Advanced quantum-chemistry methods for solids in the numeric atom-centered orbital framework

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The 1st USTC-FHI workshop

Electronic Structure Theory

Materials science and engineering: Properties of solids
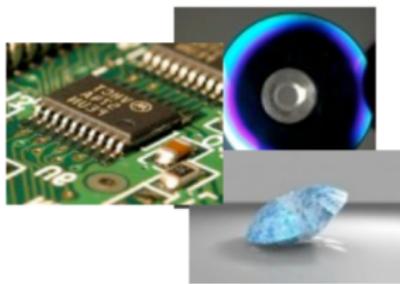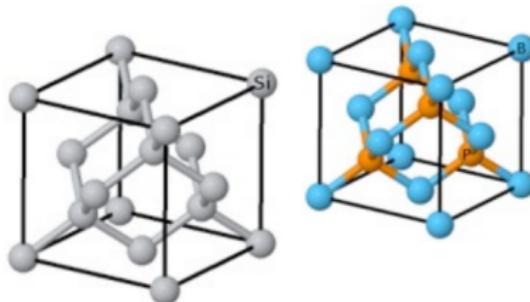
Solve many-electron Schrödinger Equation

$$\hat{H}\psi(\vec{r}_1, ..., \vec{r}_N) = \left[-\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N v(\vec{r}_i) + \sum_{i<j}^N \frac{1}{r_{ij}} \right] \psi(\vec{r}_1, ..., \vec{r}_N) = E\psi(\vec{r}_1, ..., \vec{r}_N)$$

3N-dimensional problem.

Find a good approximation!

Simplicity, efficacy and speed

Wave-function Theory (WFT)
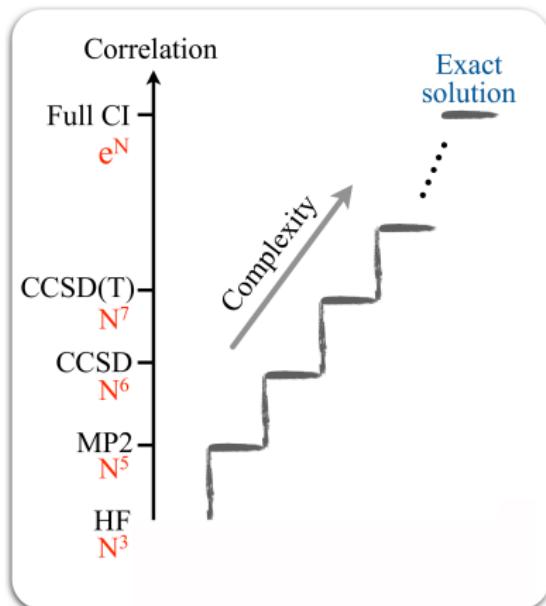
Density-functional Theory (DFT)
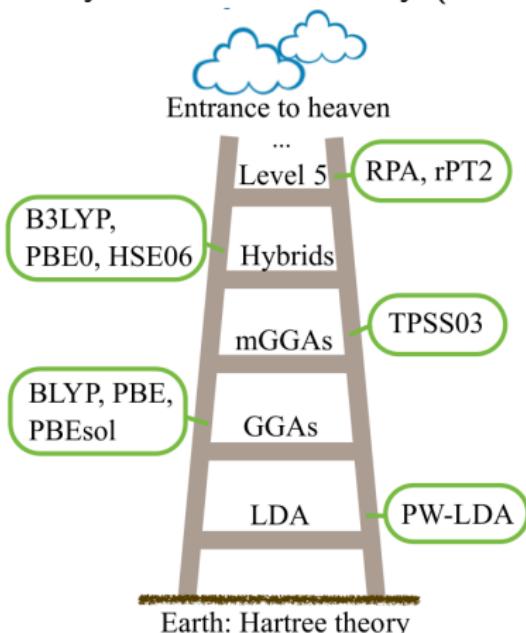
Combination of WFT and DFT?

Double-hybrid density functional approximation

Becke:

$$E_{xc}^{H}[\rho] = E_{xc}^{LDA} + a\left(E_x^{HF} - E_x^{LDA}\right) + b\Delta E_x^{GGA} + c\Delta E_c^{GGA}$$

Igor Ying Zhang, Xin Xu and William A. Goddard:

$$E_{xc}^{DH}[\rho] = E_x^{LDA} + a\left(E_x^{HF} - E_x^{LDA}\right) + b\Delta E_x^{GGA} + cE_c^{GGA} + (1-c)E_c^{PT2}$$

Three parameters $\{a, b, c\}$ were optimized against 223 molecules in G3/99 set

$$\textbf{XYG3} \ \{a = 0.8033; b = 0.2107; c = 0.6789\}$$

Ying Zhang, Xin Xu, and William A. Goddard III. **Proc. Natl. Acad. Sci. USA**, 2009, 106:4963-4968

Performance of XYG3
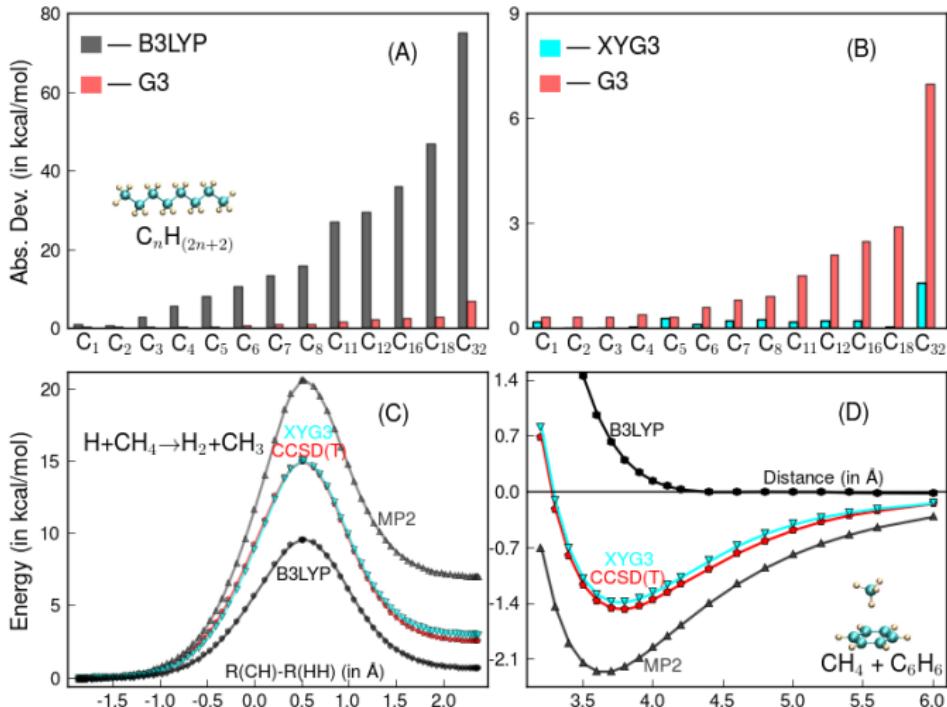
Basis set: 6-311+G(3df,2p)

Challenge of seeking for advanced methods in Solids

- ▶ PT2 fails completely for the systems with closing energy gaps

- ▶ Slow basis set convergence

- ▶ Computational complexity, particularly in reciprocal space

- ▶ Parallelization efficiency

- ▶ Lower-scaling approximation

Advanced first-principle methods for materials science and engineering
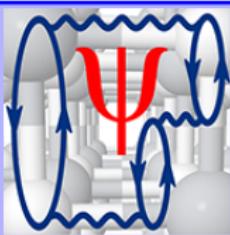
http://th.fhi-berlin.mpg.de/site/index.php?n=Groups

- ▶ **NAO-VCC-nZ**: NAO basis sets with correlation consistency

  I.Y. Zhang, *et al.* New J. Phys. **15**, 123033 (2013).

- ▶ **sBGE2**: Wave-function inspired functional for the H_2/H_2^+ challenge

  I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016).

- ▶ **ZRPS**: An efficient, general purpose orbital-dependent DFA

  I.Y. Zhang, P. Rinke, J.P. Perdew and M. Scheffler. submitted (2016).

- ▶ **MP2 for solids**: Numerical convergence in real and reciprocal spaces
- ▶ **CCSD** implementation for both cluster and periodic systems

  Parts of the MSE project; Papers in writing.

NAO-VCC-nZ:

Numeric atom-centered orbital (NAO) basis sets with valence-correlation consistency

Cusps of electronic wave functions

1) uncorrelated models require an accurate representation of the one-electron density
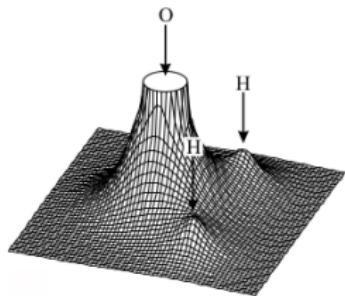
2) correlated models require also an accurate representation of the two-electron density
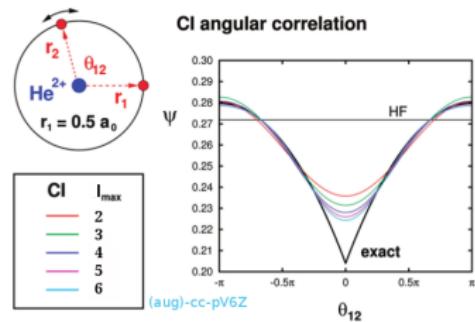
Copyright 2007 John Wiley and Sons.

$$\lim_{r_{iA} \to 0} \left[\frac{\partial}{\partial r} + 2Z_A \right] \bar{n}(r) = 0$$

$$E^{\mathrm{cor}}_{l_{max}} = E^{\mathrm{cor}}_{\infty} + A/(l_{max}+1)^3 + \cdots$$

D.P. Tew, W. Klopper, T.J. Helgaker, J. Comput. Chem. **28**, 1307-1320 (2007).

Numeric atom-centered orbital (NAO) basis sets

$$\Psi(\mathbf{r}) = \frac{u(r)}{r} Y_{lm}(\Omega); \qquad \left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}}(r) \right] u_i(r) = \epsilon_i u_i(r)$$

NAO-aims-2009 (tier-N) is the default choice of FHI-aims.

1) Satisfy the first cusp condition. **2) Slow basis set convergence.**
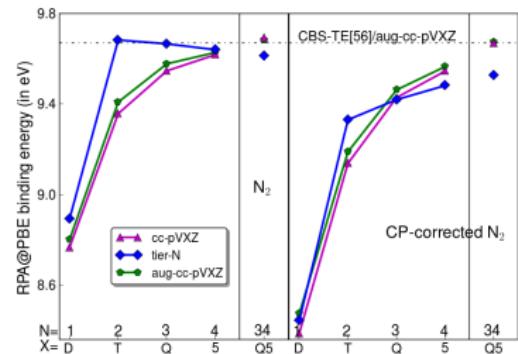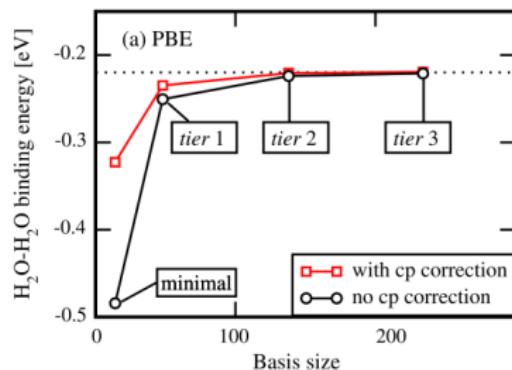
V. Blum *et al*, Comput. Phys. Comm. **180**, 2175-2196 (2009)

X. Ren *et al*, New. J. Phys. **14**, 053020 (2012)

NAO-VCC-nZ: Inherit from cc-pVnZ

Valence Correlation Consistency strategy proposed by Dunning:

1. Polarization set (VCC-nZ), where n=2,3,4,5

   VCC-DZ: $(1d)$
   VCC-TZ: $(1d)+(1d1f)=(2d1f)$
   VCC-QZ: $(1d)+(1d1f)+(1d1f1g)=(3d2f1g)$
   VCC-5Z: $(1d)+(1d1f)+(1d1f1g)+(1d1f1g1h)=(4d3f2g1h)$

2. Even-tempered expansions are used to determine the radial functions
   $u(r)$ with the same angular momentums, for example $l = d, f, g \cdots$.

$$\zeta_i = \alpha\beta^{i-1}, \text{where}, \ i = 1, \ldots, N_f$$

   Here N_f is the number of the functions in the set.

T. H. Dunning, J. Chem. Phys. 90, 1007−1023 (1989)

NAO-VCC-nZ: Differ from cc-pVnZ

	cc-pVXZ	**NAO-VCC-XZ**
Functions:	Analytical Gaussian-type atom-centered orbitals (GTO)	Numeric atom-centered orbitals (NAO)
Method:	Frozen-core (FC) CISD method	Frozen-core (FC) RPA method
minimal basis:	a combination of a set of GTOs	Occupied orbitals of spherically symmetric free atoms
Polarization set:	Primitive GTOs	Hydrogen-like orbitals
Enhenced minimal basis:	None	A group of s- and p-type (sp) hydrogen-like orbitals with the same basis size as the minimal

I.Y. Zhang, *et al.* New J. Phys. **15**, 123033 (2013).

NAO-VCC-nZ: Basis size
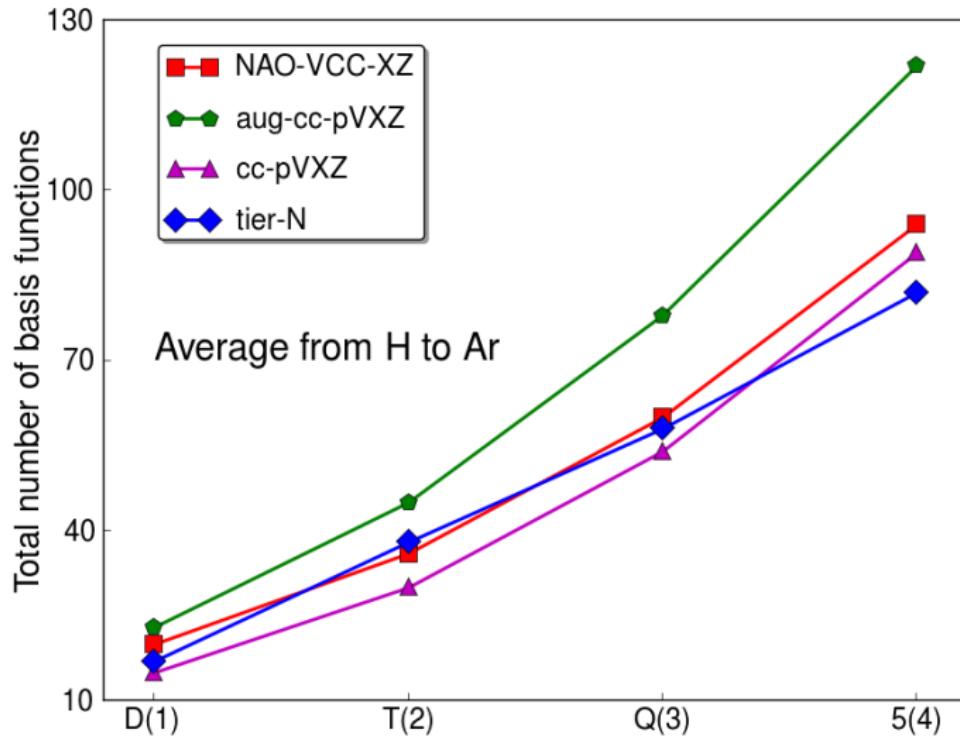
NAO-VCC-nZ: RPA@PBE total energies for atoms
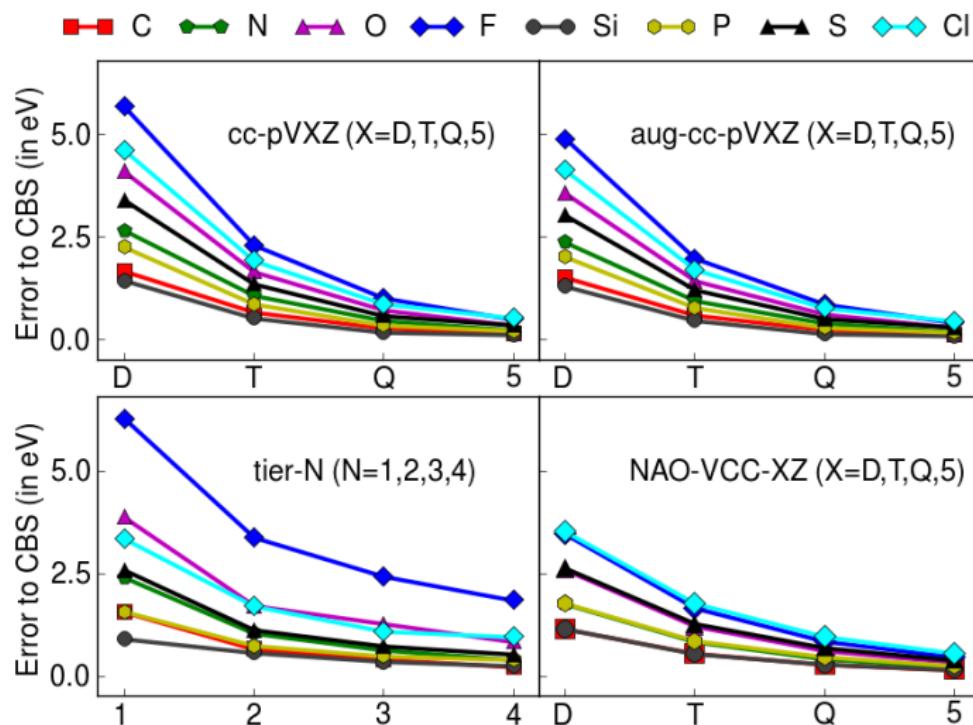
NAO-VCC-nZ: A logarithmic scale
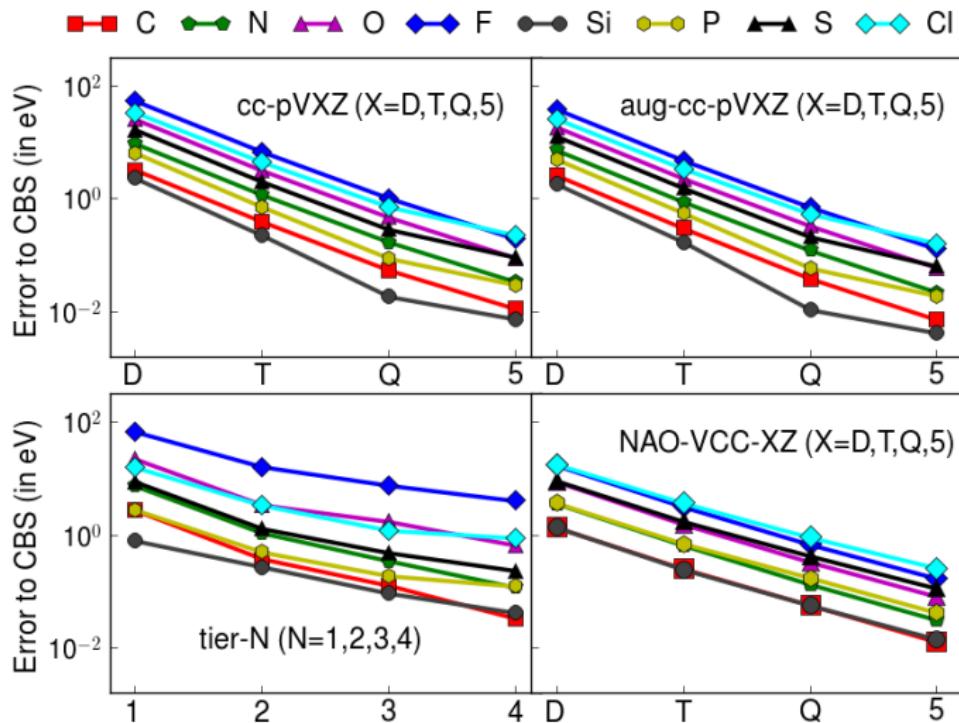
NAO-VCC-nZ: Transferability to MP2 and rPT2
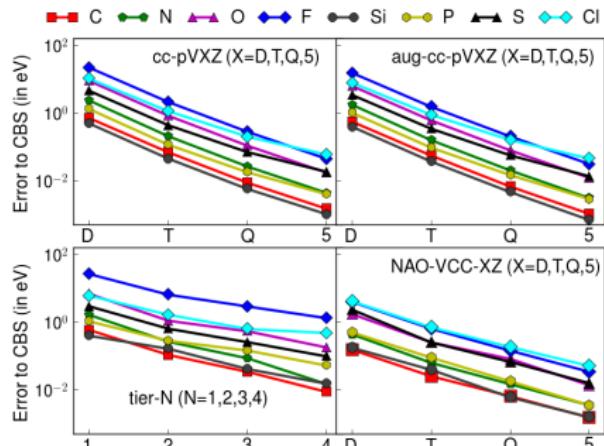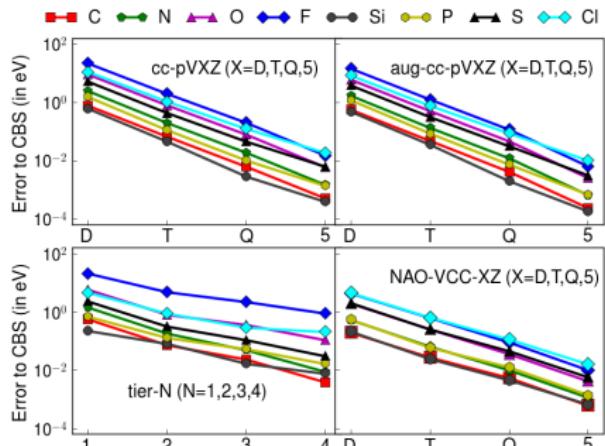
Frozen-core MP2   Frozen-core rPT2

NAO-VCC-nZ: RPA@PBE binding energies of N_2 and F_2
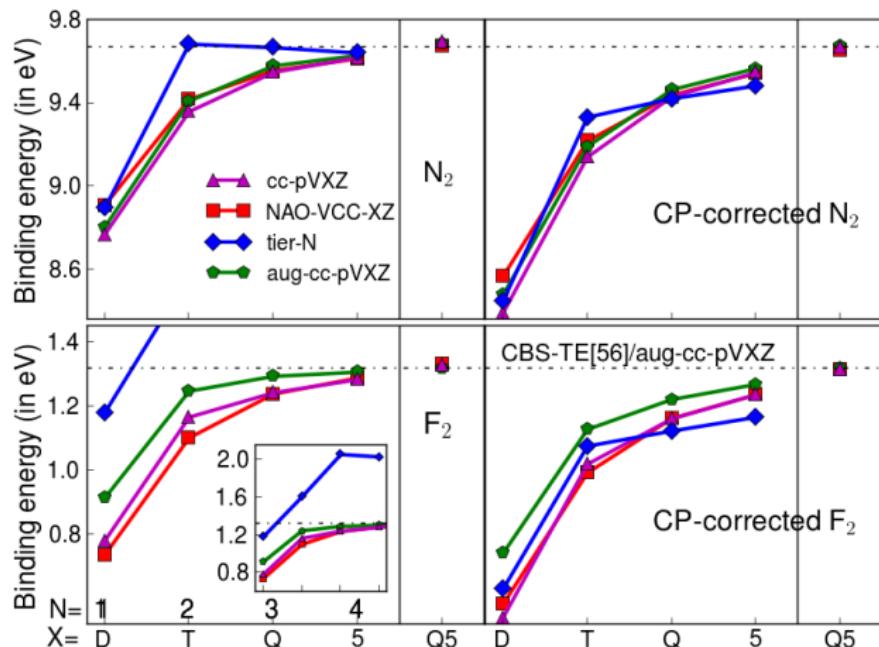
NAO-VCC-nZ: A logarithmic scale
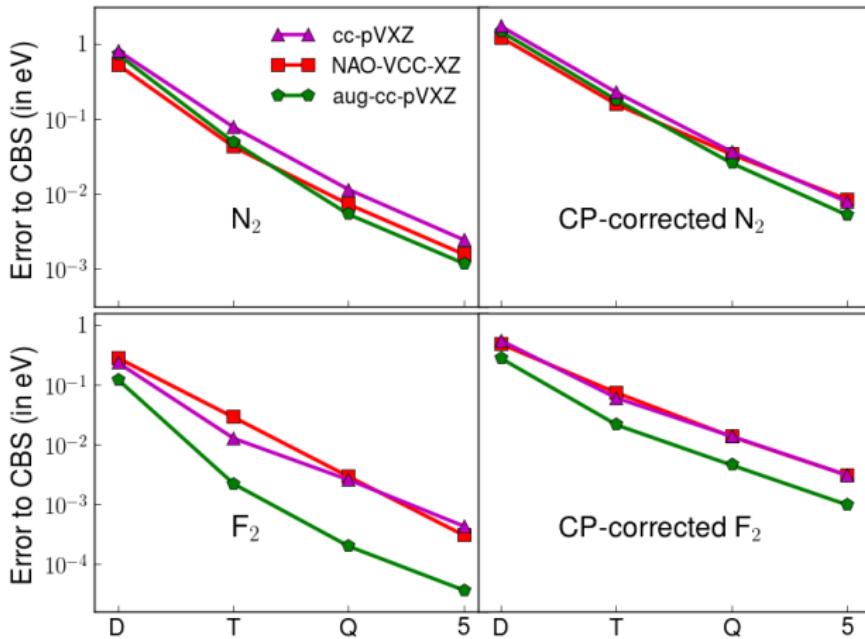
NAO-VCC-nZ: Covalent bond systems
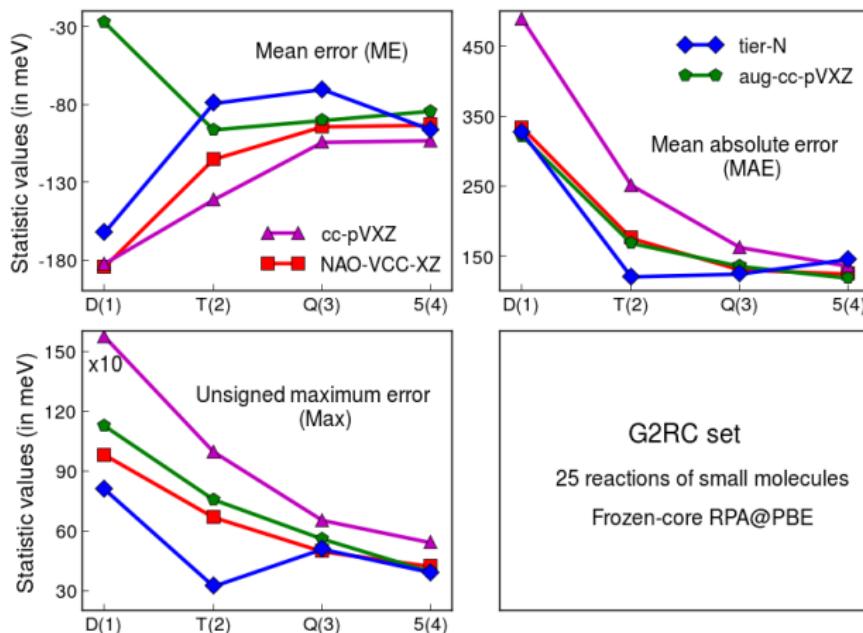
Basis set convergence of three criterions in RPA@PBE reaction energies of the G2RC test set. (in meV)

NAO-VCC-nZ: Non-covalent bond systems
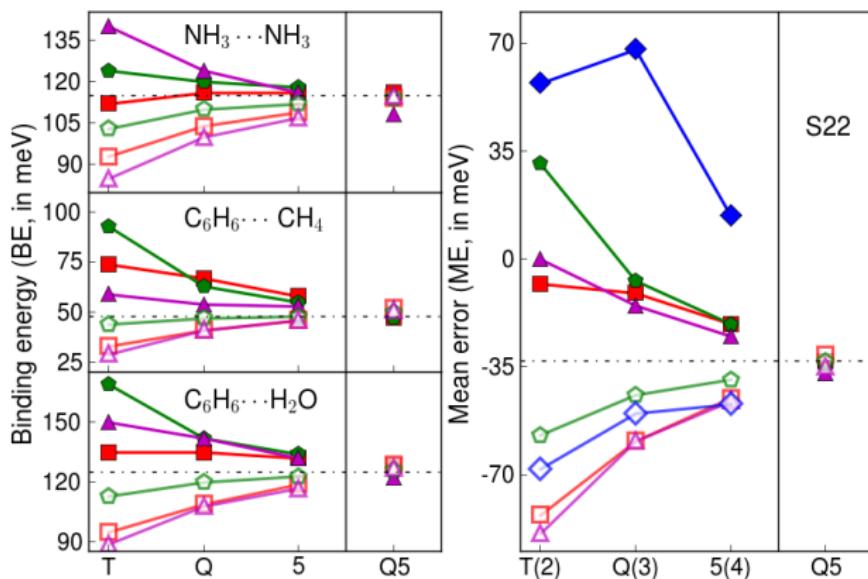
Basis set convergence of mean errors in frozen-core RPA@PBE reaction energies of the S22 test set. (in meV)

NAO-VCC-nZ: Summary

1. A series of NAO basis sets with **V**alance **C**orrelation **C**onsistency from H to Ar, named NAO-VCC-nZ
2. NAO-VCC-nZ is suitable for the frozen-core correlated methods, including RPA, MP2 and rPT2.
3. The basis set incompleteness error of NAO-VCC-nZ, including the notorious basis set superposition error, can be removed using the extrapolation scheme.

1. Core-correlation basis functions for all-electron calculations.
2. Diffuse basis functions for anion systems.
3. Extending NAO-VCC-nZ to heavy elements.

sBGE2:

Wave-function inspired functional
for the H_2/H_2^+ challenge

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

H$_2$/H$_2^+$ dissociations: A big challenge in DFT
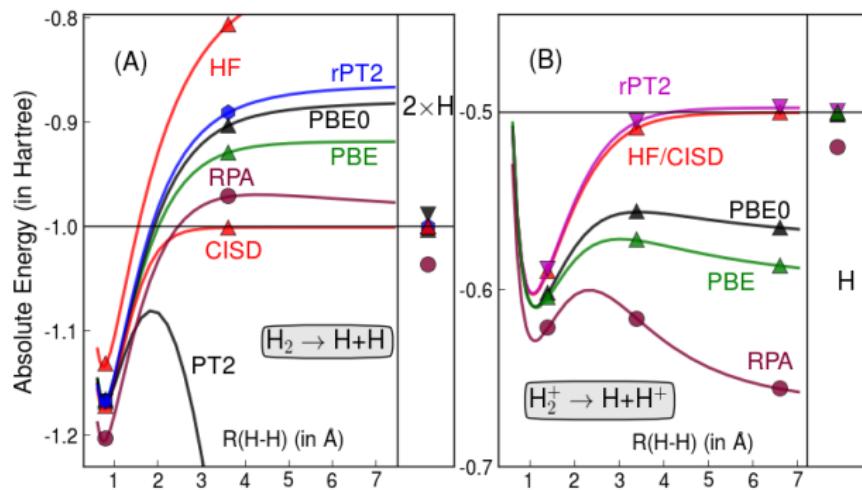
A. J. Cohen, P. Mori-Sánchez, and W. T. Yang, Chem. Rev. **112**, 289 (2011)
A. Ruzsinszky, J. P. Perdew, Comput. Theor. Chem. **963**, 2 (2011)

Some well-documented drawbacks of DFAs

- atomization energies
- conformation energies
- weak interactions
- reaction barrier heights
- molecular dissociations

- short-range correlation
- middle-range correlation
- long-range correlation
- self-interaction correlation
- (near-)degeneracy correlation

A great challenge in materials science:

- The electronic interactions are particularly difficult to describe
- Teamwork among different types of correlation is essential
- Transition metals and their strong correlated oxides

Bethe-Goldstone equation (BGE)

$$\Psi_{ab}(\lambda) = \Phi_{ab} - \sum_{r<s}^{vir} \frac{\Phi_{rs}}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)} \left\langle \Phi_{rs} | \lambda \hat{V}_{ee} | \Psi_{ab} \right\rangle ; \textbf{pp-Ladder}$$

$$e_{ab}([n];\lambda) = \int_0^\lambda d\lambda V_{xc}([n];\lambda)$$
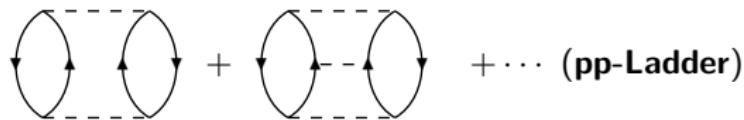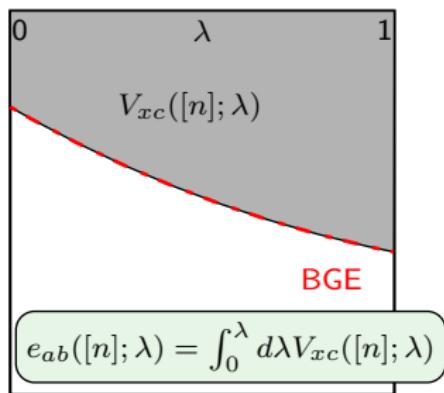
A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1996)

Bethe-Goldstone equation (BGE)

$$\Psi_{ab}(\lambda) = \Phi_{ab} - \sum_{r<s}^{vir} \frac{\Phi_{rs}}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)} \left\langle \Phi_{rs} | \lambda \hat{V}_{ee} | \Psi_{ab} \right\rangle ; \textbf{pp-Ladder}$$

$$e_{ab}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left\langle \Phi_{ab} | \hat{V}_{ee} | \Phi_{rs} \right\rangle \left\langle \Phi_{rs} | \hat{V}_{ee} | \Psi_{ab} \right\rangle}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)} ; \ \ e_{ab}\textbf{-coupling}$$

$$e_{ab}([n]; \lambda) = \int_0^\lambda d\lambda V_{xc}([n]; \lambda)$$

connected   disconnected
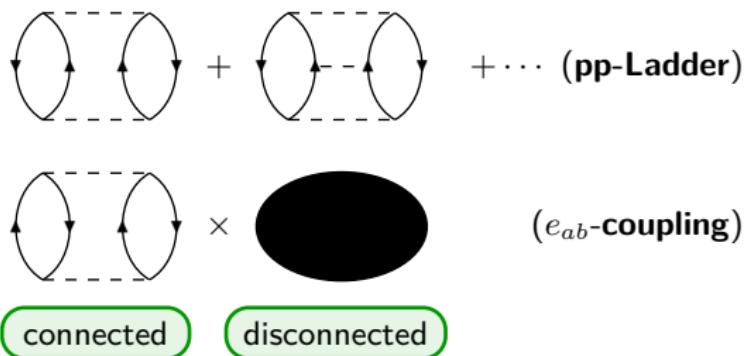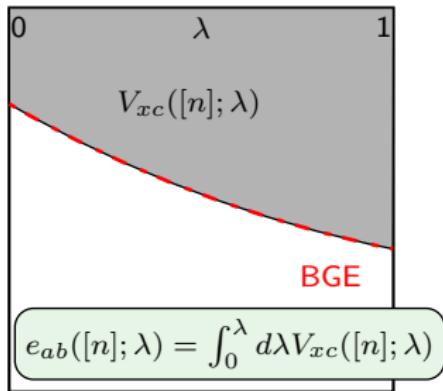
A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1996)

Second order BGE expansion (BGE2)

1. The e_{ab}-coupling procedure does not introduce connected diagrams.

$$\Psi_{ab}(\lambda) = \Phi_{ab} - \sum_{r<s}^{vir} \frac{\Phi_{rs}}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)} \left\langle \Phi_{rs}|\lambda\hat{V}_{ee}|\Psi_{ab}\right\rangle$$

$$\approx \Phi_{ab} - \sum_{r<s}^{vir} \frac{\Phi_{rs}}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)} \left\langle \Phi_{rs}|\lambda\hat{V}_{ee}|\Phi_{ab}\right\rangle$$

Second order BGE expansion (BGE2)

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$$\Psi_{ab}(\lambda) = \Phi_{ab} - \sum_{r<s}^{vir} \frac{\Phi_{rs}}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)} \left\langle \Phi_{rs}|\lambda\hat{V}_{ee}|\Psi_{ab}\right\rangle$$

$$\approx \Phi_{ab} - \sum_{r<s}^{vir} \frac{\Phi_{rs}}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)} \left\langle \Phi_{rs}|\lambda\hat{V}_{ee}|\Phi_{ab}\right\rangle$$

2. The BGE2 correlation energy E_c^{BGE2} exhibits a simple **sum-over-state (SOS)** formula similar to standard PT2.

$$e_{ab}(\lambda) \approx - \sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle\phi_a\phi_b||\phi_r\phi_s\rangle\right|^2}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)}; \quad E_c^{\mathrm{BGE2}}(\lambda) = \sum_{a<b}^{occ} e_{ab}(\lambda)$$

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

BGE2 for H_2 and H_2^+ curves
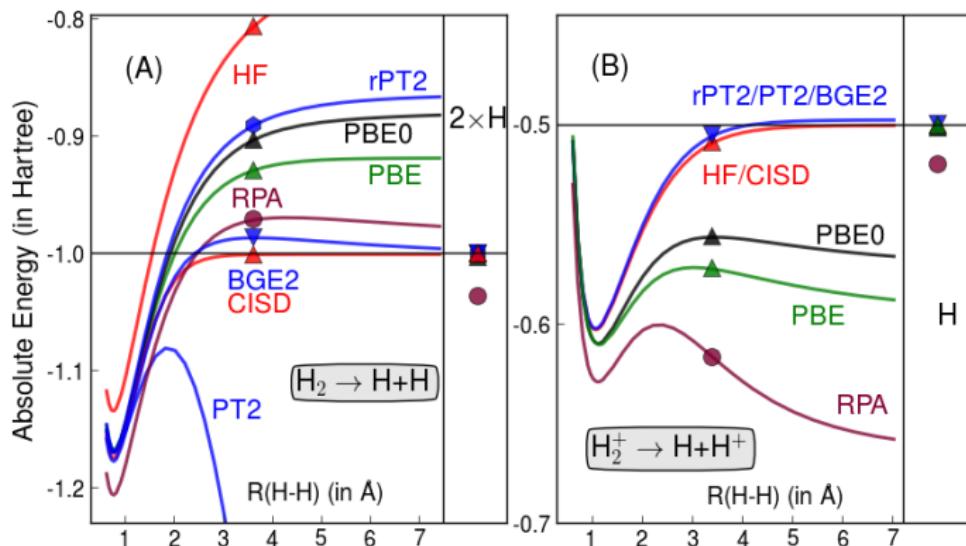
$$e_{ab}^{\text{BGE2}} = -\sum_{r<s}^{vir} \frac{|\langle \phi_a \phi_b || \phi_r \phi_s \rangle|^2}{\Delta \epsilon_{ab}^{rs} - e_{ab}^{\text{BGE2}}}; \quad E_c^{\text{BGE2}} = \sum_{a<b}^{occ} e_{ab}^{\text{BGE2}}$$

Rationale of the e_{ab}-coupling effect in BGE2

$$e_{ab}^{\mathrm{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left| \langle \phi_a \phi_b || \phi_r \phi_s \rangle \right|^2}{\Delta \epsilon_{ab}^{rs} - e_{ab}^{\mathrm{BGE2}}(\lambda)}$$

Questions:

- (Near-)degeneracy correlation?

- Higher-order connected Goldstone diagrams?

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

Geometric series expansion of e_{ab}-coupling effect in BGE2

$$e_{ab}^{\mathrm{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left| \langle \phi_a \phi_b || \phi_r \phi_s \rangle \right|^2}{\Delta \epsilon_{ab}^{rs} - e_{ab}^{\mathrm{BGE2}}(\lambda)}$$

Geometric series expansion of e_{ab}-coupling effect in BGE2

$$e_{ab}^{\text{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left| \langle \phi_a \phi_b || \phi_r \phi_s \rangle \right|^2}{\Delta \epsilon_{ab}^{rs} - e_{ab}^{\text{BGE2}}(\lambda)}$$

$$= -\sum_{r<s}^{vir} \frac{\lambda^2 \left| \langle \phi_a \phi_b || \phi_r \phi_s \rangle \right|^2}{(\Delta \epsilon_{ab}^{rs} + L) - (e_{ab}^{\text{BGE2}}(\lambda) + L)}$$

Geometric series expansion of e_{ab}-coupling effect in BGE2

$$
\begin{aligned}
e_{ab}^{\mathrm{BGE2}}(\lambda) &= -\sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle \phi_a \phi_b || \phi_r \phi_s \rangle\right|^2}{\Delta \epsilon_{ab}^{rs} - e_{ab}^{\mathrm{BGE2}}(\lambda)} \\
&= -\sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle \phi_a \phi_b || \phi_r \phi_s \rangle\right|^2}{(\Delta \epsilon_{ab}^{rs} + L) - (e_{ab}^{\mathrm{BGE2}}(\lambda) + L)} \\
&= -\sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle \phi_a \phi_b || \phi_r \phi_s \rangle\right|^2}{(\Delta \epsilon_{ab}^{rs} + L)} \left(1 - x(L)\right)^{-1}
\end{aligned}
$$

where

$$
x(L) = \frac{e_{ab}^{\mathrm{BGE2}}(\lambda) + L}{\Delta \epsilon_{ab}^{rs} + L}
$$

e_{ab}-coupling effect: (near-)degeneracy correlation?

$$e_{ab}^{\mathrm{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle\phi_a\phi_b||\phi_r\phi_s\rangle\right|^2}{(\Delta\epsilon_{ab}^{rs} + L)} (1 - x(L))^{-1}$$

In order to expand this equation in geometric series, it requires:

$$\boxed{-1 < x(L) < 1}$$

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

e_{ab}-coupling effect: (near-)degeneracy correlation?

$$e_{ab}^{\text{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left| \langle \phi_a \phi_b || \phi_r \phi_s \rangle \right|^2}{(\Delta \epsilon_{ab}^{rs} + L)} \left(1 - x(L)\right)^{-1}$$

In order to expand this equation in geometric series, it requires:

$$L > \max \left\{ 0, \tfrac{1}{2} \left(\left| e_{ab}^{\text{BGE2}}(\lambda) \right| - \left| \Delta \epsilon_{ab}^{rs} \right| \right) \right\}$$

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

e_{ab}-coupling effect: (near-)degeneracy correlation?

$$e_{ab}^{\text{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle\phi_a\phi_b||\phi_r\phi_s\rangle\right|^2}{(\Delta\epsilon_{ab}^{rs} + L)} \left(1 - x(L)\right)^{-1}$$

In order to expand this equation in geometric series, it requires:

$$L > \max\left\{0, \tfrac{1}{2}\left(\left|e_{ab}^{\text{BGE2}}(\lambda)\right| - |\Delta\epsilon_{ab}^{rs}|\right)\right\}$$

For insulators:
$$|\Delta\epsilon_{ab}^{rs}| > \left|e_{ab}^{\text{BGE2}}(\lambda)\right|$$

The single-reference many-body perturbation theory is valid

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

e_{ab}-coupling effect: (near-)degeneracy correlation?

$$e_{ab}^{\mathrm{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle\phi_a\phi_b||\phi_r\phi_s\rangle\right|^2}{(\Delta\epsilon_{ab}^{rs} + L)} \left(1 - x(L)\right)^{-1}$$

In order to expand this equation in geometric series, it requires:

$$L > \max\left\{0, \tfrac{1}{2}\left(\left|e_{ab}^{\mathrm{BGE2}}(\lambda)\right| - |\Delta\epsilon_{ab}^{rs}|\right)\right\}$$

For small-gap systems: $\quad |\Delta\epsilon_{ab}^{rs}| \leq \left|e_{ab}^{\mathrm{BGE2}}(\lambda)\right|$

Critical point of switching off the perturbative treatment of correlation

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

e_{ab}-coupling effect: higher-order connected diagrams?

$$e_{ab}^{\mathrm{BGE2}}(\lambda) = -\sum_{n=0}^{\infty} \sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle \phi_a \phi_b || \phi_r \phi_s \rangle\right|^2}{(\Delta \epsilon_{ab}^{rs})^{n+1}} e_{ab}^{\mathrm{BGE2}}(\lambda)^n$$
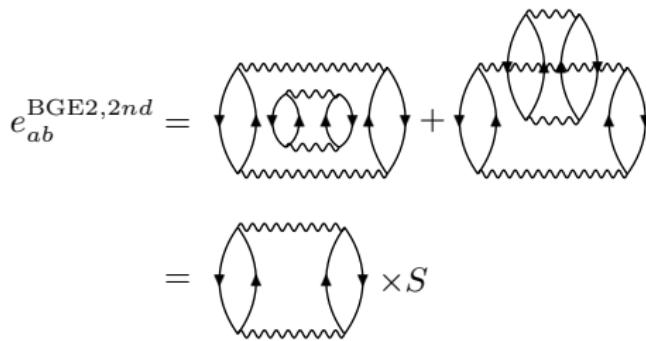
The e_{ab}-coupling effect at the second-order BGE expansion does not produce higher-order connected Goldstone diagrams.
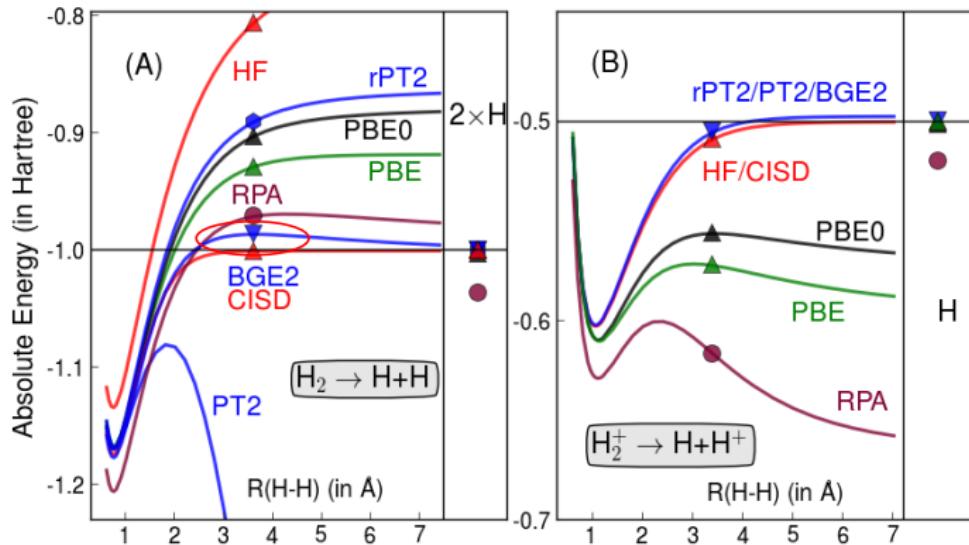
I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

H$_2$ and H$_2^+$ dissociations

All calculations, including the configuration interaction method with singles and doubles (CISD), are carried out in FHI-aims with the NAO-VCC-5Z basis set.

A. Ruzsinszky, J. P. Perdew, Comput. Theor. Chem. **963**, 2 (2011).
A. J. Cohen, P. Mori-Sánchez, and W. T. Yang, Chem. Rev. **112**, 289 (2011).

A screening effect to BGE2: sBGE2

$$e_{ab}^{\text{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left|\langle \phi_a \phi_b || \phi_r \phi_s \rangle\right|^2}{\Delta\epsilon_{ab}^{rs} - e_{ab}^{\text{BGE2}}(\lambda)}; \ E_c^{\text{BGE2}} = \sum_{a<b}^{occ} e_{ab}^{\text{BGE2}}$$

1) Higher order diagrams (BGE)
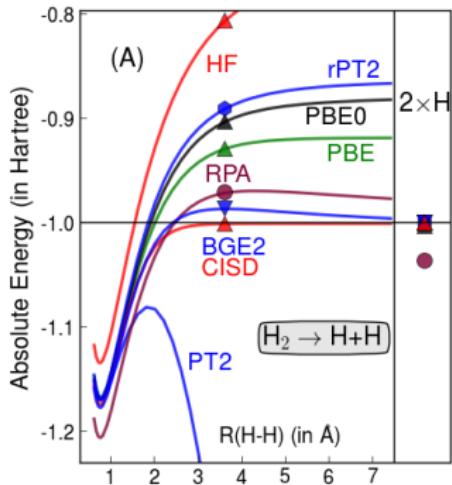
$$e_{ab}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \left\langle \Phi_{ab}|\hat{V}_{ee}|\Phi_{rs}\right\rangle \left\langle \Phi_{rs}|\hat{V}_{ee}|\Psi_{ab}\right\rangle}{\Delta\epsilon_{ab}^{rs} - e_{ab}(\lambda)}$$

A screening effect to BGE2: sBGE2

$$e_{ab}^{\text{BGE2}}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 |\langle \phi_a \phi_b || \phi_r \phi_s \rangle|^2}{\Delta \epsilon_{ab}^{rs} - e_{ab}^{\text{BGE2}}(\lambda)}; \; E_c^{\text{BGE2}} = \sum_{a<b}^{occ} e_{ab}^{\text{BGE2}}$$
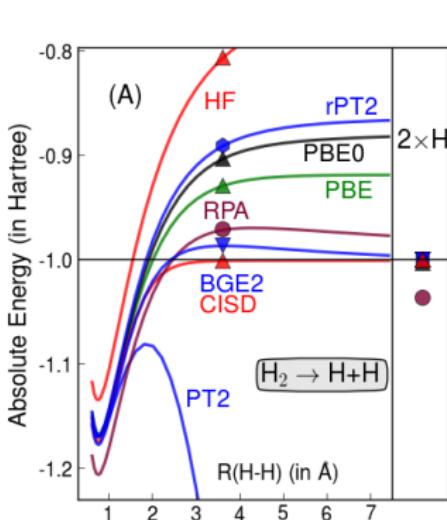
1) Higher order diagrams (BGE)

$$e_{ab}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 \langle \Phi_{ab}|\hat{V}_{ee}|\Phi_{rs}\rangle \langle \Phi_{rs}|\hat{V}_{ee}|\Psi_{ab}\rangle}{\Delta \epsilon_{ab}^{rs} - e_{ab}(\lambda)}$$

2) A screening factor $s_{ab}^{rs} = \text{Erfc}(\Delta \epsilon_{ab}^{rs})$:

$$e_{ab}(\lambda) = -\sum_{r<s}^{vir} \frac{\lambda^2 |\langle \psi_a \psi_b || \psi_r \psi_s \rangle|^2}{\Delta \epsilon_{ab}^{rs} - s_{ab}^{rs} e_{ab}(\lambda)}$$

sBGE2: Wave-function inspired functional
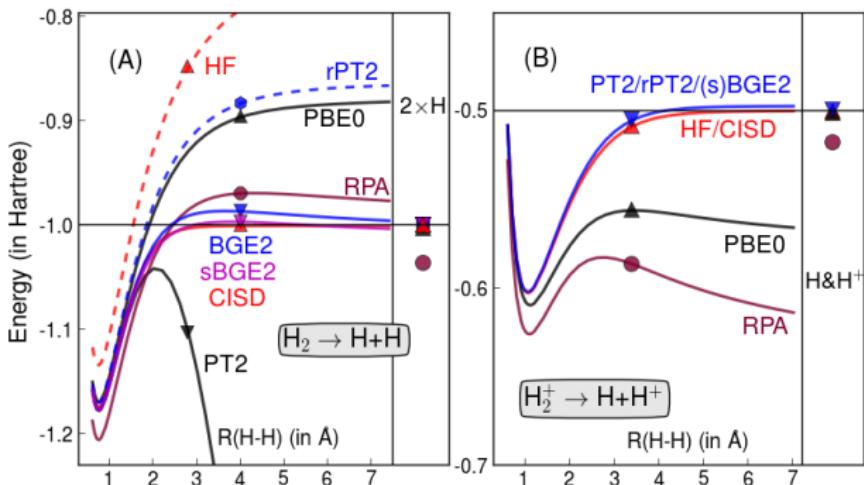
$$e_{ab}^{\text{sBGE2}} = -\sum_{r<s}^{vir} \frac{|\langle \psi_a \psi_b || \psi_r \psi_s \rangle|^2}{\Delta \epsilon_{ab}^{rs} - s_{ab}^{rs} e_{ab}^{\text{sBGE2}}}; \quad E_c^{\text{sBGE2}} = \sum_{a<b}^{occ} e_{ab}^{\text{sBGE2}}$$

I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016)

Go beyond the electron-pair approximation

- One- and Two-electron correlation problem: **sBGE2**

$$e_{ab}^{\mathrm{sBGE2}} = -\sum_{r<s}^{vir} \frac{|\langle \psi_a \psi_b || \psi_r \psi_s \rangle|^2}{\Delta\epsilon_{ab}^{rs} - s_{ab}^{rs} e_{ab}^{\mathrm{sBGE2}}}; \; E_c^{\mathrm{sBGE2}} = \sum_{a<b}^{occ} e_{ab}^{\mathrm{sBGE2}}$$

- Correlation involving more than two electrons (MAE in meV):

MAD	G2-1	RH76	ISO34	S22	Overall
PBE0-TS	124	178	74	15	124
RPA	405	88	44	33	167
rPT2	159	101	51	21	100
PT2	1570	483	116	137	695
sBGE2	1555	480	113	145	695

G2-1 : 55 atomization energies   **BH76** : 76 reaction barriers
ISO34 : 34 isomerization energies   **S22** : 22 bio-oriented weak interactions

Lars Goerigk and Stefan Grimme JCTC, 7, 727 (2011).

ZRPS:

An efficient, general purpose orbital-dependent density functional approximation

I.Y. **Z**hang, P. **R**inke, J.P. **P**erdew and M. **S**cheffler. submitted (2016)

A challenge for both DFT and WFT
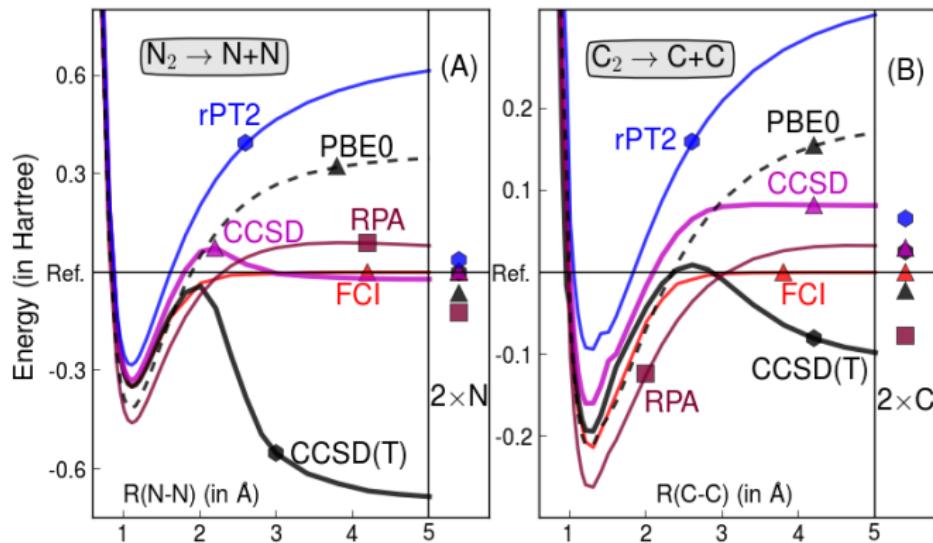
- ▶ CCSD and CCSD(T) results are obtained by using GAMESS
- ▶ PBE0, RPA, and rPT2 calculations using FHI-aims
- ▶ Full configuration interaction (FCI) within quantum Monte Carlo (QMC) using FHI-aims
- ▶ Ref's are the FCI-QMC results; The basis set used is cc-pV3Z

A challenge for both DFT and WFT
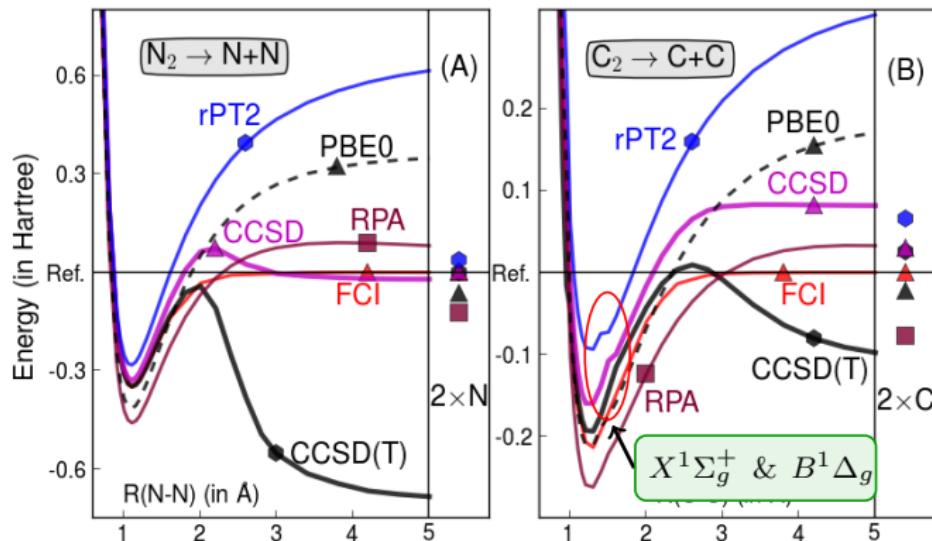
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- ▶ Ref's are the FCI-QMC results; The basis set used is cc-pV3Z

ZRPS: Adiabatic connection model for level-5 DFAs

$$
\begin{aligned}
V_{xc}^{\text{L5}}(\lambda) &= V_{xc}^{\text{GGA}}(\lambda) + (E_x^{\text{HF}} - E_x^{\text{GGA}})(1 - \lambda) \\
&\quad + (E_c^{\text{L5}} - E_c^{\text{GGA}})(\lambda - \lambda^3)
\end{aligned}
$$

- Satisfy the exact constraints in the low-density limit ($\lambda \to 0$)
  $$V_{xc}^{\text{L5}}(0) = V_{xc}^{\text{GGA}}(0) + (E_x^{\text{HF}} - E_x^{\text{GGA}})$$
- The exact-exchange depends on λ linearly
- The highest order λ-dependence is cubic in the correlation part λ
- Include the correlation of many particles in an approximated fourth-order correction

I.Y. Zhang, P. Rinke, J. P. Perdew and M. Scheffler. submitted (2016)

ZRPS: Adiabatic connection model for level-5 DFAs

$$V_{xc}^{\text{L5}}(\lambda) = V_{xc}^{\text{GGA}}(\lambda) + (E_x^{\text{HF}} - E_x^{\text{GGA}})(1 - \lambda)$$
$$+ (E_c^{\text{L5}} - E_c^{\text{GGA}})(\lambda - \lambda^3)$$

$$\Downarrow$$

$$E_{xc}^{\text{L5}}(n) = E_{xc}^{\text{GGA}} + \frac{1}{2}(E_x^{\text{HF}} - E_x^{\text{GGA}}) + \frac{1}{4}(E_c^{\text{L5}} - E_c^{\text{GGA}})$$

I.Y. Zhang, P. Rinke, J. P. Perdew and M. Scheffler. submitted (2016)

Parameter-free hybrid-L5 approximation: ZRPS

$$E_{xc}^{\mathrm{ZRPS}} = 0.5 E_x^{\mathrm{GGA}} + 0.75 E_c^{\mathrm{GGA}} + 0.5 E_x^{\mathrm{HF}} + 0.25 E_c^{\mathrm{L5}}$$

- $E_x^{\mathrm{GGA}} = E_x^{\mathrm{PBE}}$

- $E_c^{\mathrm{GGA}} = E_c^{\mathrm{PBE}} + E_{vdw}^{\mathrm{TS}}$

I.Y. Zhang, P. Rinke, J. P. Perdew, and M. Scheffler. submitted (2016)

Parameter-free hybrid-L5 approximation: ZRPS

$$E_{xc}^{\text{ZRPS}} = 0.5 E_x^{\text{GGA}} + 0.75 E_c^{\text{GGA}} + 0.5 E_x^{\text{HF}} + 0.25 E_c^{\text{L5}}$$

- $E_x^{\text{GGA}} = E_x^{\text{PBE}}$

- $E_c^{\text{GGA}} = E_c^{\text{PBE}} + E_{vdw}^{\text{TS}}$

- $E_c^{\text{L5}} = E_{c,os}^{\text{sBGE2}} = \sum_{a<b} e_{ab}^{\text{sBGE2}}(a_\alpha \neq b_\alpha)$

  - Finite-order perturbation theory provides an unbalanced description of electron pairs with the same and different spin

    M. Gerenkampand and S. Grimme, CPL 392 229 (2004).

  - Scaling can be reduced by using the Laplace quadrature approximation.

    YS Jung, RC Lochan, AD Dutoi, M Head-Gordon, JCP 121 9793 (2004).

Parameter-free hybrid-L5 approximation: ZRPS

Mean absolute error (MAE). Max absolute error (Max) is in parentheses (in meV).

	G2-1	RH76	ISO34	S22	Overall
PBE0-TS	**124**	178	74	**15**	124
	(404)	(614)	(236)	(58)	(614)
RPA	405	**88**	**44**	33	167
	(1171)	(292)	(162)	(79)	(1171)
rPT2	159	101	51	21	**100**
	(936)	(382)	(186)	(69)	(936)
PT2	1570	483	116	137	695
	(4623)	(2038)	(451)	(537)	(4623)
sBGE2	1555	480	113	145	695
	(4602)	(2029)	(451)	(553)	(4602)
ZRPS	**73**	**92**	**47**	**10**	**69**
	(195)	(363)	(197)	(32)	(363)

G2-1 : 55 atomization energies   **BH76** : 76 reaction barriers
ISO34 : 34 isomerization energies   **S22**   : 22 bio-oriented weak interactions

ZRPS: H_2 and H_2^+ dissociations
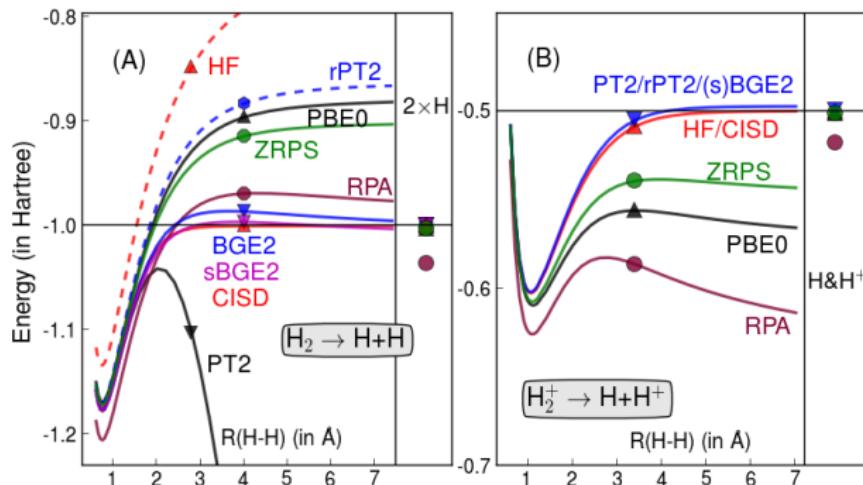
All calculations, including the configuration interaction method with singles and doubles (CISD), are carried out in FHI-aims with the NAO-VCC-5Z basis set.

A. Ruzsinszky, J. P. Perdew, Comput. Theor. Chem. **963**, 2 (2011).
A. J. Cohen, P. Mori-Sánchez, and W. T. Yang, Chem. Rev. **112**, 289 (2011).

ZRPS: N_2 and C_2 dissociations
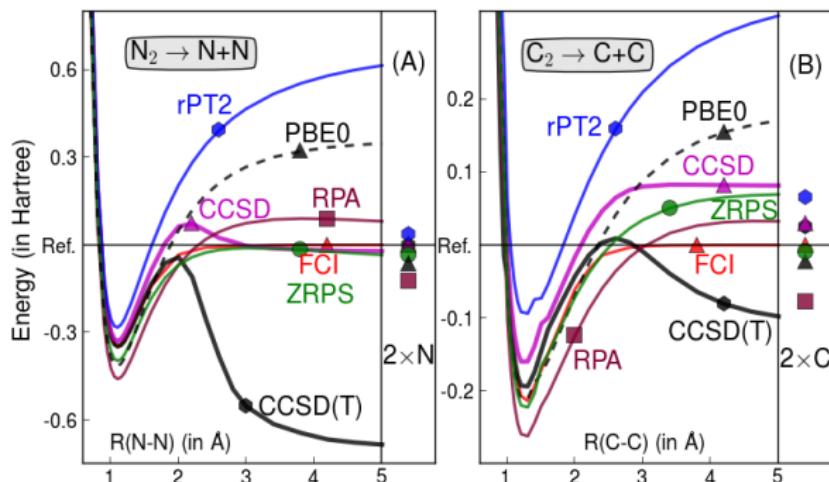
- ▶ CCSD and CCSD(T) results are obtained by using GAMESS
- ▶ PBE0, RPA, and rPT2 calculations using FHI-aims
- ▶ Full configuration interaction (FCI) within quantum Monte Carlo (QMC) using FHI-aims
- ▶ Ref's are the FCI-QMC results; The basis set used is cc-pV3Z

ZRPS: Multireference chemistry

$$E_{xc}^{\mathrm{ZRPS}} = 0.5E_x^{\mathrm{PBE}} + 0.75E_c^{\mathrm{PBE}} + 0.5E_x^{\mathrm{HF}} + 0.25E_c^{\mathrm{sBGE2}}[\{\phi_s\}, n]$$

- Parameter free
- Natural extension of PBE and PBE0
- Size consistency
- Complexity is on a par with PT2 or RPA

Errors (in meV) of various methods for O_3 involved reactions.

	PBE	→PBE0	RPA	→rPT2	ZRPS
A	65	-432	-190	-738	**41**
B	259	-311	-206	-768	**12**

A: $O_3 + C_2H_2 \rightarrow$ **B**: $O_3 + C_2H_4 \rightarrow$
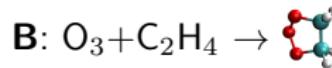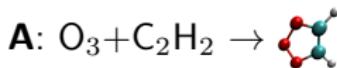
ZRPS: Conclusion

A parameter-free level-5 functional: ZRPS

$$E_{xc}^{\mathrm{ZRPS}} = 0.5 E_x^{\mathrm{GGA}} + 0.75 E_c^{\mathrm{GGA}} + 0.5 E_x^{\mathrm{HF}} + 0.25 E_c^{\mathrm{L5}}$$

- ▶ Robustness
  - Parameter free
  - Natural extension of PBE and PBE0
  - Constraint satisfaction
- ▶ Accuarcy:
  - Surpass (hybrid) GGAs, e.g. PBE0, for varying interactions:
  1. Atomization enegies (G2-1)
  2. Reaction barrier heights (BH76)
  3. Isomerization energies (ISO34)
  4. Weak interactions (S22)
  5. Molecular dissociations (H_2^+, H_2, C_2, N_2)
- ▶ Efficiency:
  - Complexity is on a par with PT2 or RPA

MP2 for solids:

Numerical convergence
in both real space and reciprocal space

Parts of the MSE project; Papers in writing

Periodic MP2 implementations

CRYSCOR: [1]

- ▶ Methods: Local MP2
- ▶ Basis set: Gaussian-type orbitals
- ▶ Core states: considered explicitly
- ▶ K-grid: Gamma-only

CP2K [2]

- ▶ Methods: Canonical MP2
- ▶ Basis set: Gaussian & plane waves
- ▶ Core states: Pseudo potentials
- ▶ K-grid: Gamma-only

VASP [3,4]

- ▶ Methods: Canonical MP2 and CCSD(T)
- ▶ Basis set: plane waves
- ▶ Core states: Pseudo potentials
- ▶ K-grid: Gamma-center k-mesh

[1] C. Pisani, et al., J. Comput. Chem. **29**, 2113 (2008).

[2] M. Del Ben, et al. J. Chem. Theory Comput. **8**, 4177 (2012).

[3] A. Grüneis, et al. J. Chem. Phys. **133**, 074107 (2010).

[4] G. H. Booth, et al. Nature, **493**, 365 (2013).

Finite cluster, Gamma only and Periodic approaches

Atom   Molecule   Nanostructure   Bulk

C

Benzene

Graphene

Graphite
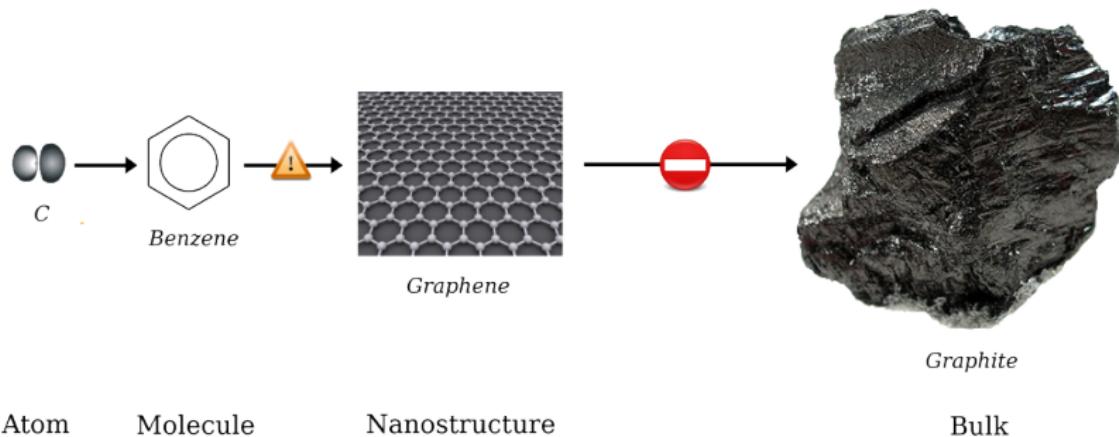
Finite cluster, Gamma only and Periodic approaches

- Correlation convergence: cluster, supercell, and k-grid sizes?

- Influence of boundary effect and pseudo-potential?

- Numeric convergence: basis set and k-grid?

Finite cluster, Gamma only and Periodic approaches

- ▶ All-electron full-potential electronic structure code
- ▶ Localized numerical atom-centered (NAO) basis sets
- ▶ Periodic HF, PBE0, HSE06, and RPA

Carry out simulations in a single computational environment

The periodic implementation of MP2

$$E_c^{\mathrm{MP2}} = \frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_{a,b}^{occ.} \sum_{n,m}^{vir.} \frac{2\,|(a\boldsymbol{k}n\boldsymbol{q}|b\boldsymbol{k'}m\boldsymbol{q'})|^2 - (a\boldsymbol{k}n\boldsymbol{q}|b\boldsymbol{k'}m\boldsymbol{q'})^* \,(a\boldsymbol{k}m\boldsymbol{q'}|b\boldsymbol{k'}n\boldsymbol{q})}{\epsilon_{a\boldsymbol{k}} + \epsilon_{b\boldsymbol{k'}} - \epsilon_{n\boldsymbol{q}} - \epsilon_{m\boldsymbol{q'}}}$$

- Formal scaling is $K^3 N^5$
- K is the number of k-points
- N represents the system size

The periodic implementation of MP2

$$E_c^{\mathrm{MP2}} = \frac{1}{N_{\boldsymbol{q}}^3} \sum_{\boldsymbol{\delta k k q'}} \sum_{a,b}^{occ.} \sum_{n,m}^{vir.} \frac{2\left|(a\boldsymbol{k}n\boldsymbol{q}|b\boldsymbol{k'}m\boldsymbol{q'})\right|^2 - (a\boldsymbol{k}n\boldsymbol{q}|b\boldsymbol{k'}m\boldsymbol{q'})^* \, (a\boldsymbol{k}m\boldsymbol{q'}|b\boldsymbol{k'}n\boldsymbol{q})}{\epsilon_{a\boldsymbol{k}} + \epsilon_{b\boldsymbol{k'}} - \epsilon_{n\boldsymbol{q}} - \epsilon_{m\boldsymbol{q'}}}$$

- Formal scaling is $K^3 N^5$
- K is th
- N repre

> K=6X6X6 $\to \sim 10^7$ times MP2
> or even higher-level calculations
>
> comparing to the calculation of finite
> molecules with the same system size N.

The periodic implementation of MP2

$$E_c^{\mathrm{MP2}} = \frac{1}{N_q^3} \sum_{\delta k k q'} \sum_{a,b}^{occ.} \sum_{n,m}^{vir.} \frac{2\left|(ak n q|b k' m q')\right|^2 - (ak n q|b k' m q')^* (ak m q'|b k' n q)}{\epsilon_{ak} + \epsilon_{bk'} - \epsilon_{nq} - \epsilon_{mq'}}$$

- Formal scaling is $K^3 N^5$
- K is th
- N repr

K=6X6X6 $\rightarrow \sim 10^7$ times MP2
or even higher-level calculations

comparing to the calculation of finite
molecules with the same system size N.

It is crucial to have a well-performed k-mesh-oriented parallelization
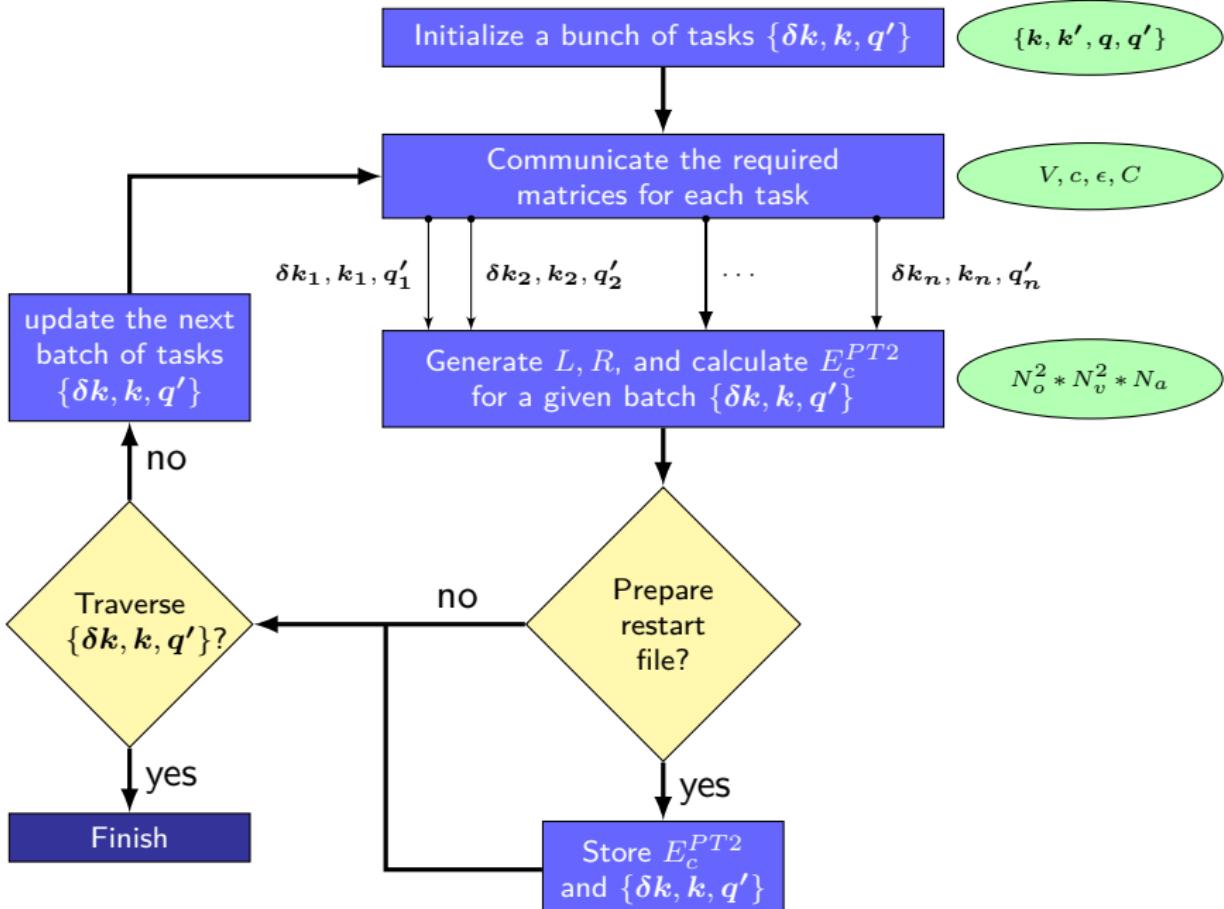
Parallelization efficiency
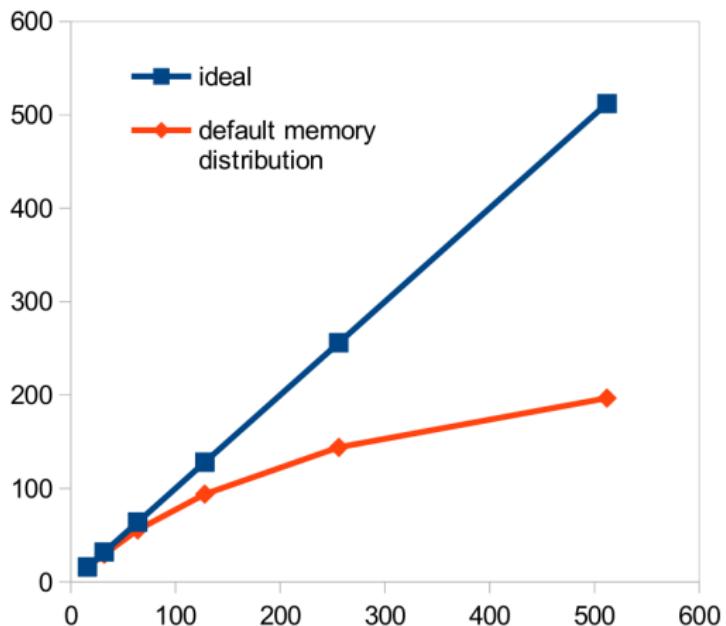
Measured speedup, Diamond, NAO-VCC-3Z, and 4X4X4

```
! =======================================================
! Duplicating the required arrays to free threads,
! which can improve the communication efficiency
! in a massive parallelization
!
! Sketch map:
!
! <--n_k_points-->                              <--A1-->
! |-----1st------|------2nd-----|------3rd-----|------|
! |-----------------------------------------------|
! <--------------------n_tasks-------------------->
!
! n_k_points : Total number of k points
! n_tasks    : Total number of threads
! A1         : The rest threads = mod(n_tasks, n_k_points)
```

Parallelization efficiency
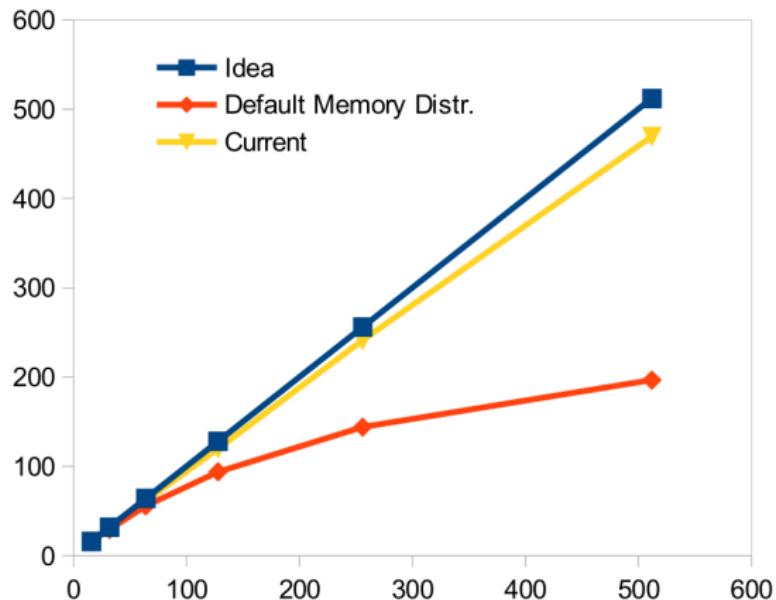
Measured speedup, Diamond, NAO-VCC-3Z, and 4X4X4

K-grid convergence
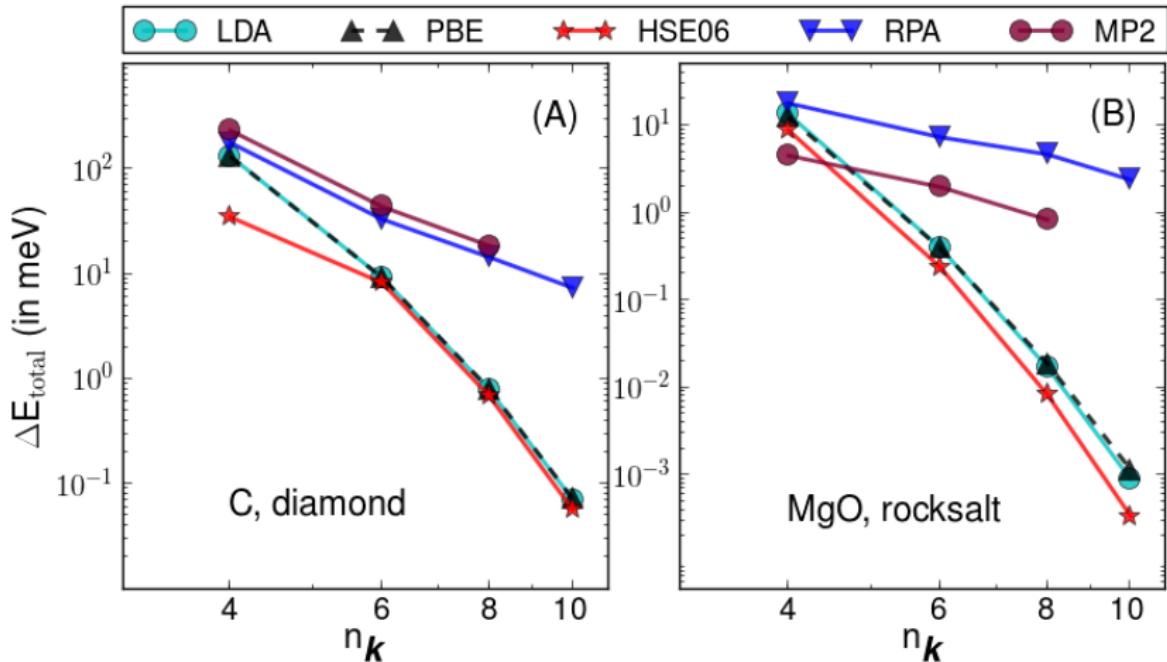
The gamma-center k-grid is used; Basis set: NAO-VCC-2Z

K-grid convergence

Complete k-mesh (CKM) extrapolation:

$$\Delta E_{\text{total}}[n_{\boldsymbol{k}}] = A/n_{\boldsymbol{k}}^{\alpha}$$

$$\log\left(\Delta E_{\text{total}}[n_{\boldsymbol{k}}]\right) = \log\left(A\right) - \alpha\log\left(n_{\boldsymbol{k}}\right)$$

G. H. Booth, *et al.* Nature, **493**, 365 (2013)
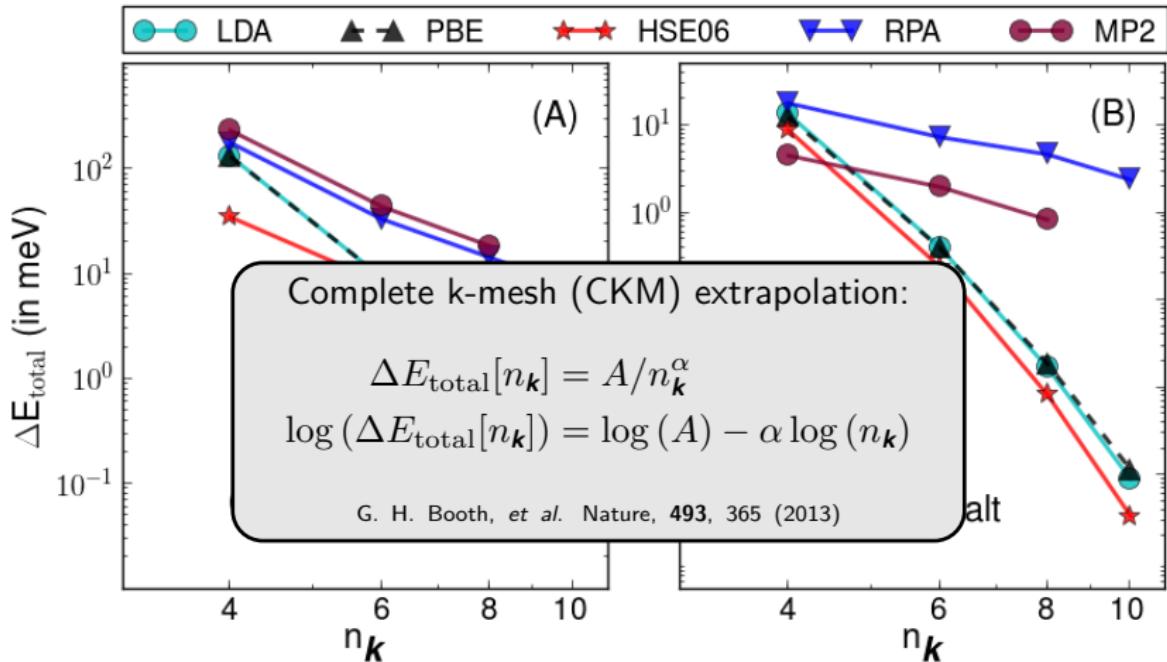
The gamma-center k-grid is used; Basis set: NAO-VCC-2Z

Downsampling concepts

Errors in the MP2 total energies per atom using different basis sets for C diamond (in meV).

k-mesh	NAO-VCC-2Z	NAO-VCC-3Z	NAO-VCC-4Z
$(4 \times 4 \times 4)$	117	114	115
$(6 \times 6 \times 6)$	22	22	22
$(8 \times 8 \times 8)$	9	9	9

[1] A. Grüneis, *et al.* J. Chem. Phys. **133**, 074107 (2010).

[1] G. H. Booth, *et al.* Nature, **493**, 365 (2013).

Downsampling concepts

Errors in the MP2 total energies per atom using different basis sets for C diamond (in meV).

k-mesh	NAO-VCC-2Z	NAO-VCC-3Z	NAO-VCC-4Z
$(4 \times 4 \times 4)$	117	114	115
$(6 \times 6 \times 6)$	22	22	22
$(8 \times 8 \times 8)$	9	9	9

$$E_{\text{total}}^{4Z}[n_{\boldsymbol{k}} = 8] = E_{\text{total}}^{4Z}[n_{\boldsymbol{k}} = 6] + \Delta E_{\text{total}}^{nZ}[n_{\boldsymbol{k}} = 8]$$

where

$$\Delta E_{\text{total}}^{nZ}[n_{\boldsymbol{k}} = 8] = E_{\text{total}}^{nZ}[n_{\boldsymbol{k}} = 8] - E_{\text{total}}^{nZ}[n_{\boldsymbol{k}} = 6]$$

[1] A. Grüneis, et al. J. Chem. Phys. **133**, 074107 (2010).

[1] G. H. Booth, et al. Nature, **493**, 365 (2013).

Basis-set convergence of the periodic MP2 method

		Diamond			Si		
		E (eV)	a_0 (Å)	B_0 (GPa)	E (eV)	a_0 (Å)	B_0 (GPa)
N2Z		7.65	3.56	451	4.62	5.44	98
N3Z		7.81	3.55	454	4.92	5.41	101
N4Z		7.96	3.54	454	5.07	5.41	101
CBS[34]		8.06	3.54	454	5.17	5.41	102
VASP	2010[1]	7.97	3.55	450	5.05	5.42	100
(PW)	2013[2]	8.04					
		MgO			AlP		
		E (eV)	a_0 (Å)	B_0 (GPa)	E (eV)	a_0 (Å)	B_0 (GPa)
N2Z		5.11	4.23	160	4.06	5.48	92
N3Z		5.39	4.23	162	4.41	5.45	94
N4Z		5.47	4.24	164	4.55	5.45	95
CBS[34]		5.53	4.24	165	4.66	5.45	95
VASP	2010[1]	5.35	4.23	153	4.32	5.46	93
(PW)	2013[2]				4.63		

[1] A. Grüneis, et al. J. Chem. Phys. **133**, 074107 (2010).

[2] G. H. Booth, et al. Nature, **493**, 365 (2013).

K-grid convergence **vs** Supercell-size convergence

# K-grid convergence **vs** Supercell-size convergence

Number of atoms per supercell

| | 2 | 4 | 8 | 16 |
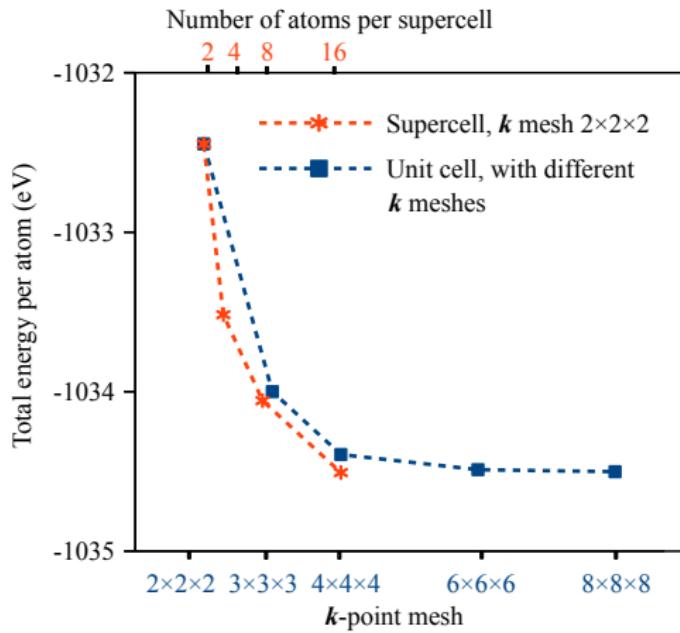
-1032

- - - - - * - - - - Supercell **k** mesh 2×2×2
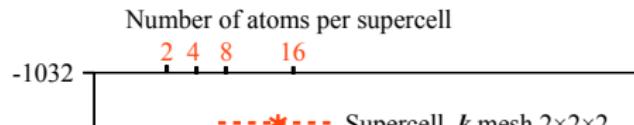
Results for diamond at MP2/NAO-VCC-2Z level

System size	**k**-mesh	Total energy per atom (eV)	Time (h)
2	$2 \times 2 \times 2$	-1032.447	0.94
	$4 \times 4 \times 4$	-1034.394	8.34
	$6 \times 6 \times 6$	-1034.489	31.29
	$8 \times 8 \times 8$	-1034.502	82.40
	Converged **k**-mesh	-1034.511	
16	$2 \times 2 \times 2$	-1034.508	1.03

The calculations are performed using 400 CPU cores of an Infiniband-connected
Intel cluster with Intel Xeon E5-2680 v2 cores (2.80GHz, 20 cores per node)

-1035

2×2×2   3×3×3   4×4×4   6×6×6   8×8×8
k-point mesh
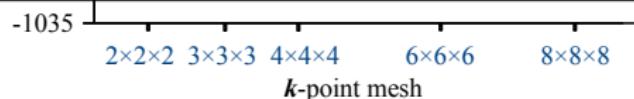
by Xiangyue Liu

Laplace-transformed MP2: Finite cluster and Gamma-only

$$E_{\mathsf{MP2}} = -2 \sum_{i,j}^{occ} \sum_{a,b}^{virt} \frac{\left[\displaystyle\sum_{s,u,t,v}^{basis} C_i^s C_j^u C_a^u C_b^v \left(su | tv \right) \right]^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

by Arvid C. Ihrig

[1] PY. Ayala, and GE. Scuseria, J. Chem. Phys. **110**, 3660 (1999).
[2] PY. Ayala, KN. Kudin, and GE. Scuseria, J. Chem. Phys. **115**, 9698 (2001).

Laplace-transformed MP2: Finite cluster and Gamma-only

$$\frac{1}{x} = \int_0^\infty e^{-xt}dt \approx \sum_q^{N_q} w_q e^{-xt_q}$$

$$E_{\mathsf{MP2}} = -2 \sum_{i,j}^{occ} \sum_{a,b}^{virt} \frac{\left[\sum_{s,u,t,v}^{basis} C_i^s C_j^u C_a^u C_b^v \left(su|tv\right) \right]^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

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Laplace-transformed MP2: Finite cluster and Gamma-only

$$\frac{1}{x} = \int_0^\infty e^{-xt}dt \approx \sum_q^{N_q} w_q e^{-xt_q}$$

$$E_{\mathsf{MP2}} = -2 \sum_{i,j}^{occ} \sum_{a,b}^{virt} \frac{\left[\sum_{s,u,t,v}^{basis} C_i^s C_j^u C_a^u C_b^v \left(su|tv\right) \right]^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

$$X_{su}^q = \sum_i^{occ} C_i^s C_i^u e^{\epsilon_i t_q} \qquad Y_{su}^q = \sum_a^{virt} C_a^s C_a^u e^{-\epsilon_a t_q}$$

by Arvid C. Ihrig

[1] PY. Ayala, and GE. Scuseria, J. Chem. Phys. **110**, 3660 (1999).
[2] PY. Ayala, KN. Kudin, and GE. Scuseria, J. Chem. Phys. **115**, 9698 (2001).

Laplace-transformed MP2: Finite cluster and Gamma-only

$$\frac{1}{x} = \int_0^\infty e^{-xt} dt \approx \sum_q^{N_q} w_q e^{-xt_q}$$

$$E_{\mathsf{MP2}} = -2 \sum_{i,j}^{occ} \sum_{a,b}^{virt} \frac{\left[\sum_{s,u,t,v}^{basis} C_i^s C_j^u C_a^u C_b^v \left(su|tv\right) \right]^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

$$X_{su}^q = \sum_i^{occ} C_i^s C_i^u e^{\epsilon_i t_q} \qquad Y_{su}^q = \sum_a^{virt} C_a^s C_a^u e^{-\epsilon_a t_q}$$

$$E_{\mathsf{MP2}}^{\mathsf{LT}} = - \sum_q^{N_q} w_q \sum_{s,u,t,v}^{basis} \left(\bar{s}\underline{u}|\bar{t}\underline{v}\right)^q \left[2\left(su|tv\right) - \left(sv|tu\right)\right]^2$$

by Arvid C. Ihrig

[1] PY. Ayala, and GE. Scuseria, J. Chem. Phys. **110**, 3660 (1999).
[2] PY. Ayala, KN. Kudin, and GE. Scuseria, J. Chem. Phys. **115**, 9698 (2001).

Periodic MP2: Trans-PA
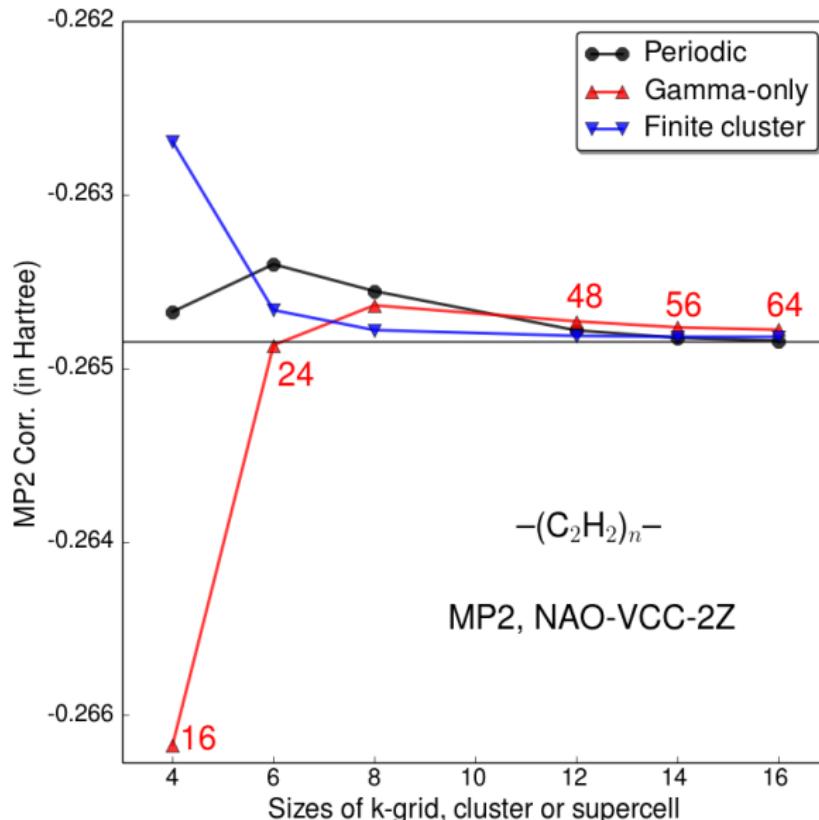
CCSD
for solids:

Finite cluster and periodic approaches

Parts of the MSE project; Papers in writing

by Dr. Tonghao Shen

Coupled-Cluster (CC) approach

Wave function
$$\Psi_{CC} = e^{\hat{T}}\Phi_0 = \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \frac{\hat{T}^3}{3!} + \cdots\right)\Phi_0$$

Cluster operator
$$\hat{T} = \sum \hat{T}_n$$

$$\hat{T}_1\Phi_0 = \sum_{i,a} t_i^a \Phi_i^a \qquad \hat{T}_2\Phi_0 = \sum_{i<j,a<b} t_{ij}^{ab} \Phi_{ij}^{ab} \qquad \cdots$$

Correlation energy
$$E_{corr} = \langle \Phi_0 | \bar{H}_N e^{\hat{T}} | \Phi_0 \rangle_C$$

CC equations
$$\langle \Phi_i^a | \bar{H}_N e^{\hat{T}} | \Phi_0 \rangle_C = 0,$$

$$\langle \Phi_{ij}^{ab} | \bar{H}_N e^{\hat{T}} | \Phi_0 \rangle_C = 0,$$

$$\langle \Phi_{ijk}^{abc} | \bar{H}_N e^{\hat{T}} | \Phi_0 \rangle_C = 0$$
$$\cdots$$

R. J. Bartlett and M. Musiał, *Rev. Mod. Phys.*, **79**, 291 (2007)

Challenges in the implementation

- High computational cost

- Large storage space demand

- Low parallel efficiency

	Cluster model		Periodic model	
	CCSD	CCSD(T)	CCSD	CCSD(T)
Cost	$O(N^6)$	$O(N^7)$	$O(N^6K^4)$	$O(N^7K^5)$
Storage	$O(N^4)$	$O(N^4)$	$O(N^4K^3)$	$O(N^4K^3)$
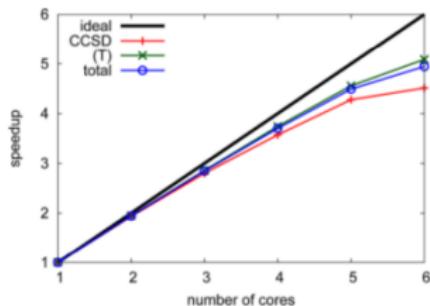
A. E. DePrince and C. D. Sherrill, *JCTC*. **9**, 2687(2013)
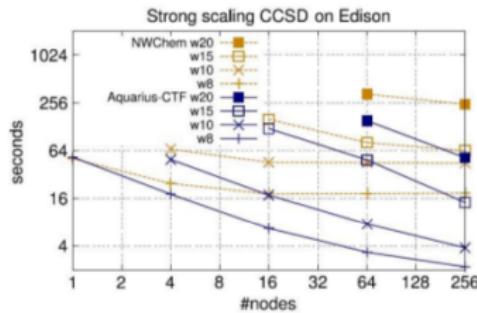
E. Solomonik, *et. al.* *J. Parallel Distrib. Comput.* **74**, 3176 (2014)

Tensor construction and contraction

Amplitude tensor

$$t_i^a \quad \longleftarrow \quad \langle \Phi_i^a | \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle_C = 0$$

$$t_{ij}^{ab} \quad \longleftarrow \quad \langle \Phi_{ij}^{ab} | \hat{H}_N e^{\hat{T}} | \Phi_0 \rangle_C = 0$$

Tensor contraction

$$a_{ij}^{kl} = \sum_{c,d} v_{cd}^{kl} t_{ij}^{cd} \qquad v_{ab}^{ij} = \langle ij | ab \rangle = (ia|jb)$$

Matrix multiplication

- Lapack
- Tensor Contraction Engine (TCE)
- Cyclops Tensor Framework (CTF)

Largest test carried out by CTF:

water 55 cluster at cc-pVDZ level by using 16384 nodes (256K cores)

N_o	N_v	N_{config}	Memory cost
275	1045	~41 billion	~262 TB

So Hirata, *J. Phys. Chem. A*, **107**, 9887 (2003)

E. Solomonik, *et. al. J. Parallel Distrib. Comput.* **74**, 3176 (2014)

Tensors needed for Finite-cluster approach

Memory and computational costs

Tensors	Memory cost	Computational cost	
		construction	contraction
t_{ij}^{ab}	$N_o^2 N_v^2$	N^6	N^6
v_{ab}^{ij}	$N_o^2 N_v^2$	N^5	N^6
v_{jb}^{ia}	$N_o^2 N_v^2$	N^5	N^5
v_{ic}^{kl}	$N_o^3 N_v$	N^5	N^5
v_{ij}^{kl}	N_o^4	N^5	-
v_{cd}^{ak}	$N_o N_v^3$	N^5	N^5
j_{ic}^{ak}	$N_o^2 N_v^2$	$N_o^3 N_v^3$	$N_o^3 N_v^3$
k_{ic}^{ka}	$N_o^2 N_v^2$	$N_o^3 N_v^3$	$N_o^3 N_v^3$
a_{ij}^{kl}	N_o^4	$N_o^4 N_v^2$	$N_o^4 N_v^2$
b_{cd}^{ab}	N_v^4	N^5	$N_o^2 N_v^4$
v_{cd}^{ab}	N_v^4	N^5	-

Tensors needed for Periodic approach

Integral tensors $\qquad v_{qs}^{pr}(k_p, k_q, k_r, k_s)$

Tensors stored in memory

| Tensors	Memory cost	Computational cost	
		construction	contraction
$t_{ik_ijk_j}^{ak_abk_b}$	$K^3 N_o^2 N_v^2$	$K^4 N^6$	$K^4 N^6$
$j_{ik_ick_c}^{ak_akk_k}$	$K^3 N_o^2 N_v^2$	$K^4 N_o^3 N_v^3$	$K^4 N_o^3 N_v^3$
$k_{ik_ick_c}^{kk_kak_a}$	$K^3 N_o^2 N_v^2$	$K^4 N_o^3 N_v^3$	$K^4 N_o^3 N_v^3$
$a_{ik_ijk_j}^{kk_klk_l}$	$K^3 N_o^4$	$K^4 N_o^4 N_v^2$	$K^4 N_o^4 N_v^2$

Parallization strategy

- MPI tasks grouping
- Hybrid MPI-OMP parallel programing

$$\mathbf{C} = \mathbf{AB}$$

$$
\begin{array}{ccc}
C_{11} & C_{12} & C_{13} \\
C_{21} & C_{22} & C_{23} \\
C_{31} & C_{32} & C_{33}
\end{array}
=
\begin{array}{ccc}
A_{11} & A_{12} & A_{13} \\
A_{21} & A_{22} & A_{23} \\
A_{31} & A_{32} & A_{33}
\end{array}
\times
\begin{array}{ccc}
B_{11} & B_{12} & B_{13} \\
B_{21} & B_{22} & B_{23} \\
B_{31} & B_{32} & B_{33}
\end{array}
$$

storage

|	Domain 1	Domain 2	Domain 3
Group 1	0	1	2
Group 2	3	4	5
Group 3	6	7	8

$$
\begin{array}{cccccc}
A_{11} & A_{21} & A_{31} & B_{11} & B_{12} & B_{13} \\
A_{12} & A_{22} & A_{32} & B_{21} & B_{22} & B_{23} \\
A_{13} & A_{23} & A_{33} & B_{31} & B_{32} & B_{33}
\end{array}
$$

$\mathbf{A}^T$ $\qquad\qquad$ $\mathbf{B}$

Parallization strategy

- MPI tasks grouping
- Hybrid MPI-OMP parallel programing

$$\mathbf{C} = \mathbf{AB}$$
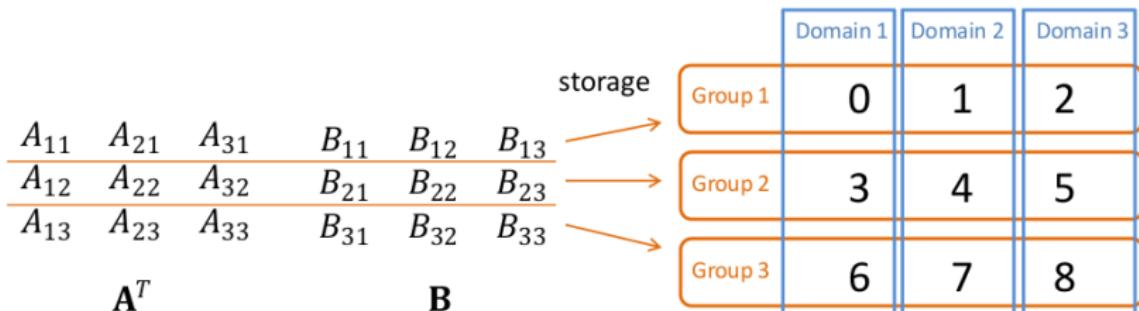
$$
\begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \times \begin{bmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{bmatrix}
$$

	Domain 1	Domain 2	Domain 3
	0	1	2
	3	4	5
	6	7	8

Calculation

$$C_{11} \begin{cases} A_{11} \times B_{11} \\ A_{12} \times B_{21} \\ A_{13} \times B_{31} \end{cases}$$

Parallization strategy

- MPI tasks grouping
- Hybrid MPI-OMP parallel programing
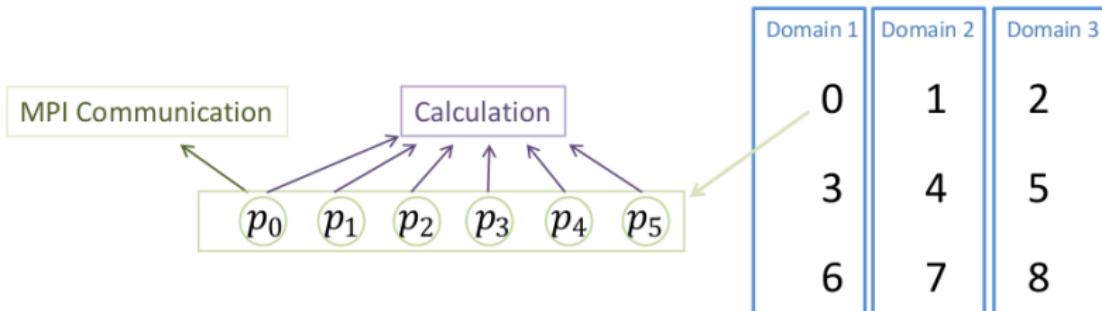
CCSD in FHI-aims: Accuracy

Correlation energies of small molecules at equilibrium geometries.

Potential energy curves of H_2 and CO
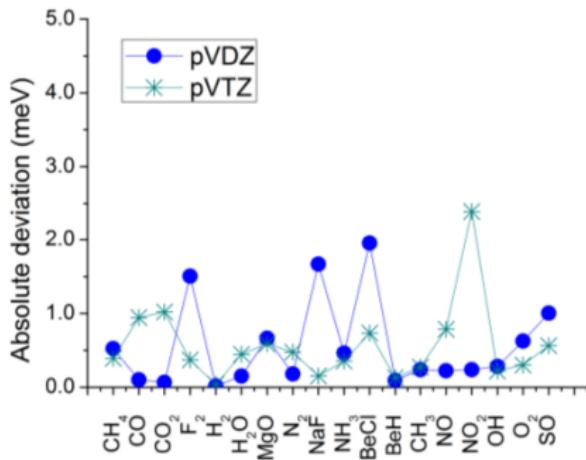
Deviations from results calculated by GAMESS program
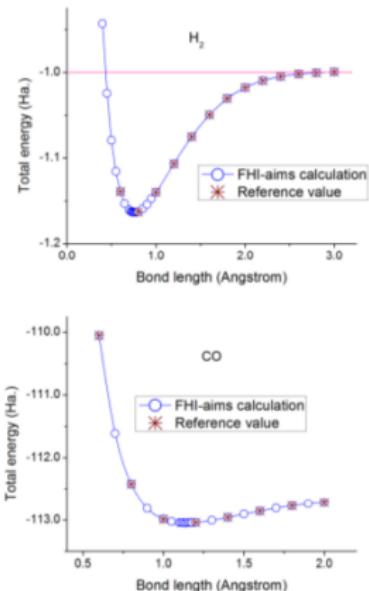
M.W.Schmidt, K.K.Baldridge, J.A.Boatz, *et al. J. Comput. Chem.*, **14**, 1347 (1993)

CCSD in FHI-aims: Parallelization efficiency

Time scaling
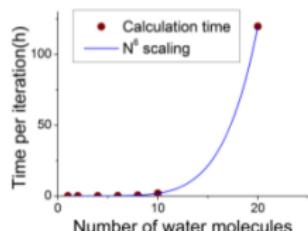
CCSD calculations of water clusters using N2Z basis set.
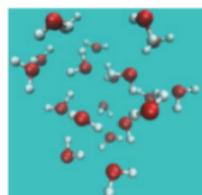
MPI Parallel efficiency
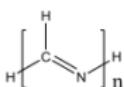
Polymethinimine (PMI)   Benzene dimer
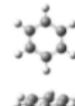
	Basis set	N excitations
PMI12	NAO-2Z	1.92E8
Benzene dimer	aug-cc-pVTZ	2.63E8

CPU utilization

$80 \times 32 = 2560$ cores
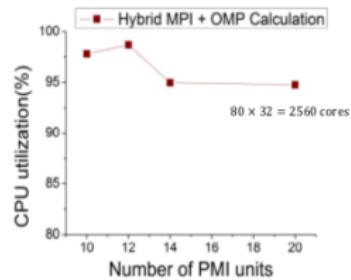
CPU utilization of PMI by using different grouping strategies
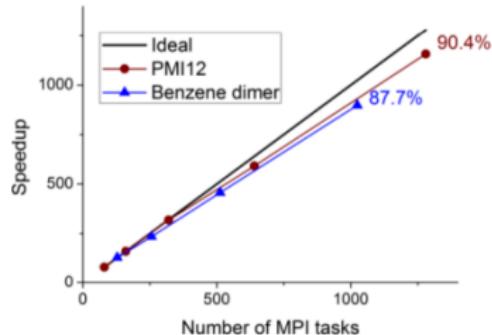
CCSD in FHI-aims: Cluster v.s. Periodic
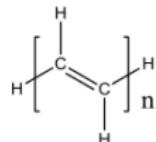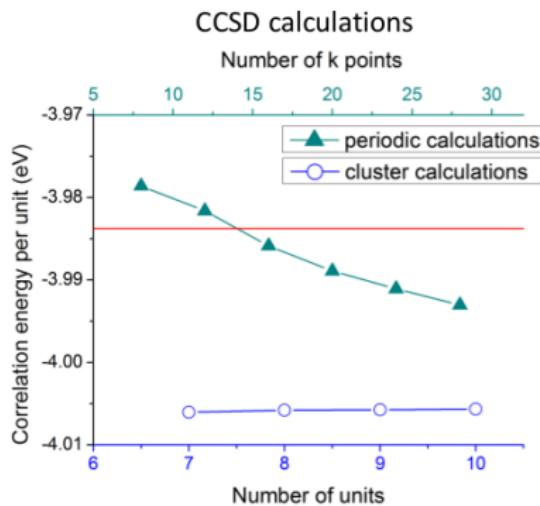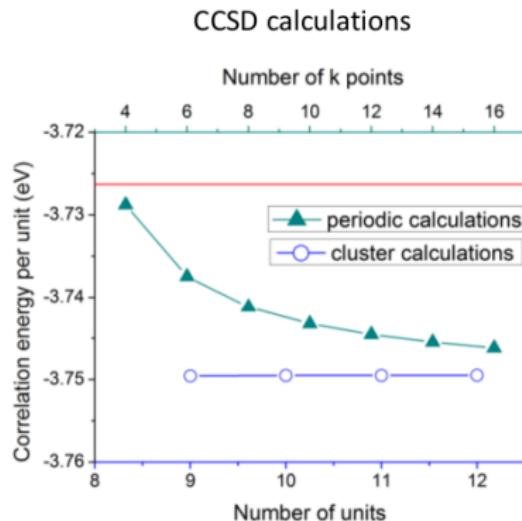
S. Hirata, R. Podeszwa, M. Tobita, *et al. JCP,* **120**, 2581 (2004)

> **Advanced first-principle methods for materials science and engineering**
>
> *http://th.fhi-berlin.mpg.de/site/index.php?n=Groups*
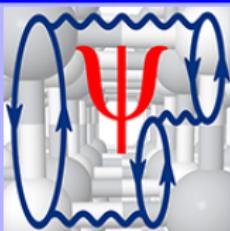
- **NAO-VCC-nZ**: NAO basis sets with correlation consistency

  I.Y. Zhang, *et al.* New J. Phys. **15**, 123033 (2013).

- **sBGE2**: Wave-function inspired functional for the H_2/H_2^+ challenge

  I.Y. Zhang, P. Rinke, and M. Scheffler. arXiv:1604.03929 (2016).

- **ZRPS**: An efficient, general purpose orbital-dependent DFA

 I.Y. Zhang, P. Rinke, J.P. Perdew and M. Scheffler. submitted (2016).

- **MP2 for solids**: Numerical convergence in real and reciprocal spaces

- **CCSD** implementation for both cluster and periodic systems

  Parts of the MSE project; Papers in writing.

Advanced first-principle methods for materials science and engineering

http://th.fhi-berlin.mpg.de/site/index.php?n=Groups
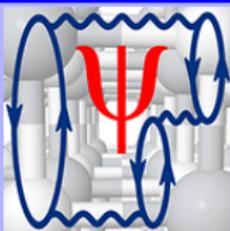
- ▸ **NAO-VCC-nZ**: To cover more heavy elements
- ▸ **F12 strategy**: Speed up the basis-set convergence

- ▸ **CCSD(T)**: Perturbative triple excitations
- ▸ **Lower-scaling MP2 and CCSD(T) for solids**

- ▸ **MSE:** Test set for materials science and engineering

- ▸ **Applications in HIOS and strongly correlated systems**

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- ▶ Prof. Xinguo Ren, USTC, China

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- ▶ Prof. John P. Perdew, Temple University, USA

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- ▶ Arvid C. Ihrig
- ▶ Xiangyue Liu