Combining Wavefunction Theory with SCAN to Describe Electron Correlation

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   - *Dynamic or short-range weak*, due to instantaneous electron repulsions.
   - *Dispersion or long-range weak,* from instantaneous multipole-multipole interactions between electrons on different centers.
   - *Static or strong*, which occurs due to degeneracies.

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Taking into account correlation is crucial for describing many physical and chemical phenomena.

The dissociation of H_2 is the paradigm for the division of static and dynamic correlation
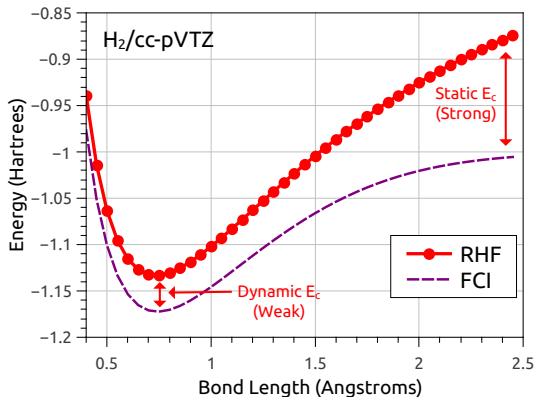

Figure 1:   Dissociation energy curves for the H_2 molecule

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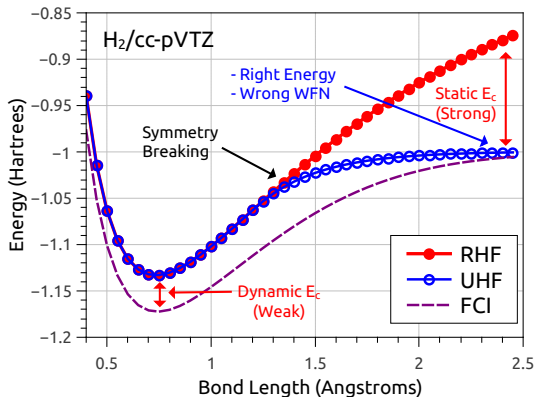

Figure 2: Dissociation energy curves for the H_2 molecule

Static and dynamic correlation are pervasive in bond breaking processes
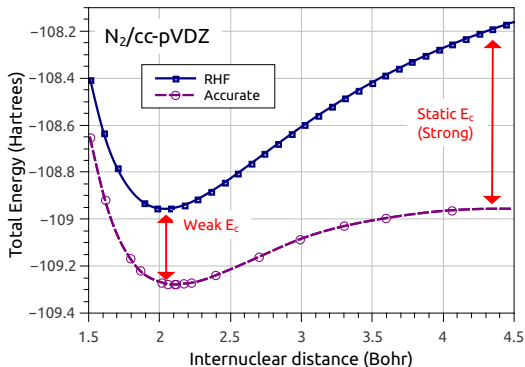

Figure 3: Dissociation energy curves for the N_2 molecule.

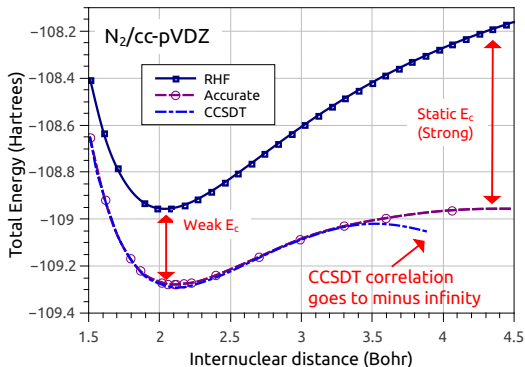# Static and dynamic correlation are pervasive in bond breaking processes

Figure 4: Dissociation energy curves for the N_2 molecule.

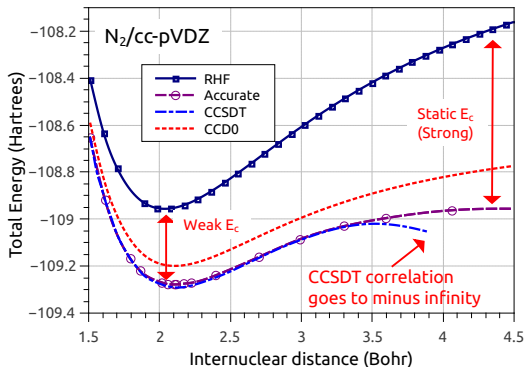# Static and dynamic correlation are pervasive in bond breaking processes
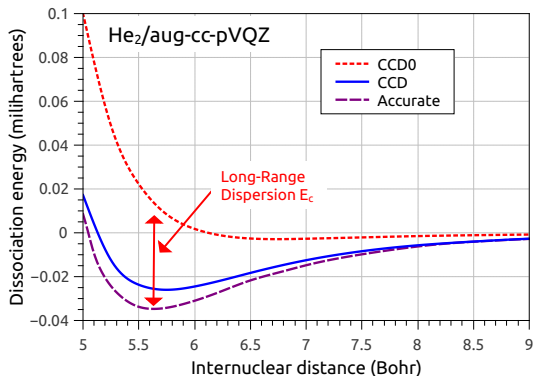

Figure 5: Dissociation energy curves for the N_2 molecule.

The correlation lost by multireference methods may be critical for weak interactions


Figure 6: He_2 dissociation curve.

CCD0 sacrifices some weak correlation in order to describe strong correlation. However, the missing correlation may be very important in case of more subtle interactions.

Roughly, we can say the following about contemporary quantum chemistry methods:

1. Good approximations exist for the short-range dynamic correlation (*e.g.*, CC and DFT).

2. Dispersion correlation is more difficult, although methods like CC and the RPA are adequate.

3. *However, practical methods for static and dynamic correlation are still out of reach.*

We attempt to tackle this problem via combinations of wavefunction and density functional theories
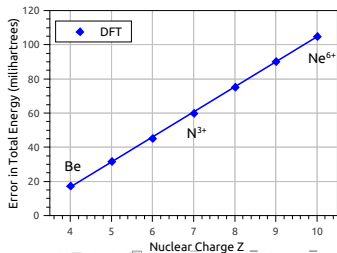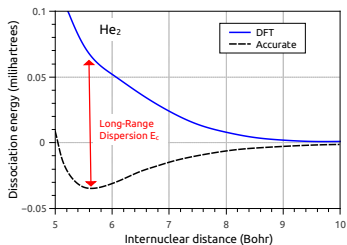
It seems logical to try to combine WFN methods with DFT to tackle the correlation problem

Roughly, we can say

WFN → Can handle static correlation

DFT → Efficiently captures dynamic correlation

Thus, we may expect a good approximation to the exact energy to be

$$E \approx \underbrace{E^{\mathrm{WFN}}}_{Static} + \underbrace{E_c^{\mathrm{DFT}}[n]}_{Dynamic}$$

However, such combinations must address three problems:

1. *WFN Method Problems*

2. *The "Symmetry Dilemma"*

3. *Double Counting*

The problems of standard WFN+DFT can be addressed by a combination of CCD0 with SCAN

SPECIAL ISSUE IN HONOUR OF ANDREAS SAVIN

Combinations of coupled cluster, density functionals, and the random phase approximation for describing static and dynamic correlation, and van der Waals interactions

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Actinide chemistry using singlet-paired coupled cluster and its combinations with density functionals

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CCD0 is a generalization of pCCD

The T_2 operator of standard CCD can be written as a sum of singlet- and triplet-pairing components

$$T_2 = T_2^{[0]} + T_2^{[1]}.$$

CCD0 uses only the singlet-pairing component:

$$|\Psi_{\text{CCD0}}\rangle = e^{T_2^{[0]}}|\Phi_{\text{RHF}}\rangle,$$

where

$$T_2^{[0]} = \frac{1}{2}\sum_{ijab}\sigma_{ij}^{ab}P_{ab}^{\dagger}P_{ij},$$

with

$$P_{ij} = \frac{1}{\sqrt{2}}\left(c_{j\uparrow}c_{i\downarrow} + c_{i\uparrow}c_{j\downarrow}\right).$$

Avoiding double counting in CCD0+DFT

Now, looking at the full T_2 operator

$$T_2 = T_2^{[0]} + T_2^{[1]},$$

The triplet-paired component is

$$T_2^{[1]} = \frac{1}{2} \sum_{ijab} \pi_{ij}^{ab} \mathbf{Q}_{\mathbf{ab}}^{\dagger} \cdot \mathbf{Q}_{\mathbf{ij}}$$

where $\mathbf{Q}_{\mathbf{ij}} = (Q_{ij}^{+}, Q_{ij}^{0}, Q_{ij}^{-})^t$ with

$$Q_{ij}^{+} = c_{j\uparrow}c_{i\uparrow}, \quad Q_{ij}^{-} = c_{j\downarrow}c_{i\downarrow}, \quad Q_{ij}^{0} = \frac{1}{\sqrt{2}}\left(c_{j\uparrow}c_{i\downarrow} - c_{i\uparrow}c_{j\downarrow}\right)$$

Because the Q_{ij}^{+}, Q_{ij}^{0}, and Q_{ij}^{-} components contribute all equally to the energy we get (for a closed shell)

$$E_{\text{total}}^{\text{CCD0+DFT}} = E^{\text{CCD0}} + 3E_{c\uparrow\uparrow}^{\text{DFA}}[n].$$

We can extract the equal spin correlation in SCAN for combination with CCD0

The SCAN functional constructs ε_c as

$$\varepsilon_c = \varepsilon_c^1 + f_c(\alpha) \left[\varepsilon_c^0 - \varepsilon_c^1 \right],$$

where $f_c(\alpha)$ is a function that depends on τ, and $\varepsilon_c^{\alpha=1}$ and $\varepsilon_c^{\alpha=0}$ are the uniform density and single orbital limits of ε_c. Hence, the parallel spin correlation density is

$$\varepsilon_c^{\uparrow\uparrow} = \varepsilon_c^{1\,\uparrow\uparrow} + f_c(\alpha) \left[\varepsilon_c^{0\,\uparrow\uparrow} - \varepsilon_c^{1\,\uparrow\uparrow} \right].$$

Furthermore, since $\varepsilon_c^{0\,\uparrow\uparrow} = 0$, we get

$$\varepsilon_c^{\uparrow\uparrow} = \varepsilon_c^{1\,\uparrow\uparrow} - f_c(\alpha)\varepsilon_c^{1\,\uparrow\uparrow},$$

and $\varepsilon_c^{1\,\uparrow\uparrow}$ has been parametrized by Gori–Giorgi and Perdew.[1]

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[1]Phys. Rev. B **69**, 041103 (2004).

CCD0+DFT is very accurate for problems dominated by dynamic correlation

Table 1: Mean absolute errors (MAEs) for various properties of small molecules for which accurate reference data are available.

Property	MAE		
	DFT	CCD0	CCD0+DFT
Bond Lengths[†] (Å)	0.024	0.013	0.007
Vibrational Frequencies[†] (cm^{-1})	68	22	18
Proton Affinities[‡] (kcal/mol)	2.65	2.69	0.66

[†]First and second row diatomics.

[‡]Standard PA8 set of proton affinities.

Static and dynamic correlation can also be described by CCD0+DFT
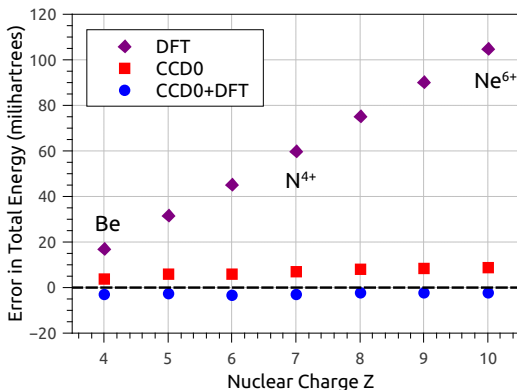

Figure 7: Errors in energy for the beryllium isoelectronic series.

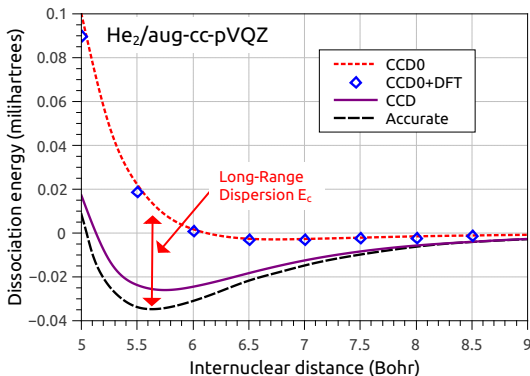# However, the long-range dispersion correlation remains missing in CCD0+DFT

Figure 8: Dissociation energy curves for the He_2 dimer

We can correct this issue by complementing with dRPA long-range correlation

The dRPA equations are:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} = \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} \begin{pmatrix} \boldsymbol{\omega} & 0 \\ 0 & -\boldsymbol{\omega} \end{pmatrix}$$

And the dRPA ground-state correlation is

$$E_c^{\mathrm{dRPA}} = \frac{1}{2} \mathrm{Tr}(\boldsymbol{\omega} - \mathbf{A}).$$

with

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + \langle ib|aj \rangle,$$

$$B_{ia,jb} = \langle ij|ab \rangle.$$

So we can take only same spin integrals to get same spin correlation, and evaluate them only in the long range.

DFT and the dRPA are good, complementary choices for evaluating residual correlation
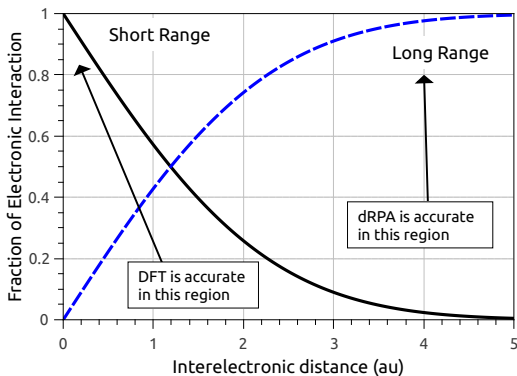

Figure 9: Separation of electron-electron interaction into short- and long-ranges.

Therefore, we have the following approximations:

1. *CCD0+DFT: For problems in which long range interactions are not important*

$$E = \underbrace{E_{\text{CCD0}}}_{\mathscr{O}(N^6)} + \frac{3}{2} \underbrace{\left(E_{c\uparrow\uparrow}^{\text{DFT}} + E_{c\downarrow\downarrow}^{\text{DFT}} \right)}_{\mathscr{O}(N^3)}.$$

2. *Long-range corrected (LC)-CCD0+DFT: For problems involving long range interactions*

$$E = \underbrace{E_{\text{CCD0}}}_{\mathscr{O}(N^6)} + \frac{3}{2} \underbrace{\left(E_{c\uparrow\uparrow}^{\text{lr-dRPA}} + E_{c\downarrow\downarrow}^{\text{lr-dRPA}} \right)}_{\approx \mathscr{O}(N^4) - \mathscr{O}(N^5)} + \frac{3}{2} \underbrace{\left(E_{c\uparrow\uparrow}^{\text{sr-DFT}} + E_{c\downarrow\downarrow}^{\text{sr-DFT}} \right)}_{\mathscr{O}(N^3)}.$$

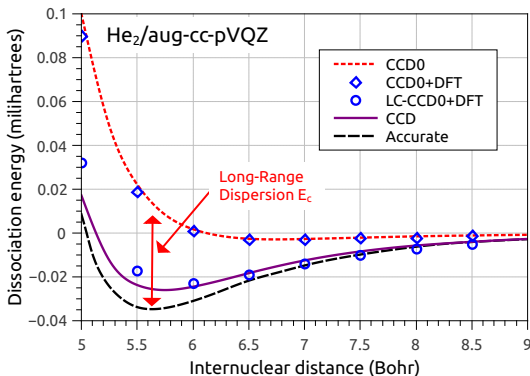# Long-range dispersion can now be described with LC-CCD0+DFT

Figure 10: Dissociation energy curves for the He_2 dimer

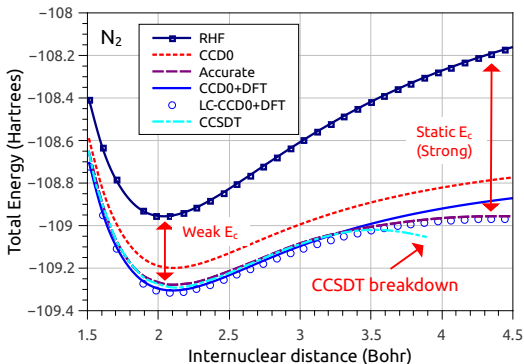# The different CCD0+DFT methods can also describe challenging bond breaking processes

Figure 11: Dissociation energy profiles for the N_2 molecule using a cc-pVDZ basis.

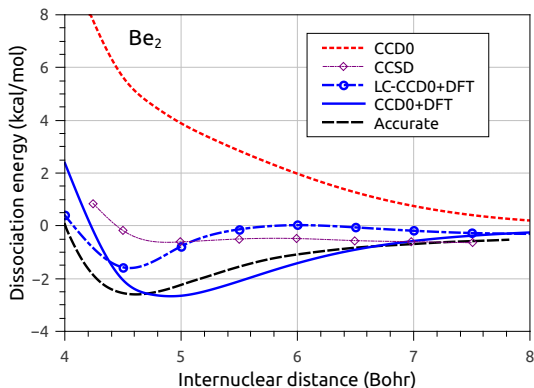# A challenging system: Beryllium dimer—an "impossible molecule"

Figure 12: Dissociation energy profiles for the Be_2 dimer using an uncontracted aug-cc-pVTZ basis.

Application of CCD0+DFT to actinide chemistry: the uranyl ion UO_2^{2+}

Table 2: Bond lengths (R_e in Å) and harmonic vibrational frequencies (ω_e in cm^{-1}) for UO_2^{2+}.

Method	R_e	ω_{as}	ω_s	ω_β
HF	1.648	1293	1220	267
DFT	1.715	1086	985	123
CCD0	1.698	1129	1053	541
CCD0+DFT	1.693	1121	1052	220
Best Estimate	1.690	1120	1035	178

Conclusions for CCD0+DFT:

Advantages

1. *Avoids the usual problems of standard WFN+DFT.*

2. *No need of empirical parameters or symmetry breaking.*

3. *Reasonable description of static and dynamic correlation.*

4. *Can also capture dispersion correlation in its LC-CDD0+DFT variant.*

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3. *Reasonable description of static and dynamic correlation.*
4. *Can also capture dispersion correlation in its LC-CDD0+DFT variant.*

Disadvantages

1. *Same computational cost as coupled cluster.*

Acknowledgments

Collaborators:

1. Prof. Gustavo Scuseria
2. Prof. John P. Perdew
3. Dr. Jianwei Sun
4. Dr. Ireneusz Bulik
5. Dr. Thomas Henderson
6. Ana G. Sousa Alencar

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