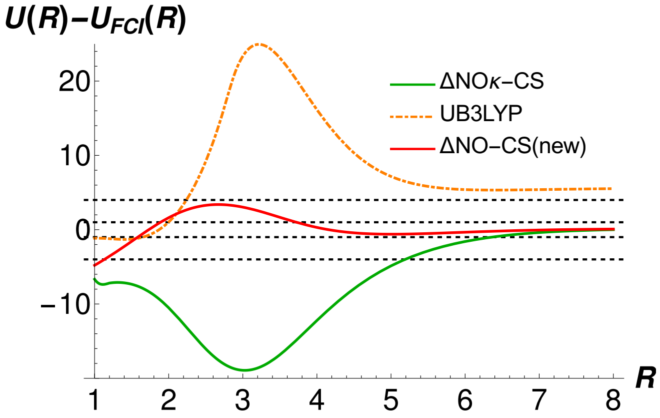
$$E_{DCC}^{\Delta\text{NO}} = c_{\text{DCC}}\pi \int \sum_i \left(\frac{\Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\Gamma^0_{ii}(\boldsymbol{R},\boldsymbol{R})}\right) \frac{\Gamma^0_{ii}(\boldsymbol{R},\boldsymbol{R}) - \Gamma_{ii}(\boldsymbol{R},\boldsymbol{R})}{\sigma(\boldsymbol{R})^2} d\boldsymbol{R}$$



$$c_{\text{DCC}} = 0.417$$

Improved double-counting correction

Error in H_2 dissociation (cc-pVTZ)



units: kJ mol^{-1}

JWH and N Pegoretti *in prep.*

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