Self-consistent many-body methods for bond-making and breaking

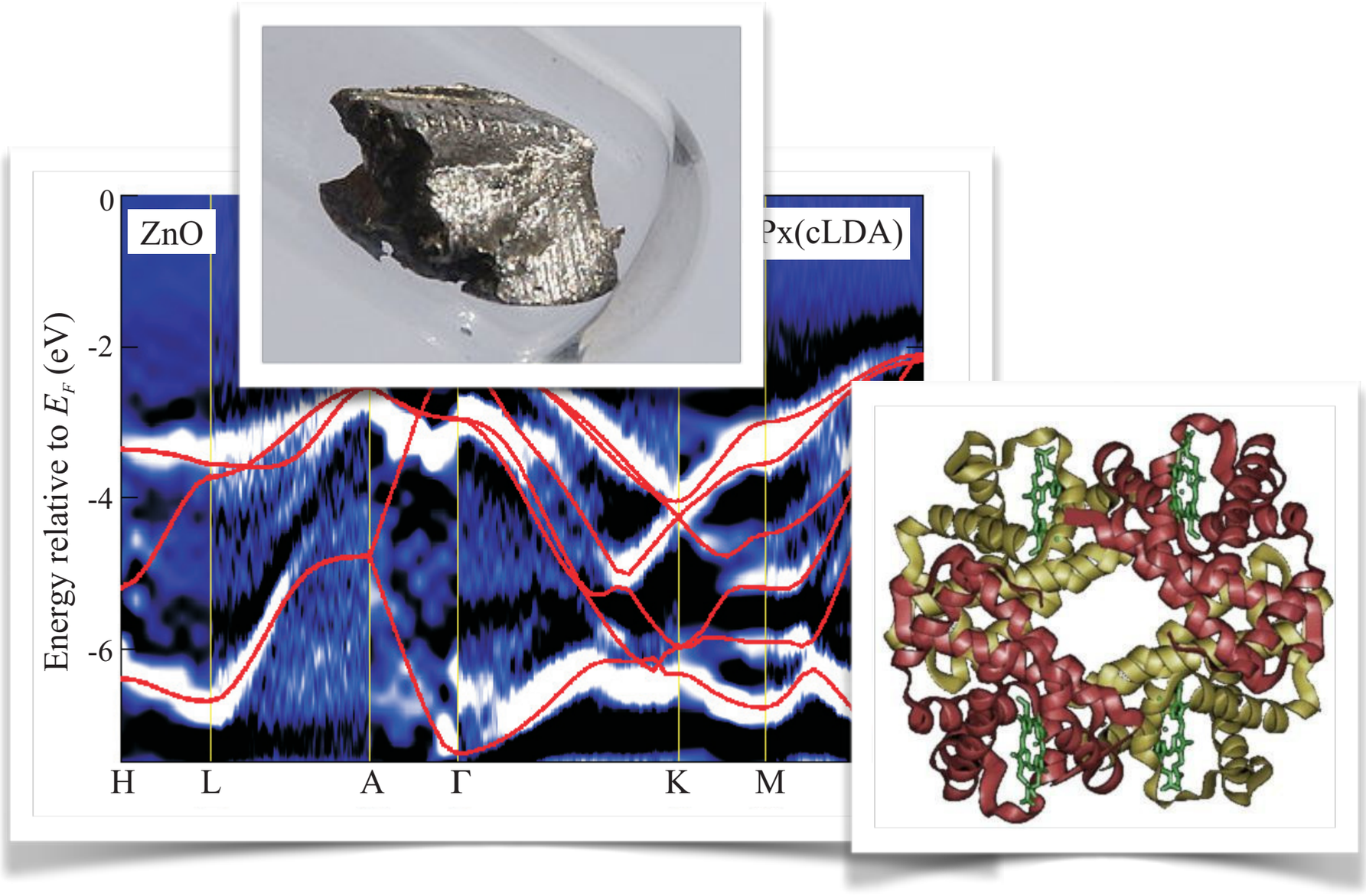
Patrick Rinke
School of Science
Department of Applied Physics
Helsinki, Finland

Aalto University
School of Science

CSC

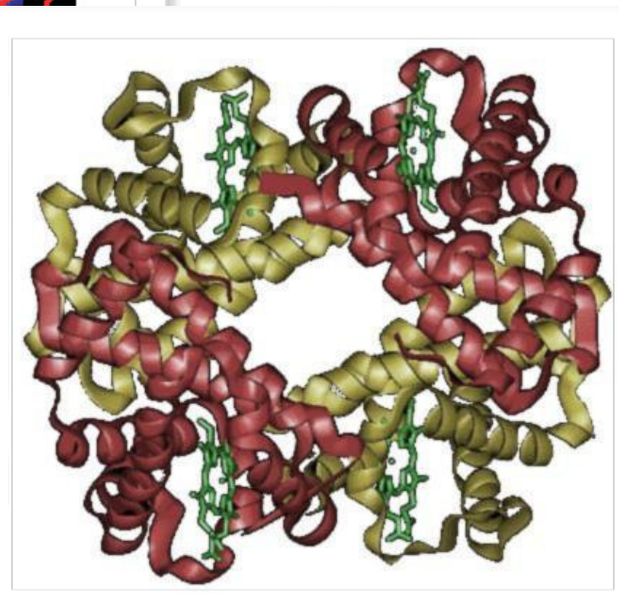
ACADEMY OF FINLAND

Wish list for electronic structure approaches



Wish list for electronic structure approaches

all dimensionalities (0D-3D)



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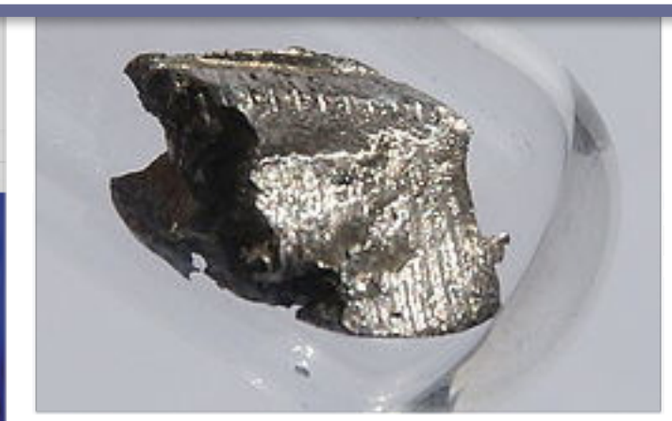
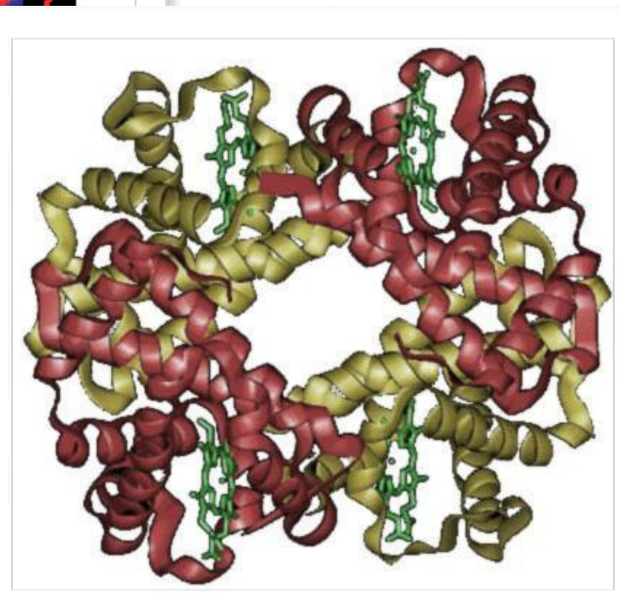
efficient





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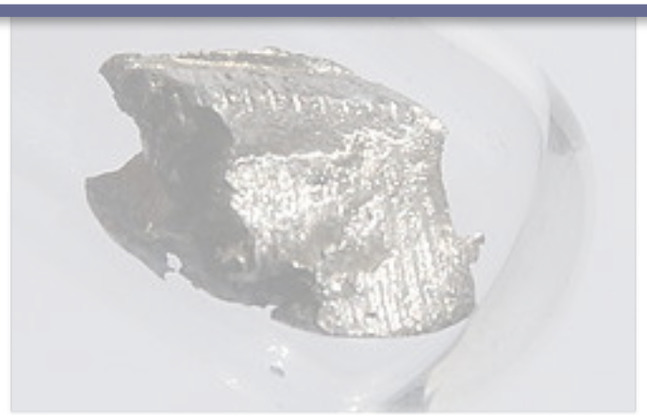

efficient

whole periodic table (including d/f)

Wish list for electronic structure approaches

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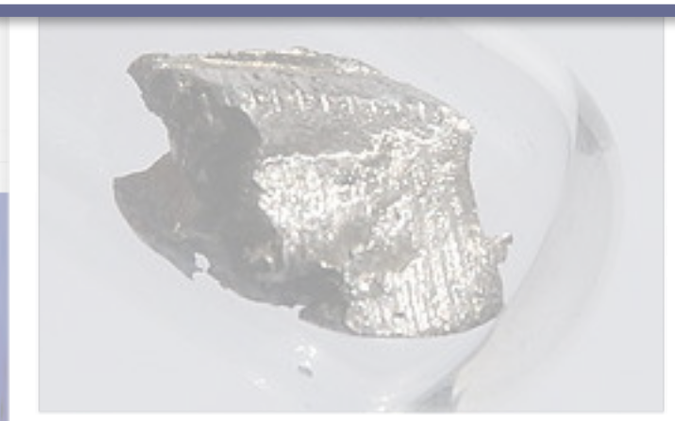

efficient

whole periodic table (including d/f)

ground+excited states

Wish list for electronic structure approaches

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efficient

free from pathologies, e.g.
- **self-interaction**
- **absence of van der Waals**
- **band-gap problem**

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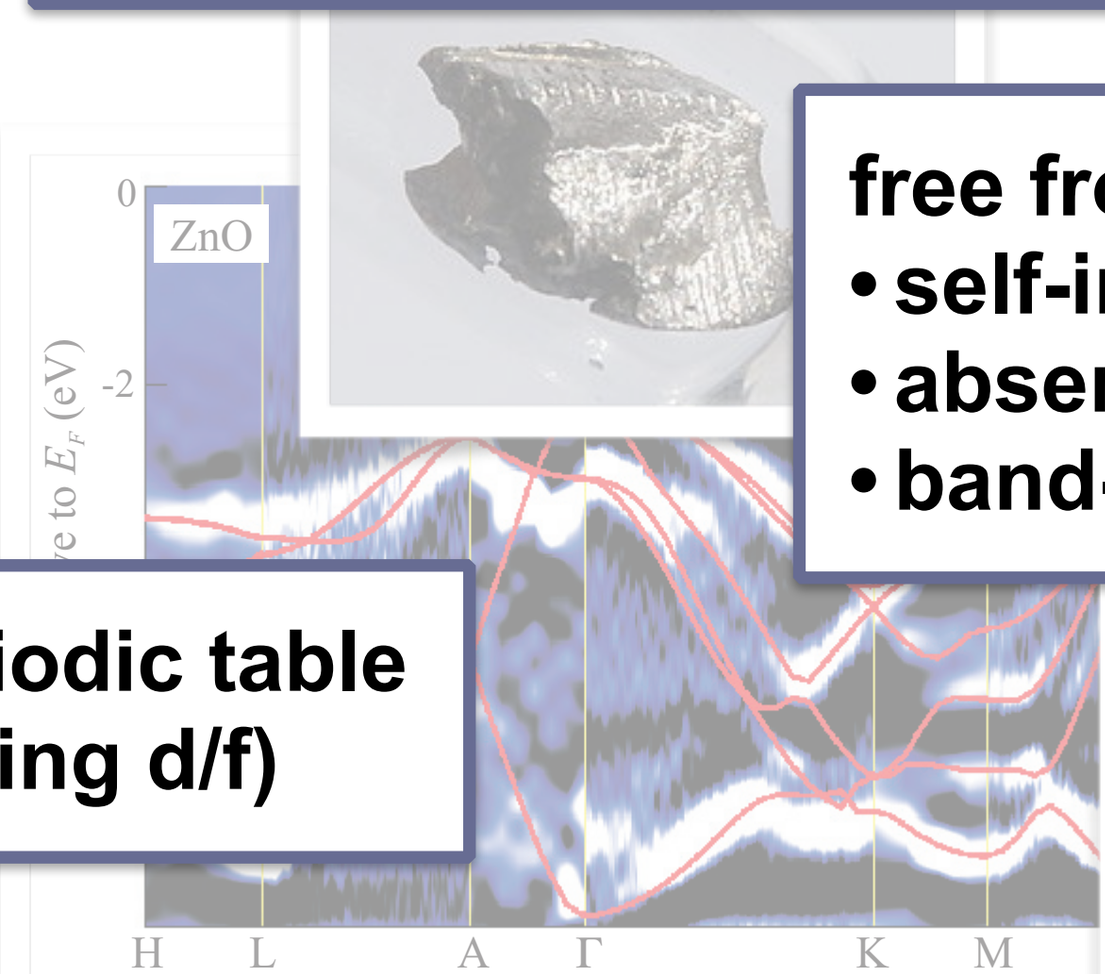

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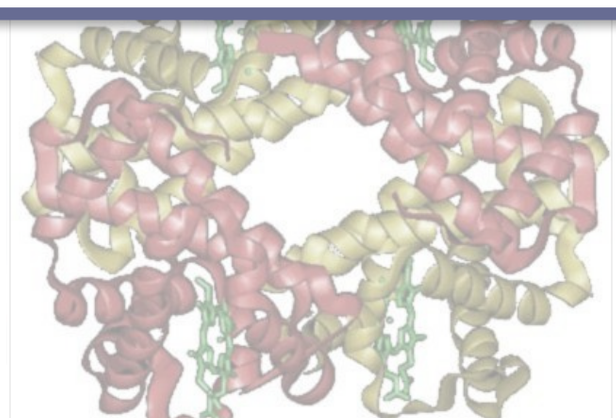

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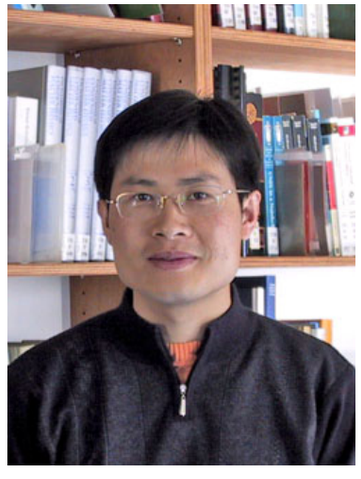
RPA applied to the f-electron metal Cerium

Marco Casadei
formerly UC Louvain
La Neuve, Belgium



Xinguo Ren
Hefei University of Technology, China

Matthias Scheffler
FHI, Berlin

Angel Rubio
MPSD, Hamburg

Aalto University
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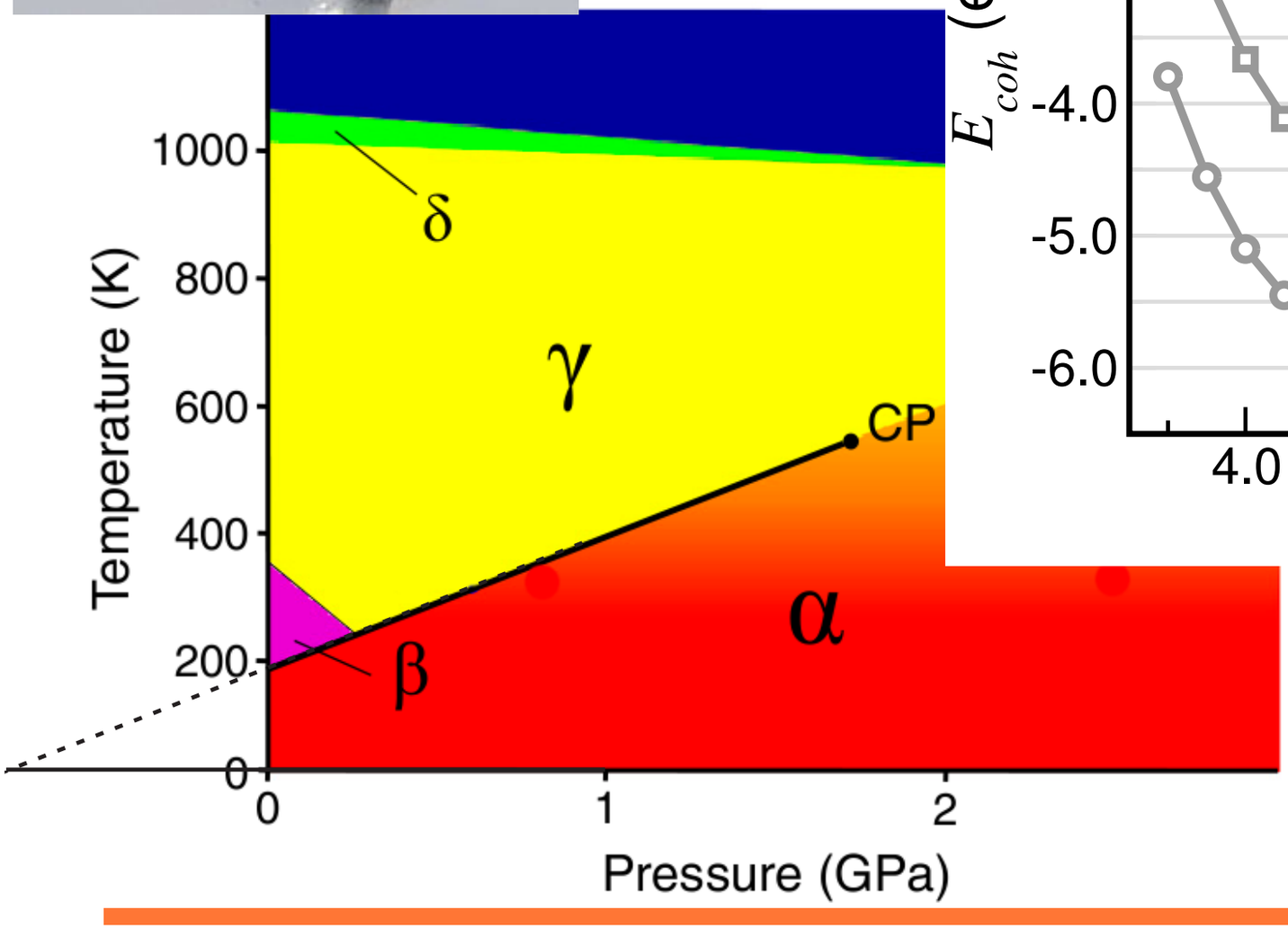
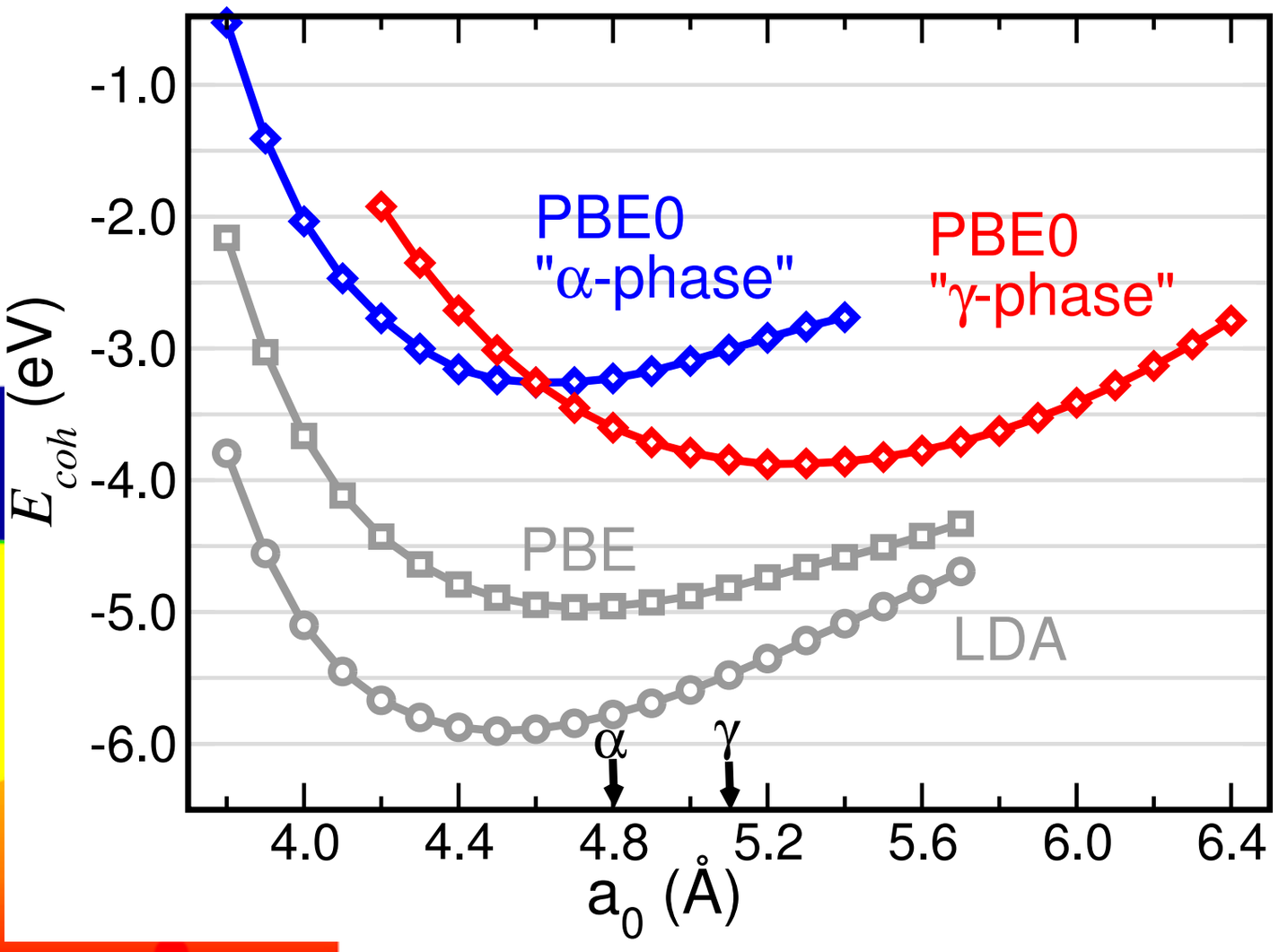
The f-electron metal Cerium





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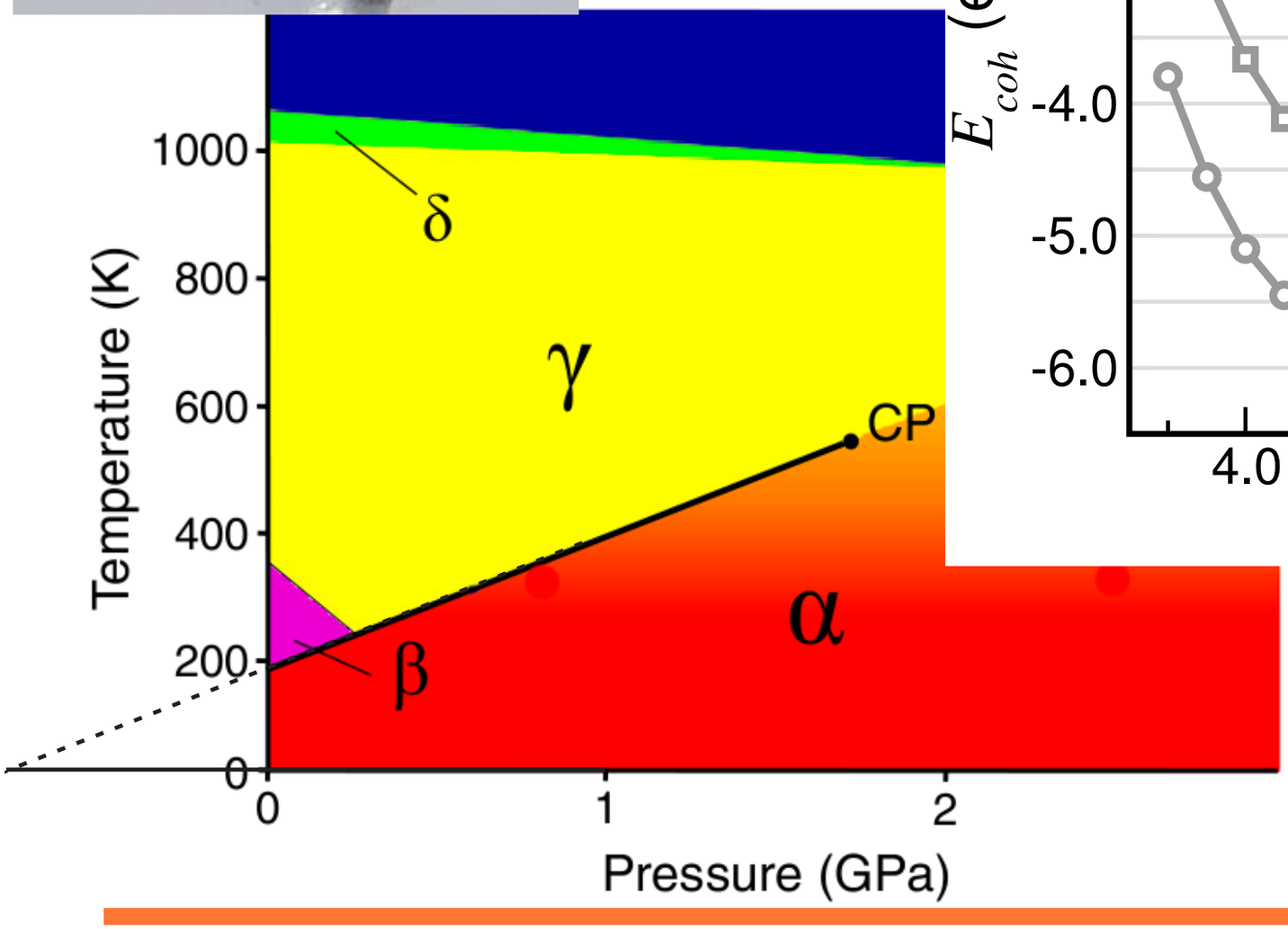
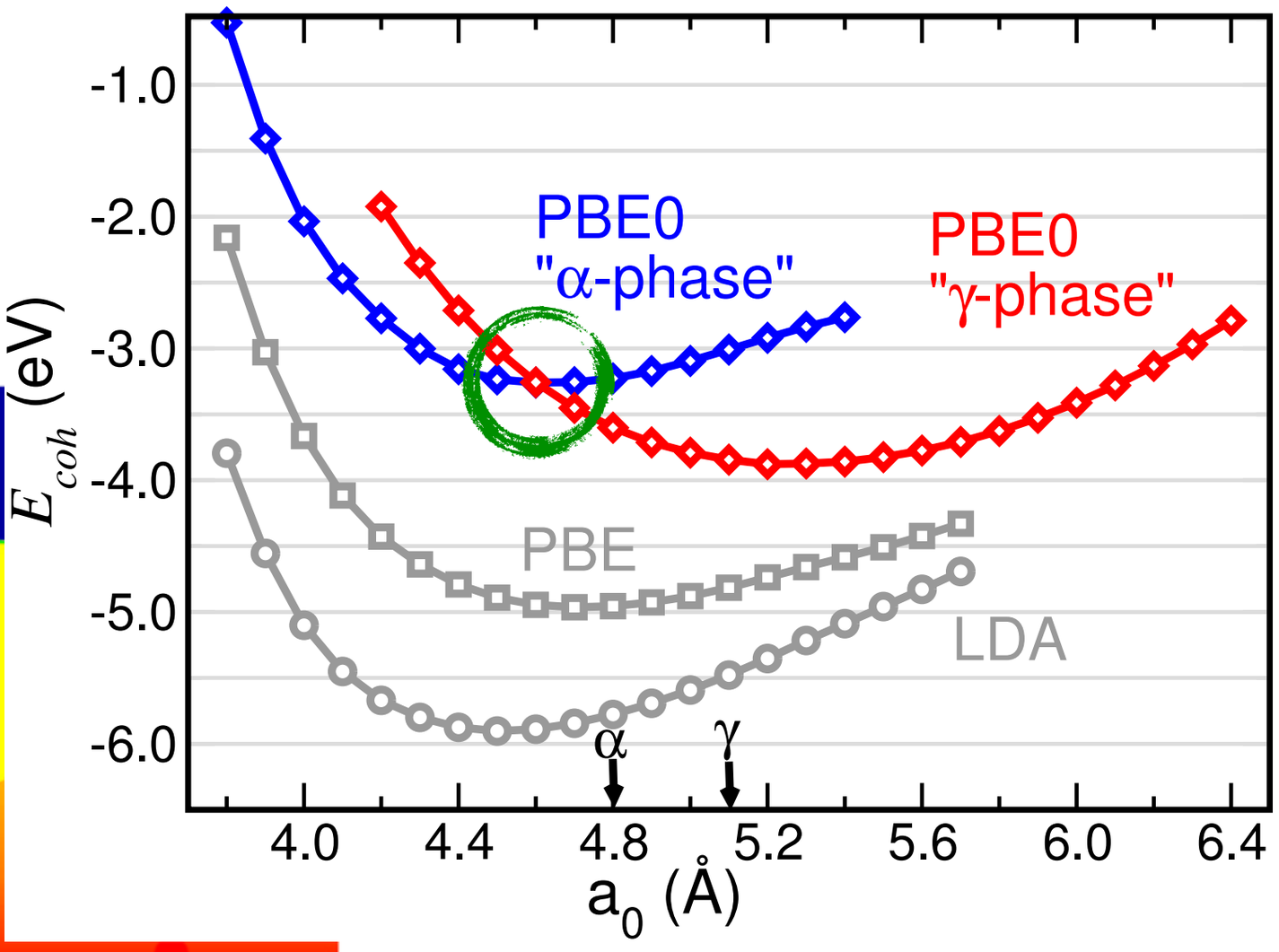
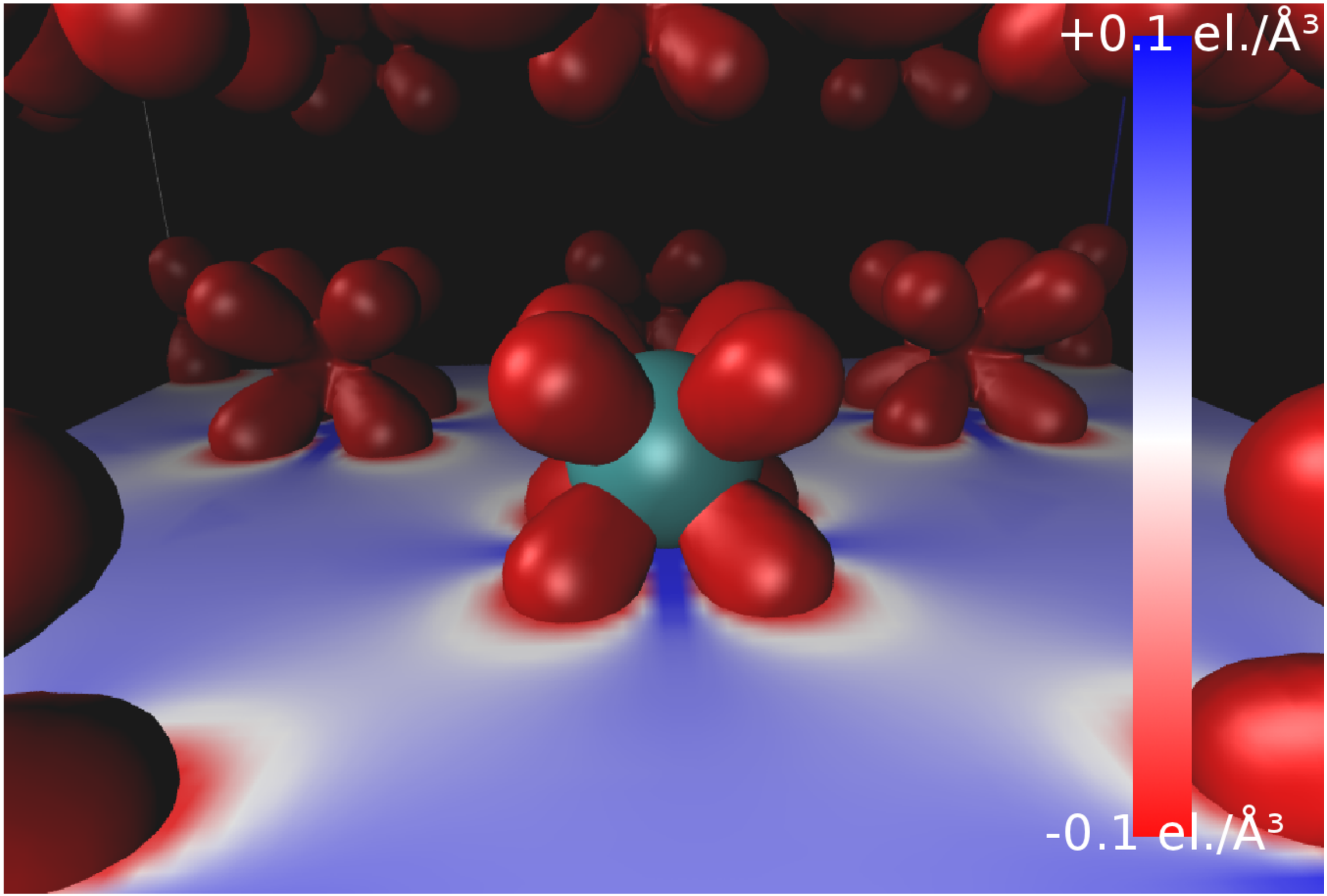




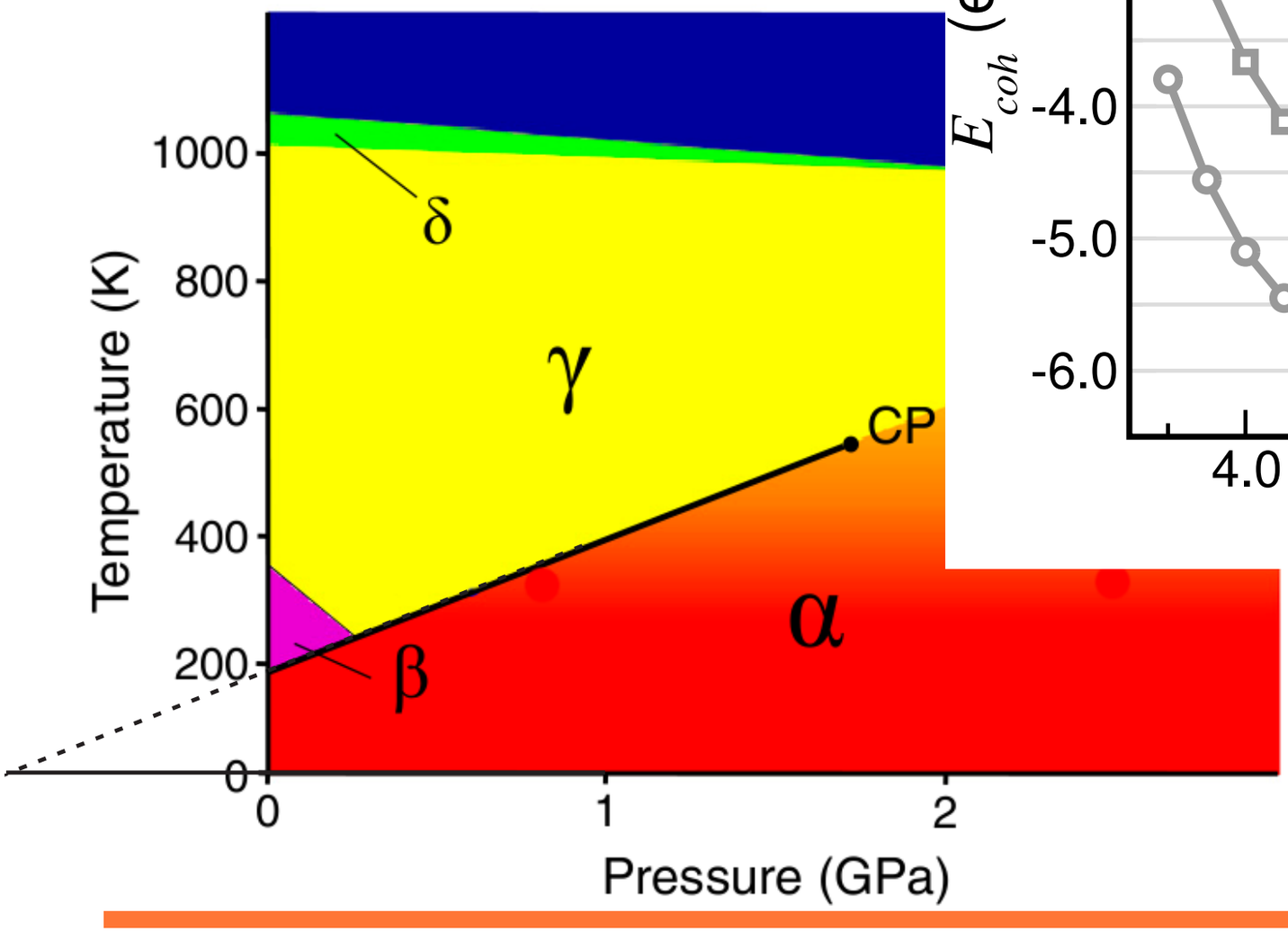
Cerium - density difference in PBE0

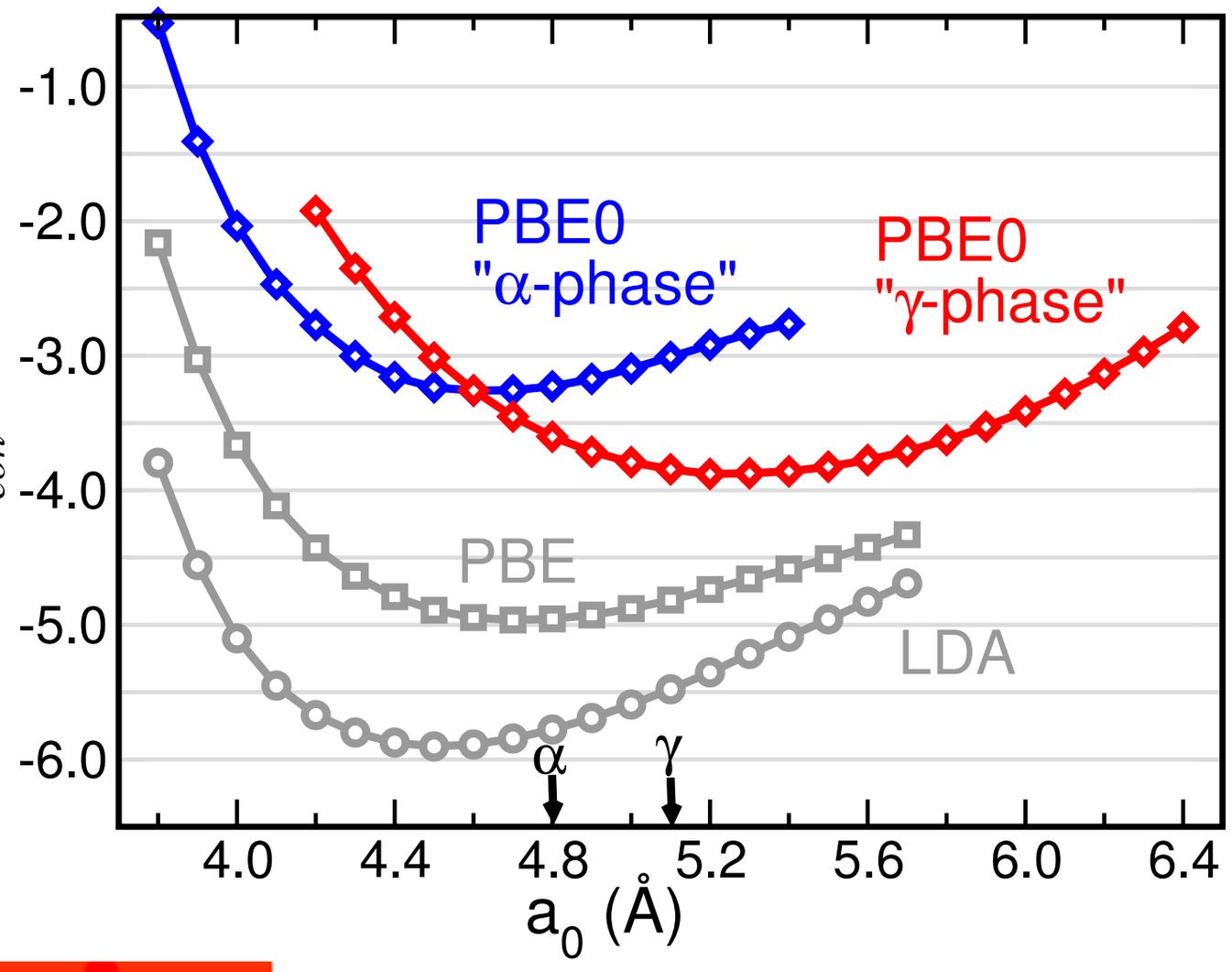
$$n(\alpha) - n(\gamma) \text{ at a=}4.6\text{Å}$$



The f-electron metal Cerium

- wrong phase ordering





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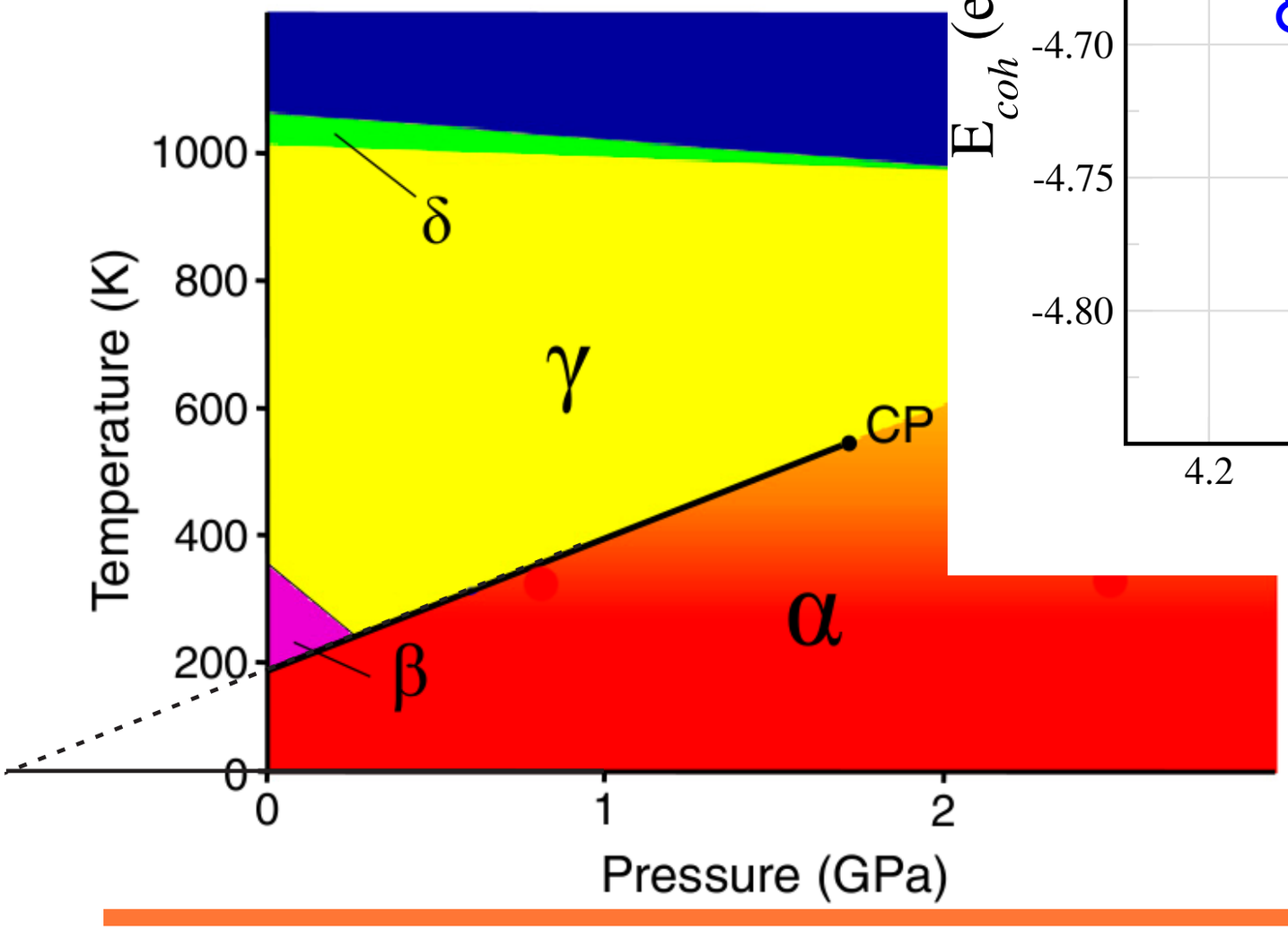
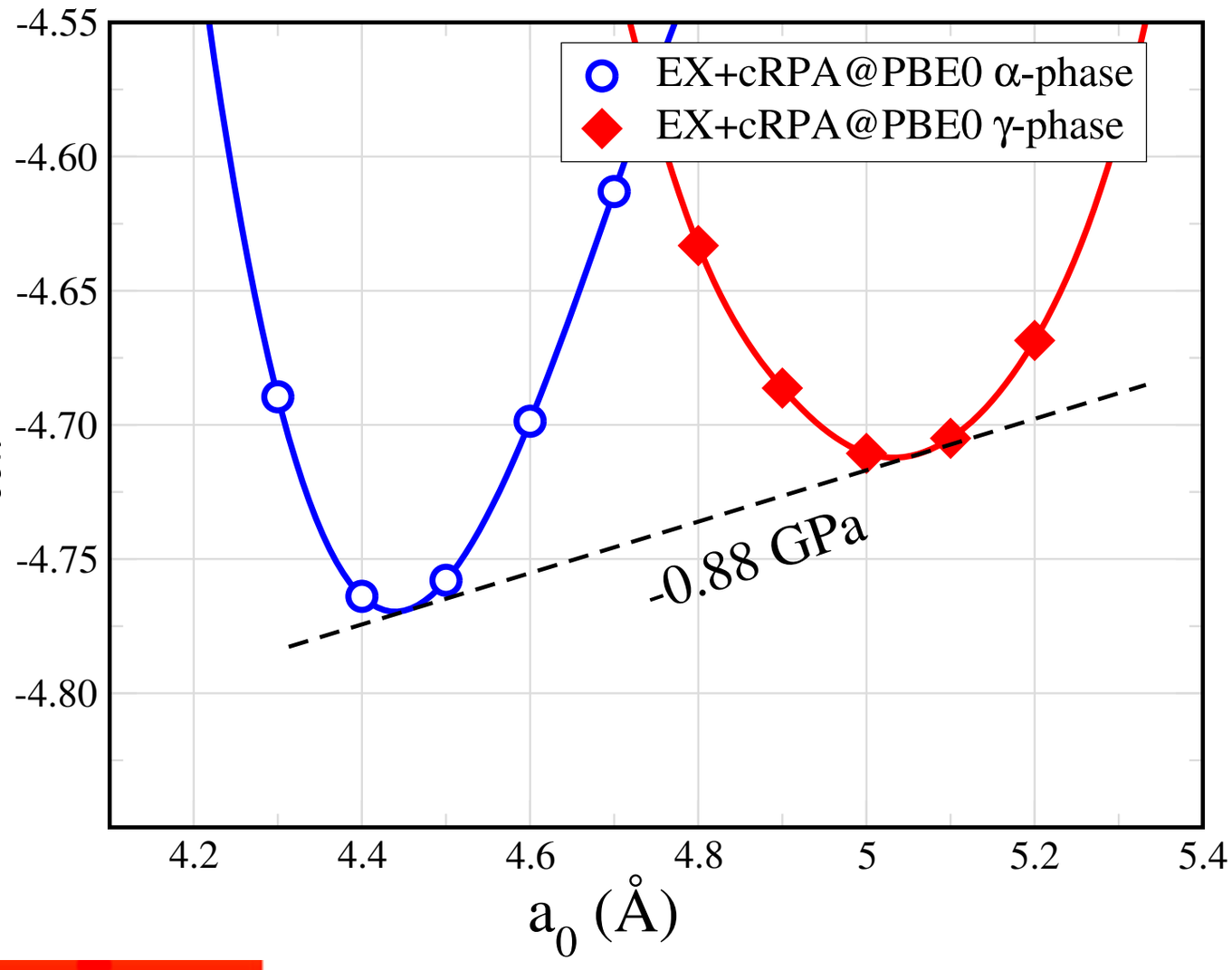
M. Casadei, X. Ren, P. Rinke, A. Rubio, M. Scheffler,
Phys. Rev. Lett. 109, 146402 (2012)

RPA applied to the f-electron metal Cerium

- correct phase ordering
- results for Ce_{19} cluster





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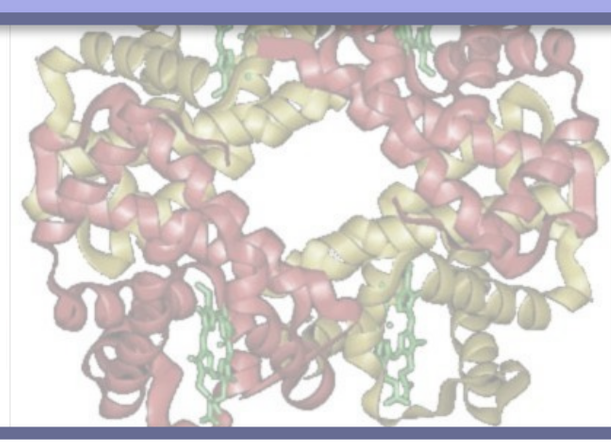


whole periodic table (including d/f)

ground+excited states

gradients+structure relaxation

Wish list for electronic structure approaches

all dimensionalities (0D-3D)

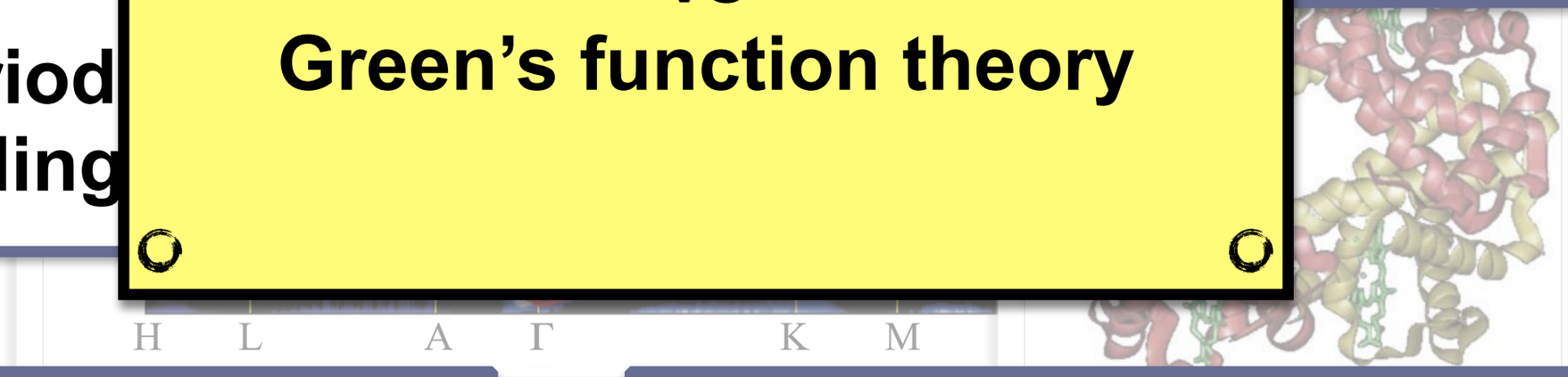
efficient

whole period
(including

Today

Density-functional theory
vs
Green's function theory

ologies, e.g.
on
an der Waals
blem



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Wish list for electronic structure approaches

all dimensionalities (0D-3D)

ef

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aals

new functional

RPA

Today

Density-functional theory vs Green's function theory

whole period (including

GW

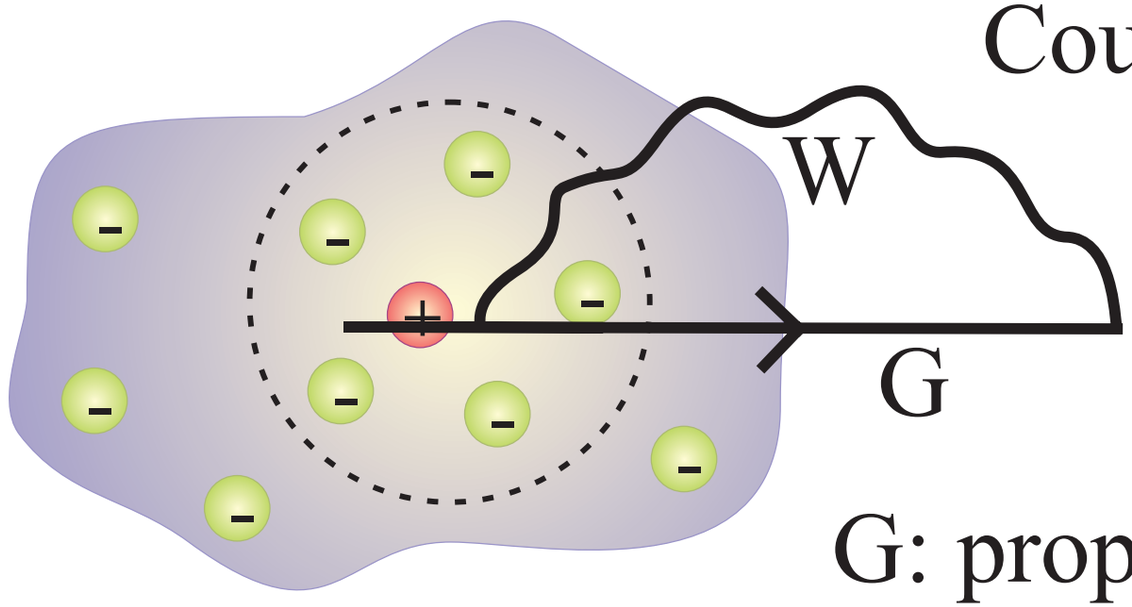
H L A Γ K M

ground+excited states

gradients+structure relaxation

Theoretical spectroscopy - *GW* approximation

$$\Sigma = iGW$$



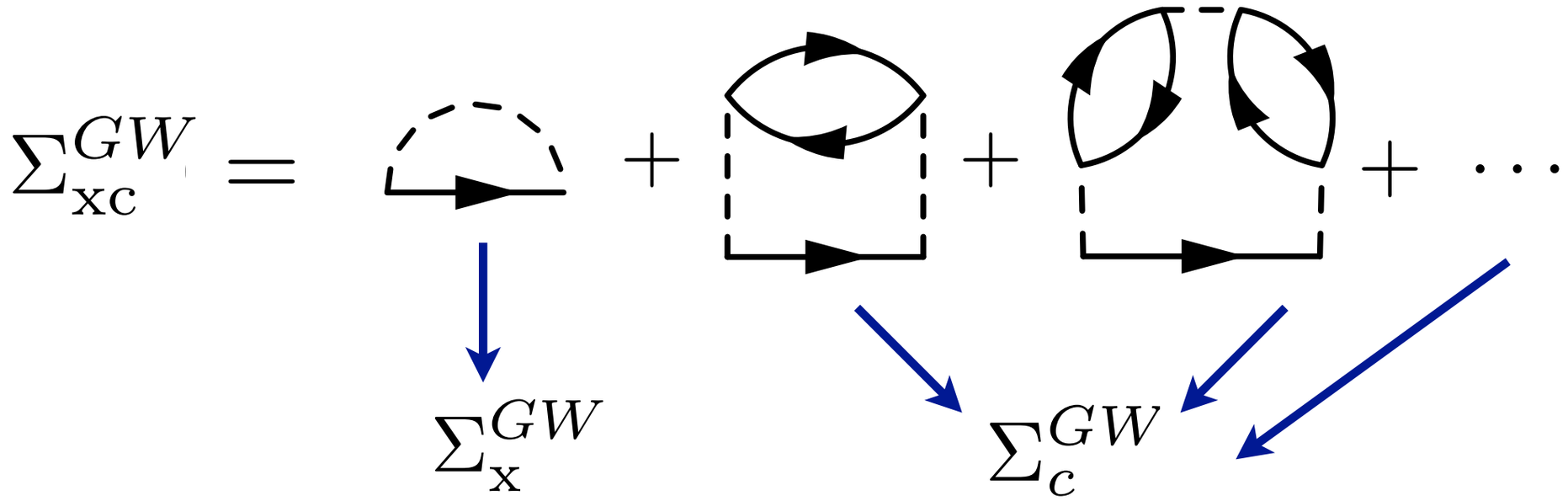
self-energy:

$$\Sigma^{GW}(\mathbf{r},\mathbf{r}',\omega) = -\frac{i}{2\pi}\int d\omega e^{i\omega\eta} G(\mathbf{r},\mathbf{r}',\omega+\omega')W(\mathbf{r},\mathbf{r}',\omega')$$

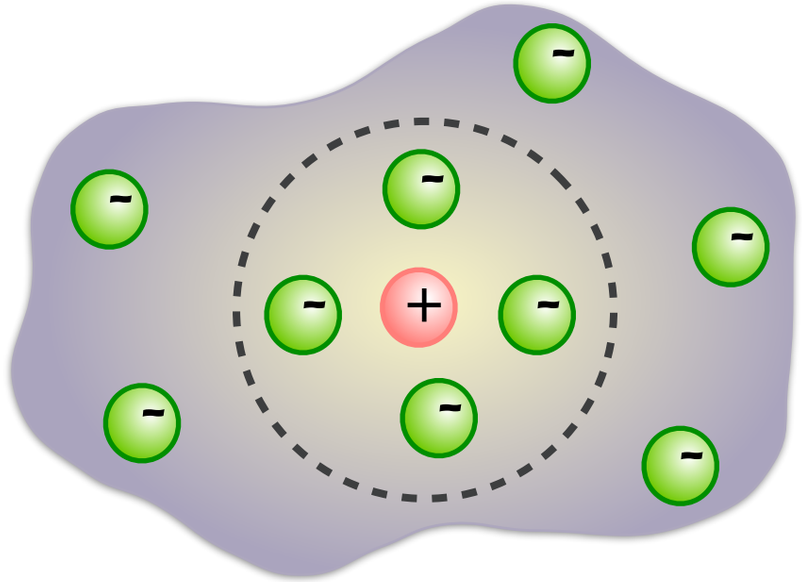
- G_0W_0: correction to eigenvalues from density-functional theory (DFT):

$$\epsilon^{qp}_{n\mathbf{k}} = \epsilon^{\mathrm{DFT}}_{n\mathbf{k}} + \Sigma^{G_0W_0}_{n\mathbf{k}}(\epsilon^{qp}_{n\mathbf{k}}) - v^{xc}_{n\mathbf{k}}$$

Return to the GW self-energy



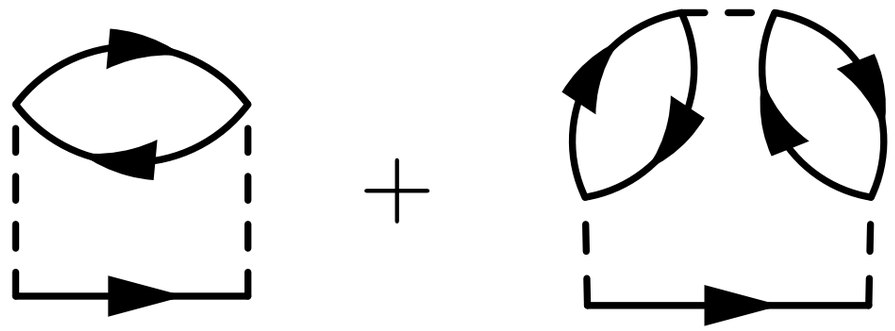
exact-exchange part (self-interaction-free)



correlation part (screening (includes van der Waals))

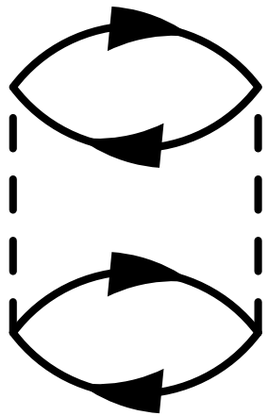
Correlation part of the GW self/total energy

$$\Sigma_c^{GW} =$$

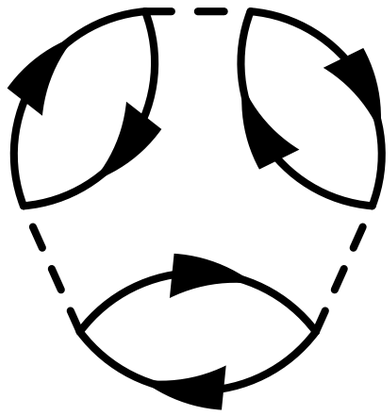


$$+ \quad + \cdots$$

$$E_c^{GW} = -\frac{1}{4}$$



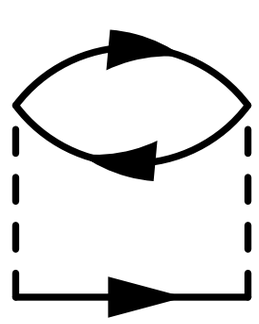
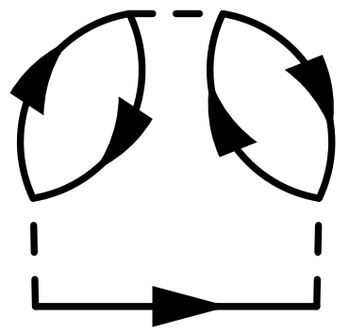
$$-\frac{1}{6}$$



$$+ \quad \cdots$$

$$E_c^{GW}[G] = \int_0^\infty \frac{d\omega}{2\pi} \mathrm{Tr}\left(\Sigma_c^{GW}(i\omega)G(i\omega)\right)$$

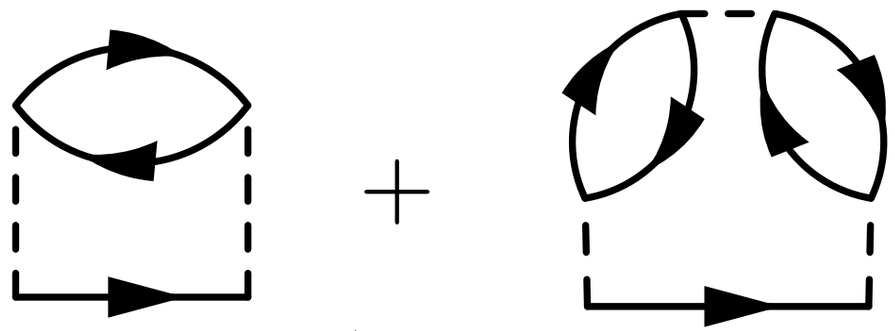
Question?

$$\Sigma_c^{GW} =$$  $+$  $+ \cdots$

Does a given correlation energy approximation uniquely define the total energy?

GW versus RPA

$$\Sigma_c^{GW} =$$



$+ \cdots$

many-body perturbation theory

density-functional theory

Dyson's equation:

$$G^{-1} = G_0^{-1} - \Sigma$$

Optimized eff. potential:

$$G_0 \left[\Sigma - v_{xc}^{\mathrm{OEP}} \right] G_0 = 0$$

GW

Random-Phase Approximation (RPA)

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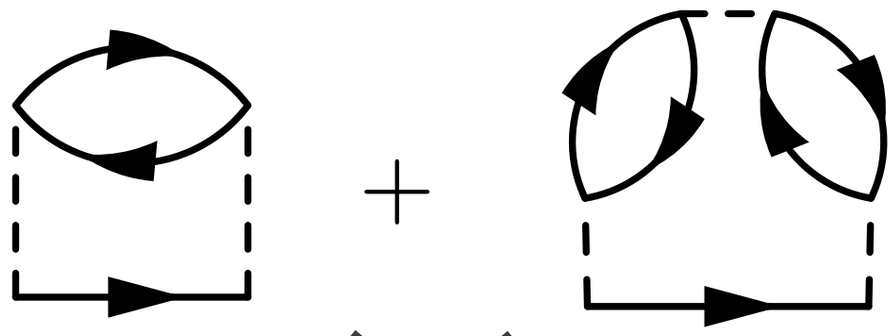
F. Caruso, D. R. Rohr, M. Hellgren, X. Ren, P. Rinke, A. Rubio, and M. Scheffler, Phys. Rev. Lett. 110, 146403 (2013)

GW versus RPA

$$\Sigma_c^{GW} =$$  $$+ \cdots$$

many-body perturbation theory

density-functional theory

total energy
e.g. Galitskii-Migdal

$$E_{\rm xc} = E_{\rm xc}[G]$$

adiabatic-connection fluctuation-dissipation theorem

$$E_{xc} = E_{xc}\left[-iG_0G_0\right]$$

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GW versus RPA

$$\Sigma_c^{GW} = \quad + \quad + \cdots$$

iterate to self-consistency

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sc*GW*

scRPA

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F. Caruso, P. Rinke, et al, Phys. Rev. Lett. 110, 146403 (2013)
F. Caruso, P. Rinke et al. Phys. Rev. B 88, 075105 (2013)
M. Hellgren, Rohr, Gross, J. Phys. Chem. 136, 034106 (2012)

GW versus RPA

implemented in FHI-aims [1]

- local atomic basis
- all-electron

Dyson's equation:

$$G^{-1} = G_0^{-1} - \Sigma$$

- Perturbative RPA in FHI-aims
- self-consistent RPA in [2]

***GW*/scGW**

RPA/scRPA

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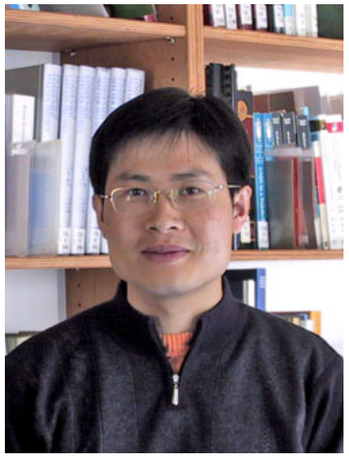
[1] Ren, Rinke, et al., New J. Phys. 14, 053020 (2012),
Caruso, Rinke et al. Phys. Rev. B 86, 081102(R) (2012)
[2] Hellgren, Rohr, Gross, J. Phys. Chem. 136, 034106 (2012)

GW versus RPA

Fabio Caruso
Humboldt University, Berlin



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IMPMC, UPMC, Paris

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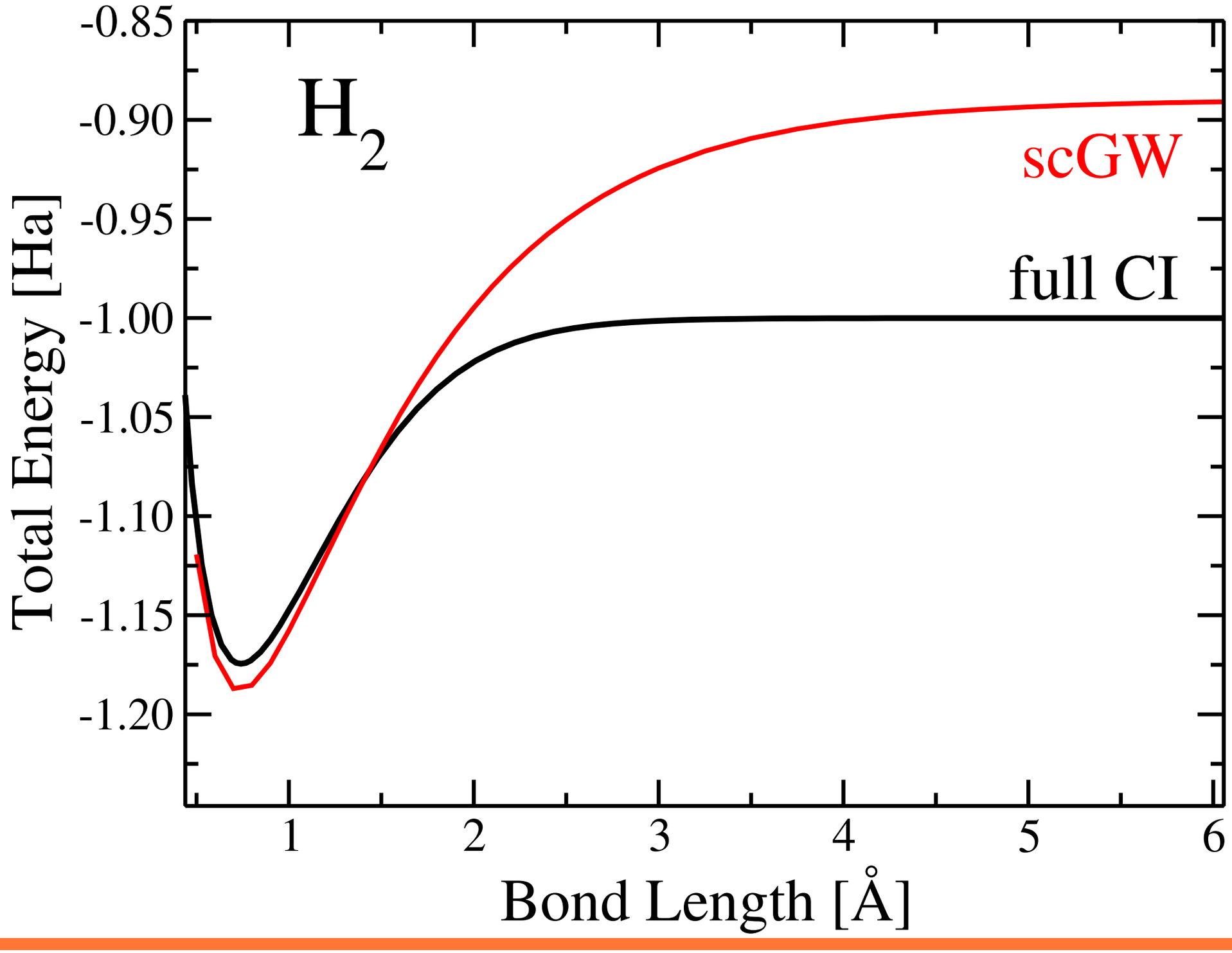
Bond-making and bond-breaking - H_2



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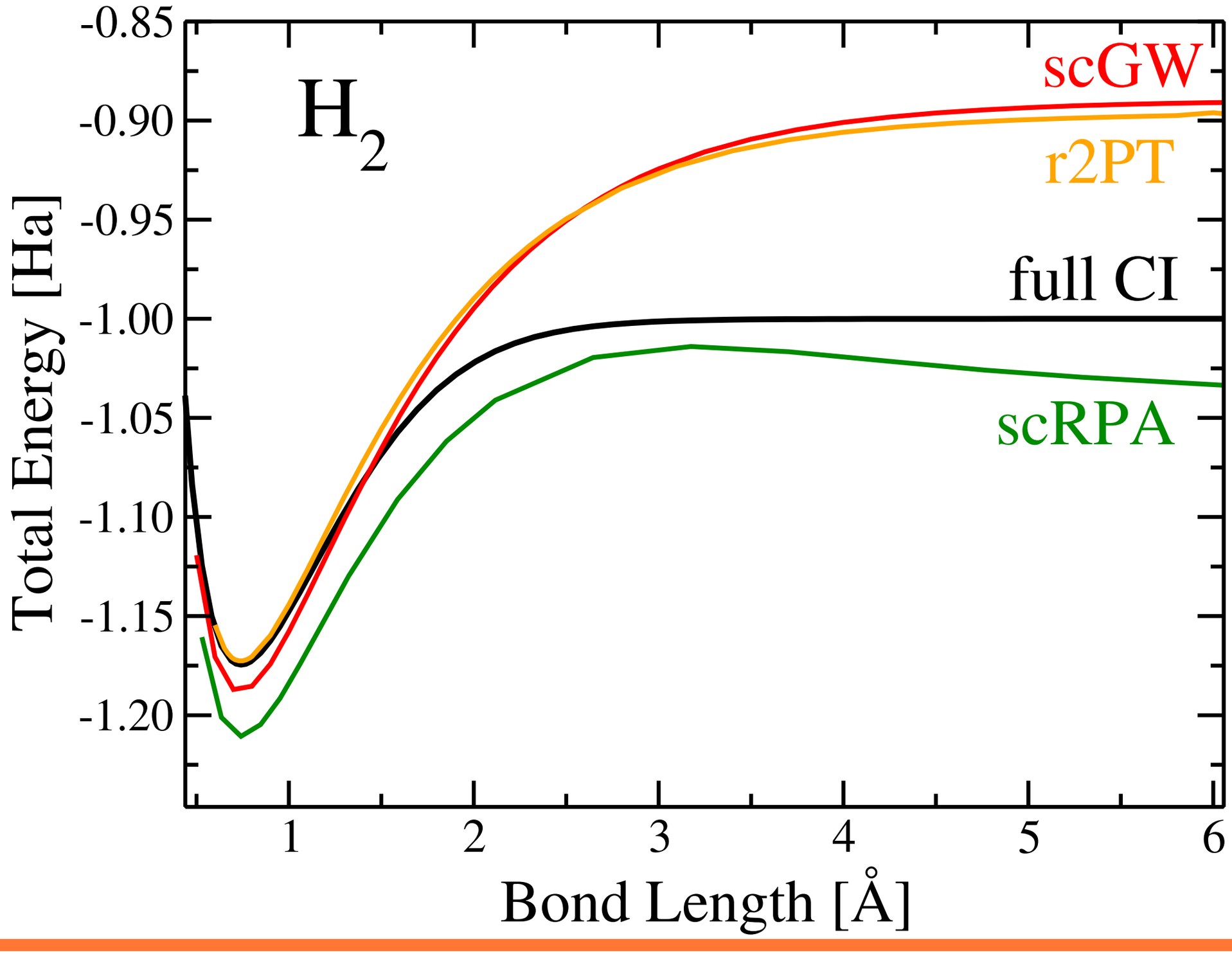

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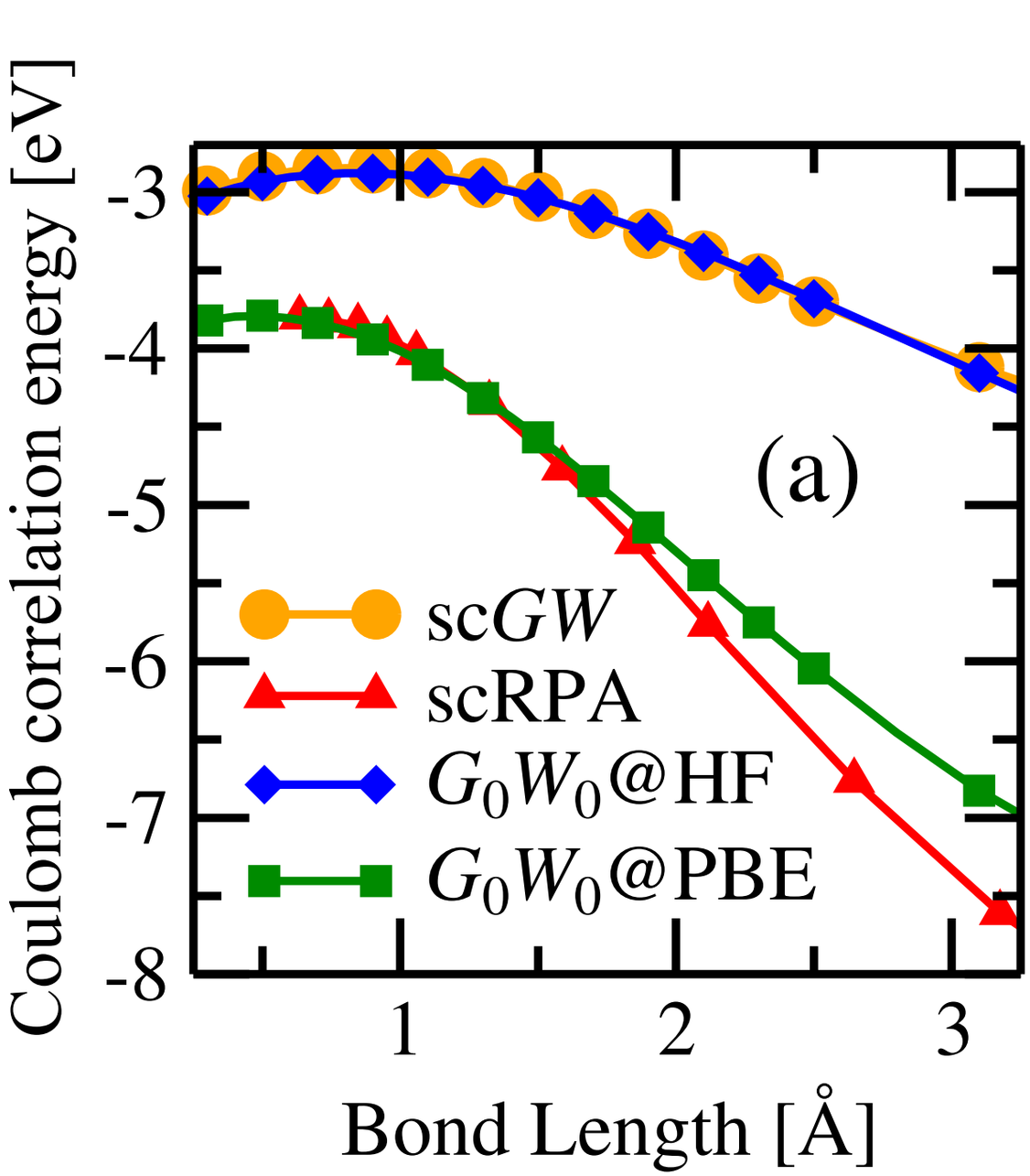

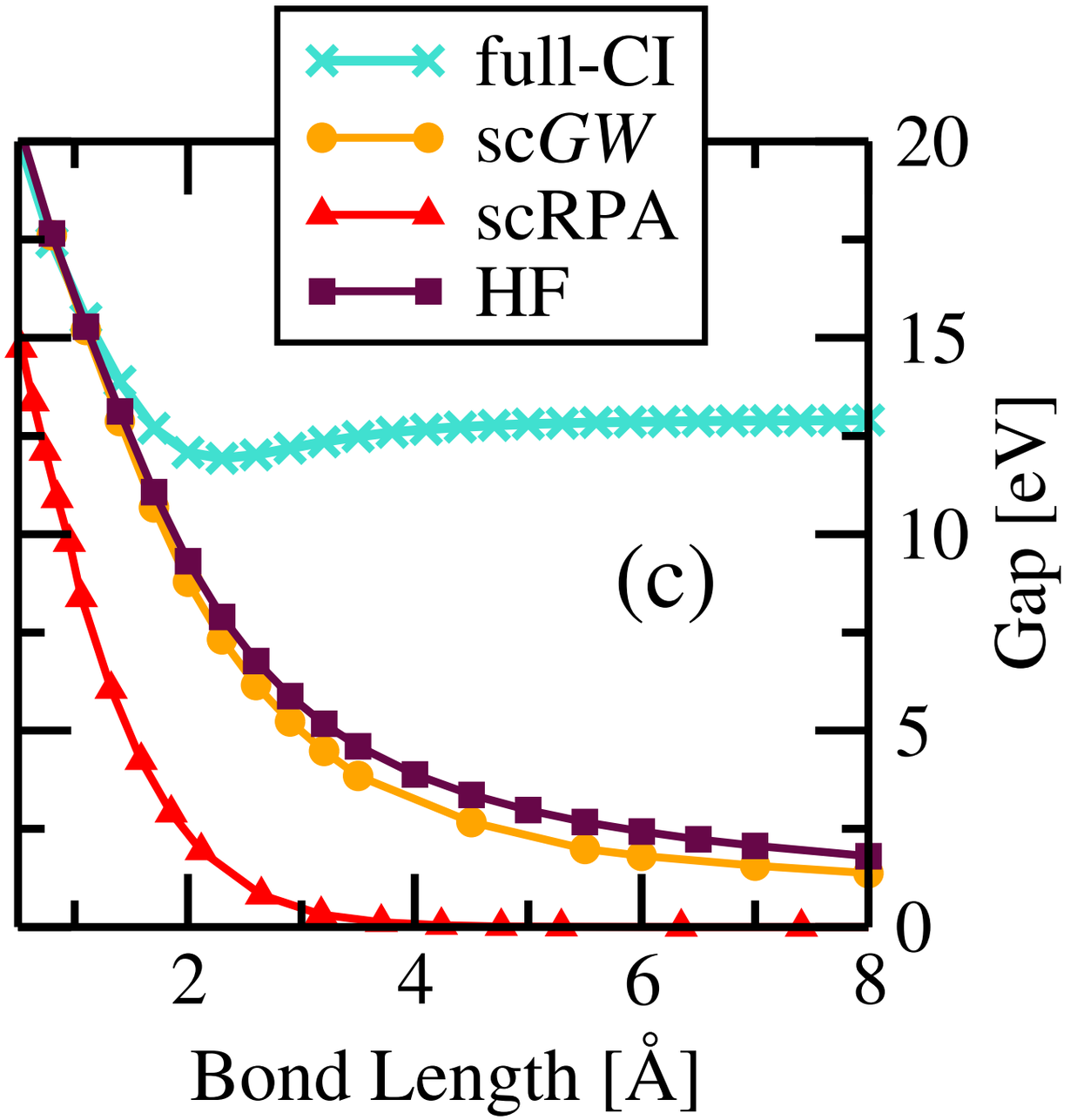

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M. Hellgren, F. Caruso, D. R. Rohr, X. Ren, A. Rubio, M. Scheffler, P. Rinke, Phys. Rev. B 91, 165110 (2015)

Kinetic energy analysis

total energy:

$$E^{GW}[G] = T[G] + E_{\mathrm{ext}}[G] + E_{\mathrm{H}}[G] + E_{\mathrm{x}}[G] + E_{\mathrm{c}}^{GW}[G]$$

$$E^{G_0W_0}[G_0] = T_s[G_0] + E_{\mathrm{ext}}[G_0] + E_{\mathrm{H}}[G_0] + E_{\mathrm{x}}[G_0] + E_{\mathrm{c}}^{GW}[G_0]$$

scGW includes interacting kinetic energy, G_0W_0 does not.

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$$E^{\rm RPA}[G_0] = T_s[G_0] + E_{\rm ext}[G_0] + E_{\rm H}[G_0] + E_{\rm x}[G_0] + E_{\rm c}^{\rm RPA}[G_0] + T_c^{\rm RPA}[G_0]$$

Kinetic correlation energy is included in RPA by means of adiabatic connection.

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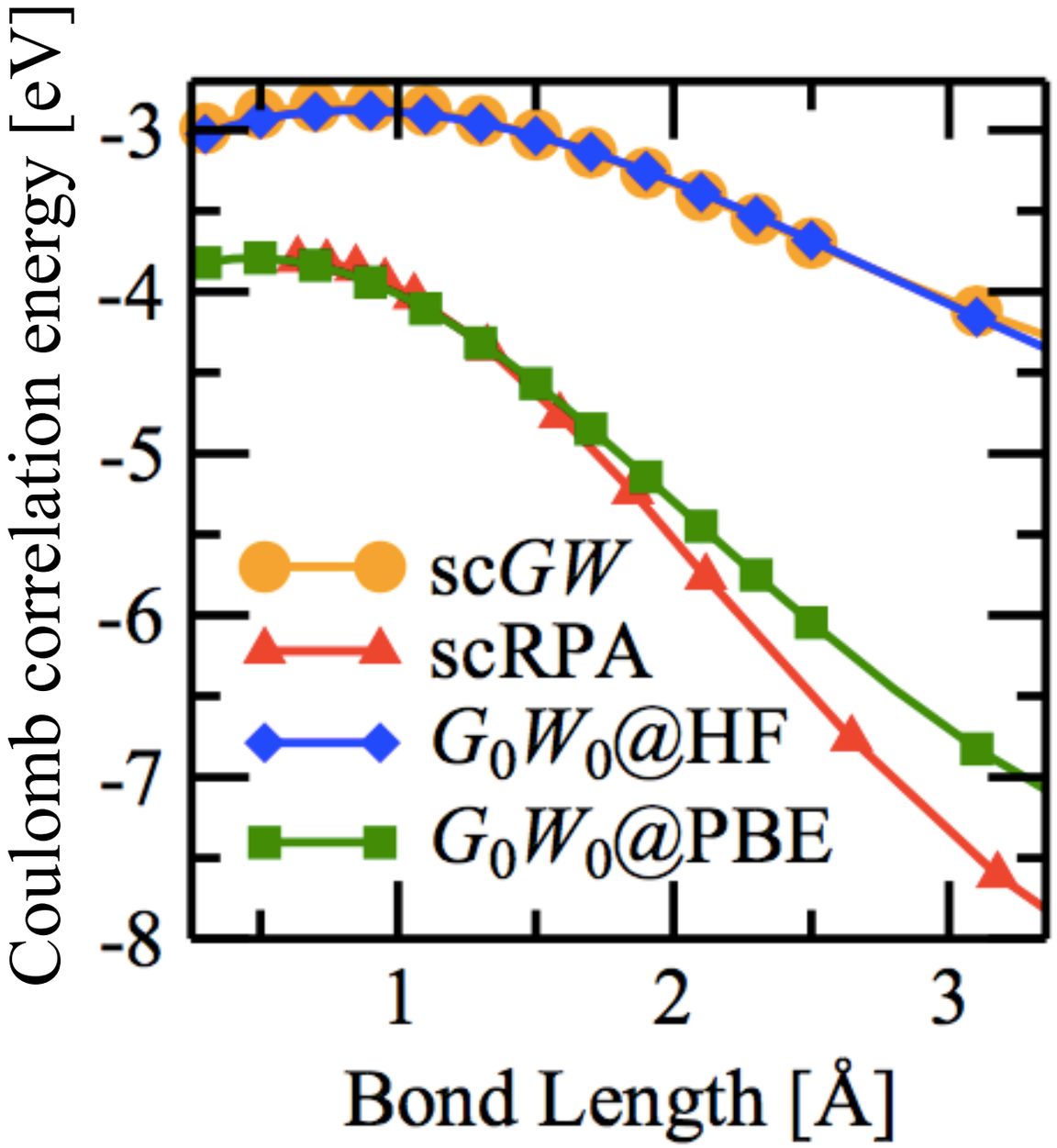

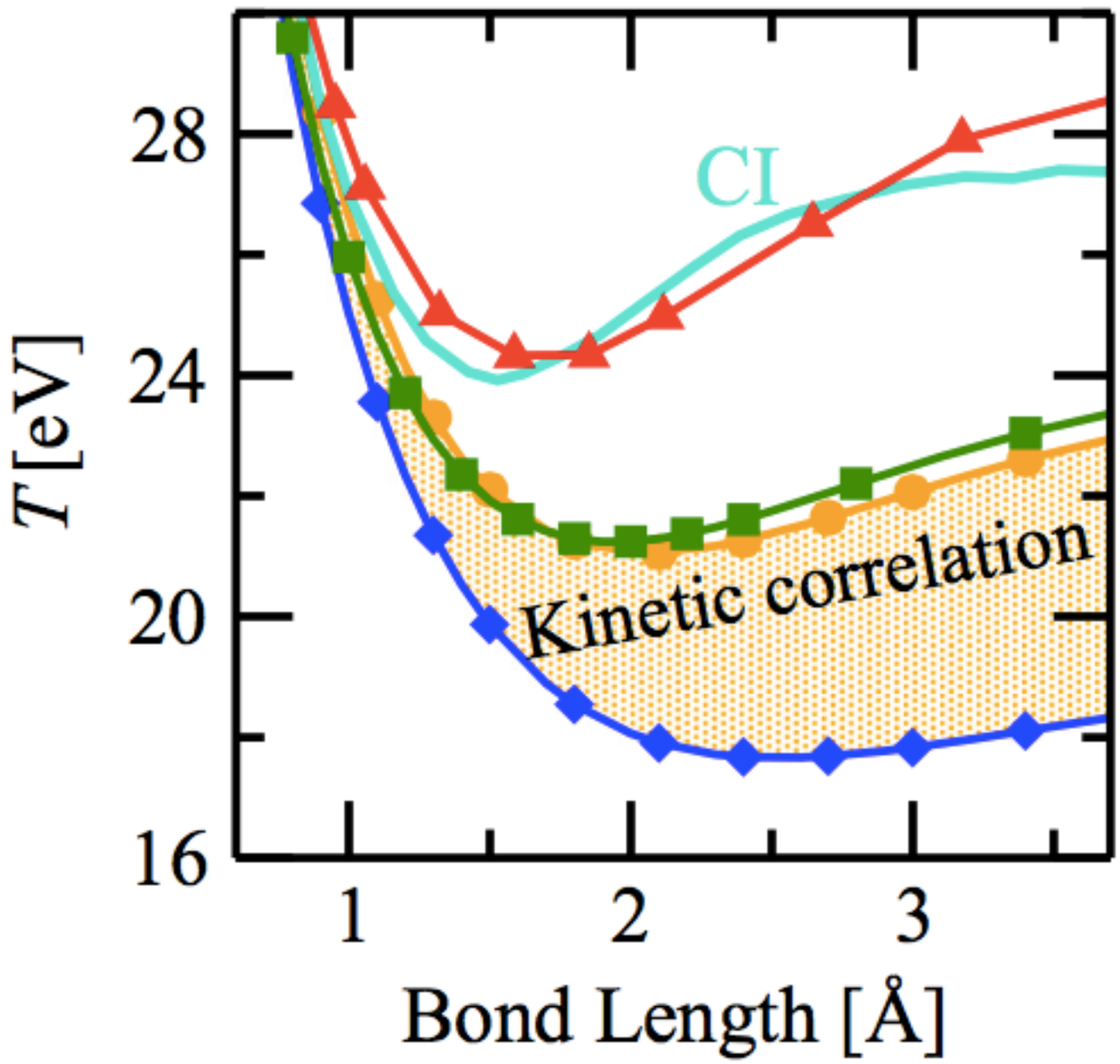

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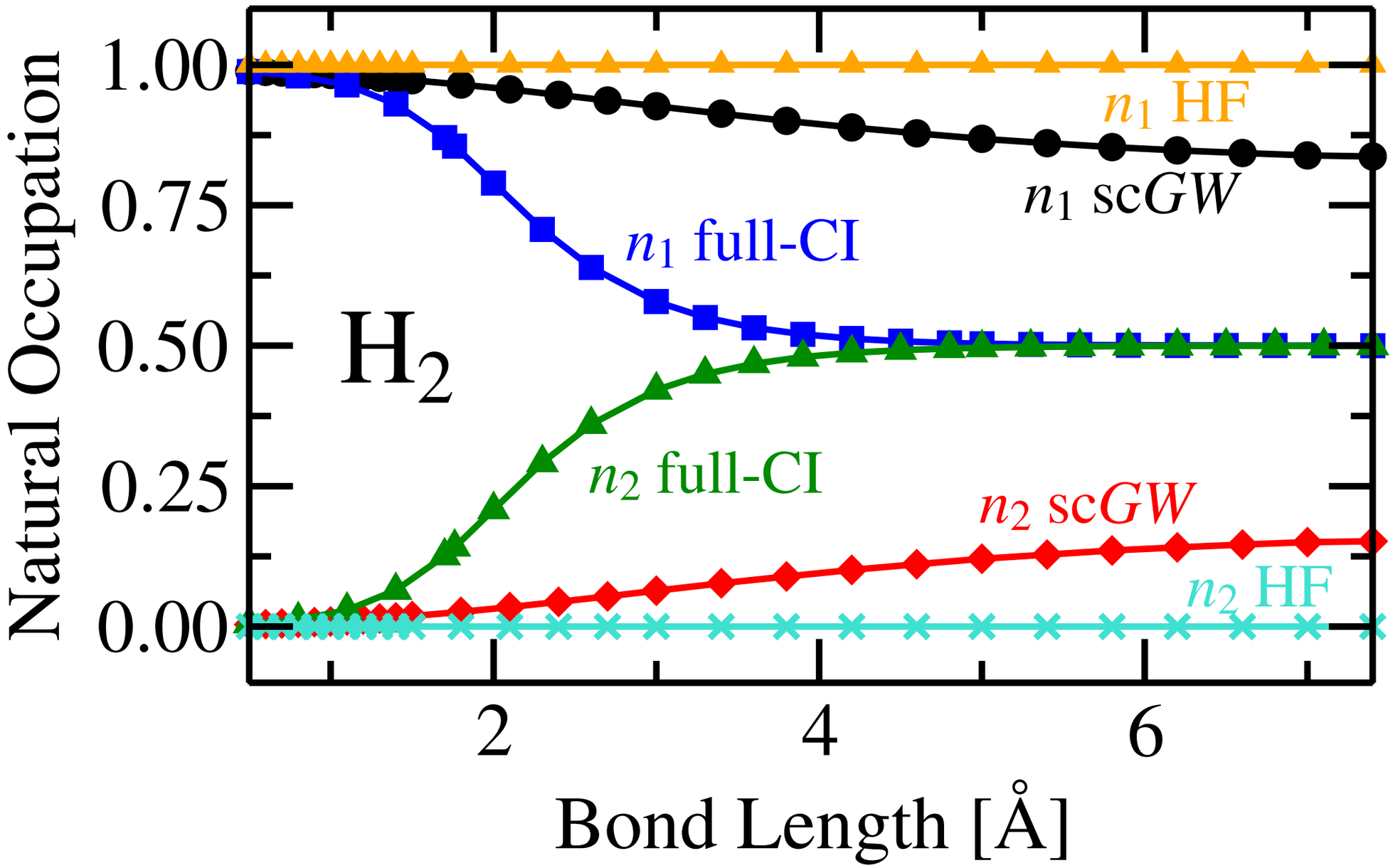
Natural orbital occupations - H_2



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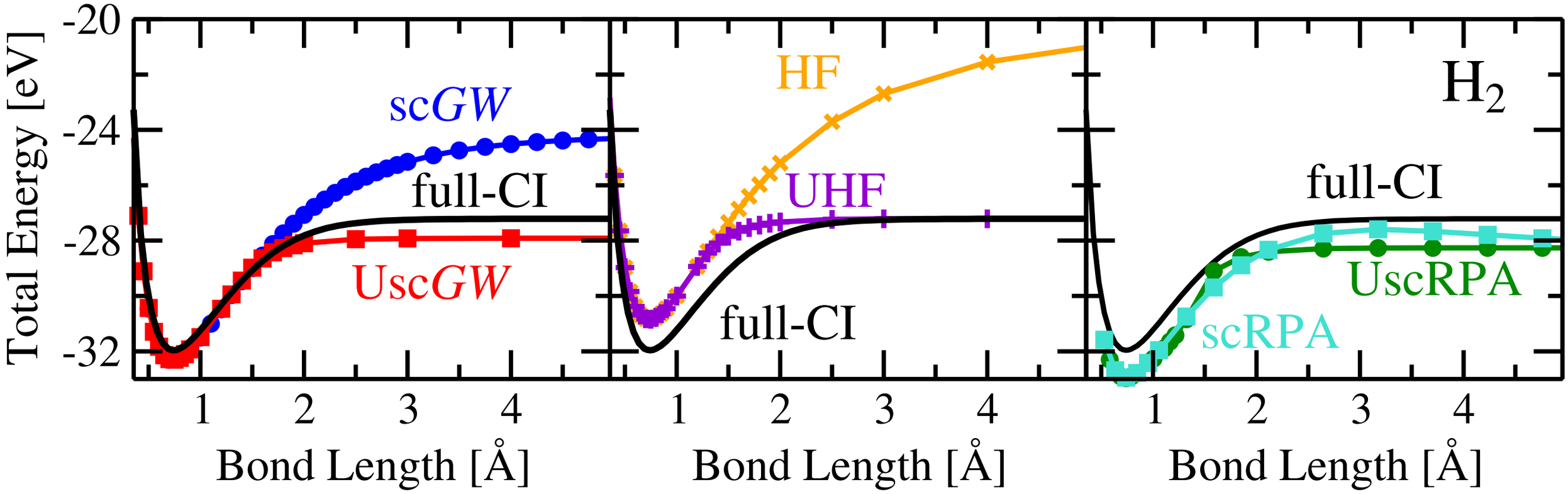
Unrestricted calculations - H_2



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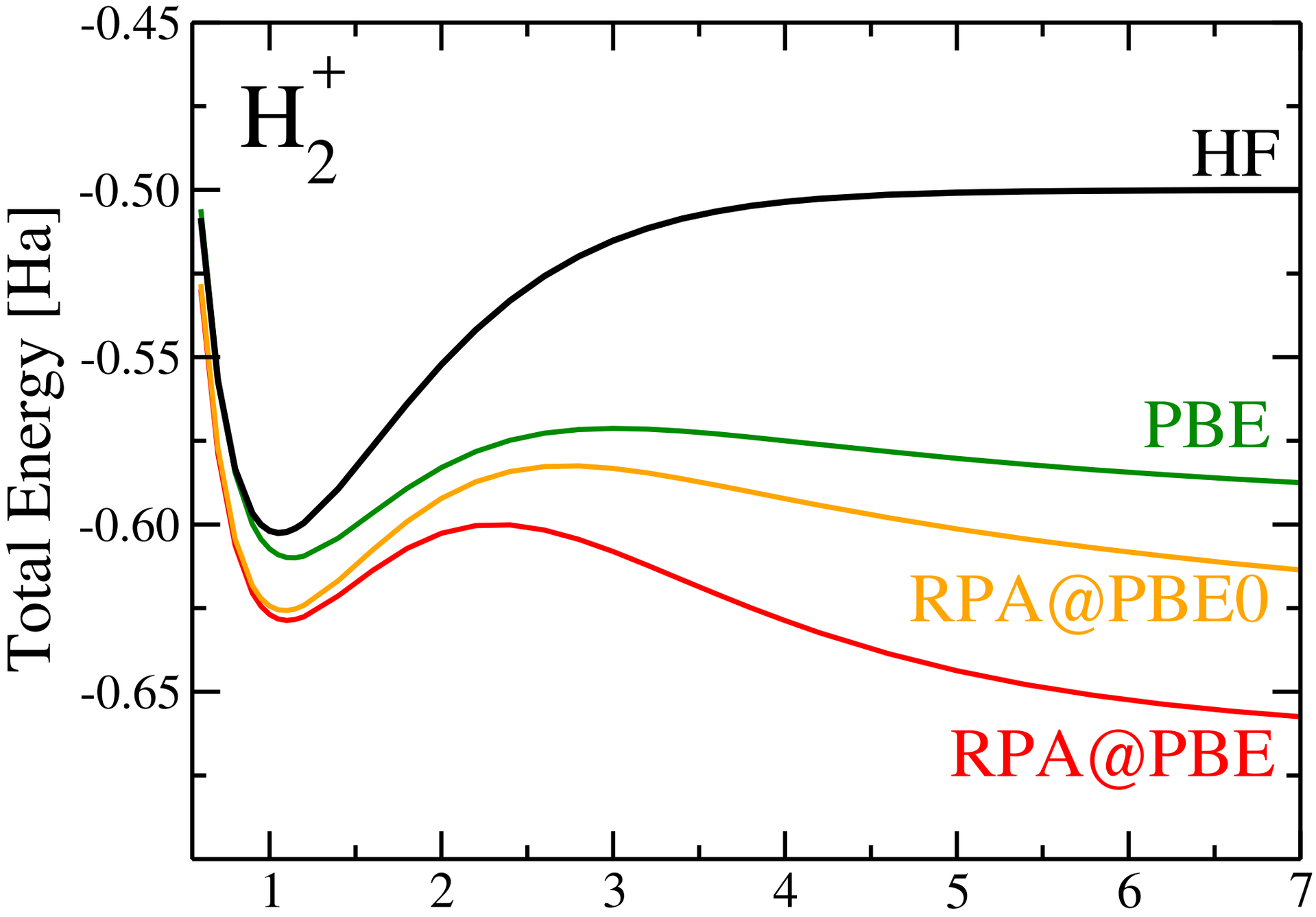
M. Hellgren, F. Caruso, D. R. Rohr, X. Ren, A. Rubio, M. Scheffler, P. Rinke, Phys. Rev. B 91, 165110 (2015)

H_2^+ is the real problem



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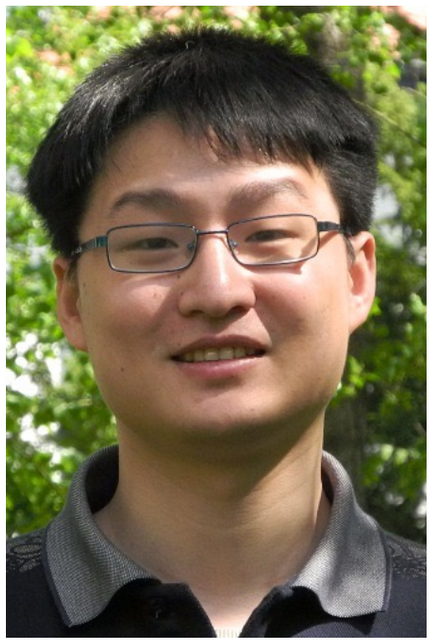
I. Y. Zhang, P. Rinke, and M. Scheffler,
New J. Phys. 18, 073026 (2016)

Correlations from the Bethe-Goldstone equation

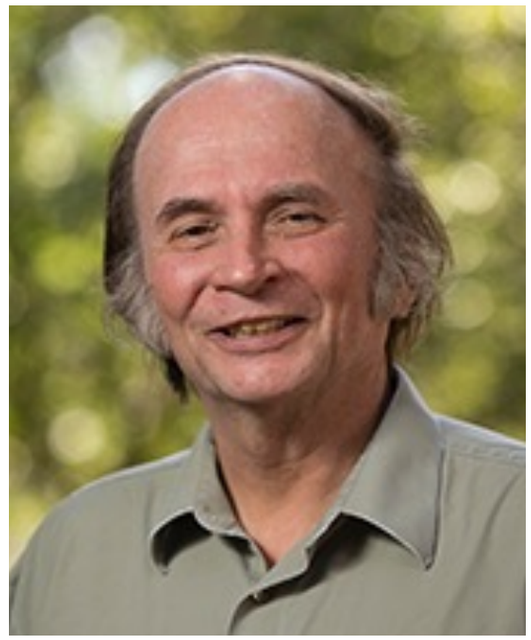


Igor Zhang

Fritz-Haber-Institut
Berlin

Matthias Scheffler

Fritz-Haber-Institut
Berlin



John Perdew

Tempel University
Philadelphia

Aalto University
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Bethe-Goldstone equation (exact for 2 electrons)

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

$$\Delta\epsilon_{ab}^{rs} = \epsilon_r + \epsilon_s - \epsilon_a - \epsilon_b$$

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

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

Bethe-Goldstone equation (exact for 2 electrons)

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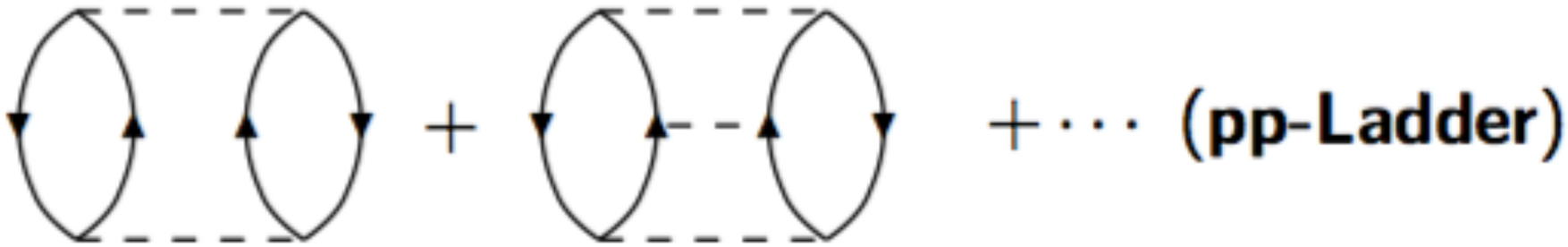

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A. L. Fetter and J. D. Walecka, Quantum Theory of Many Particle Systems, McGraw-Hill, New York (1996)

2nd order Bethe-Goldstone equation (BGE2)

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

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

but! retain coupling

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2nd order Bethe-Goldstone equation (BGE2)

pair approximation

$$E_c^{\mathrm{BGE2}} = \sum_{a<b}^{occ} e_{ab}(\lambda)$$

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

simple MP2 expression

but! self-consistent coupling

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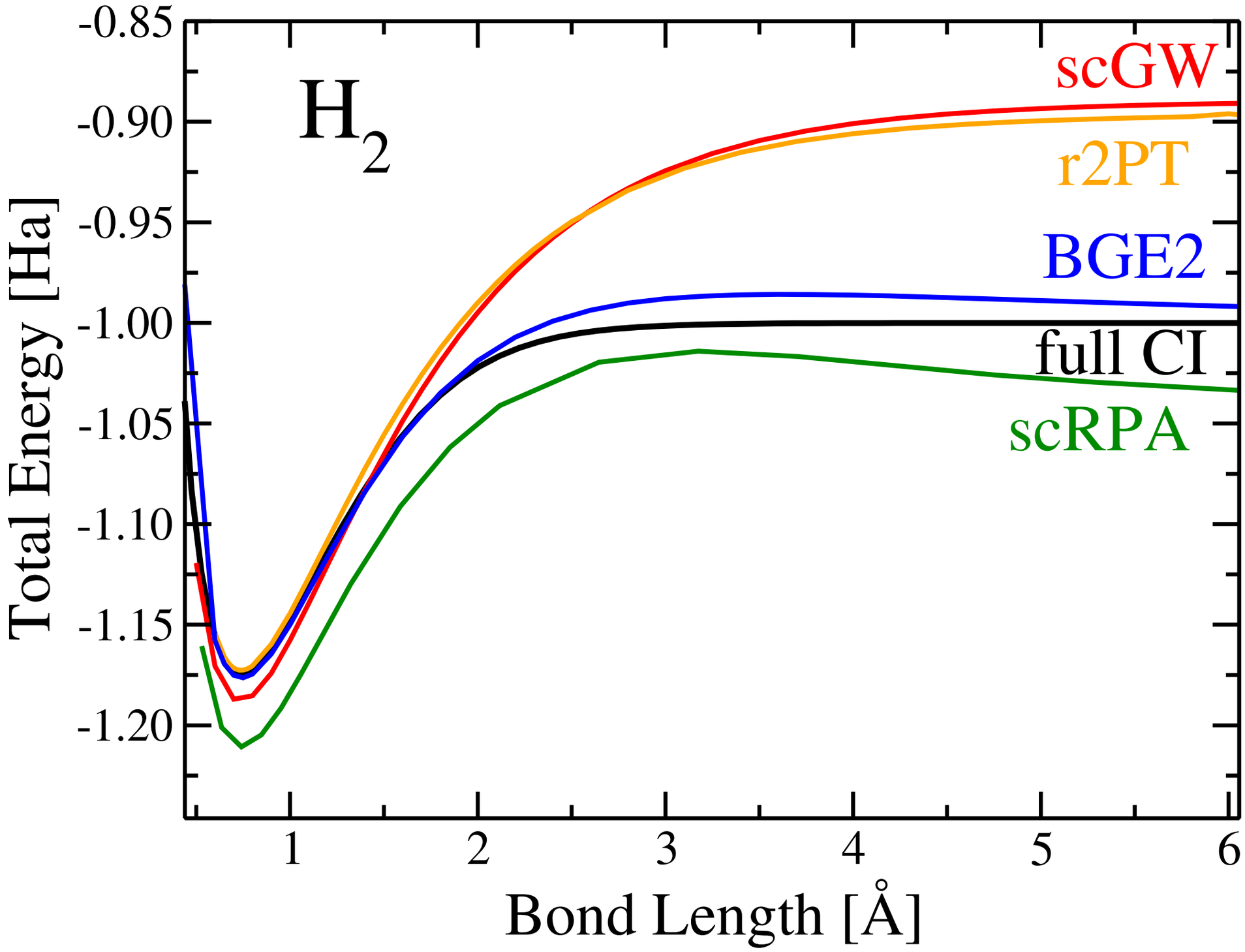
BGE2 applied to H_2 dissociation



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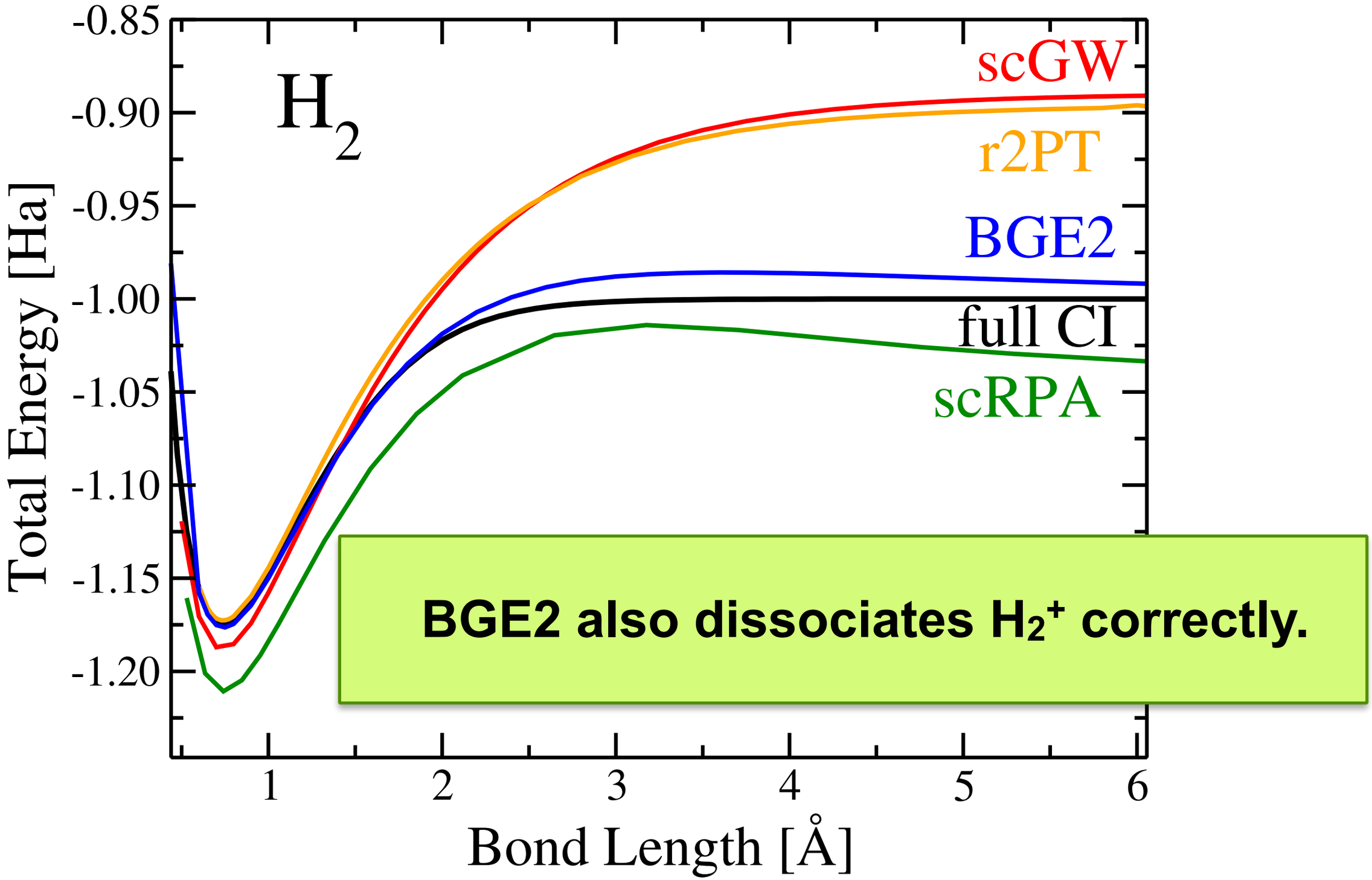

BGE2 also dissociates H_2^+ correctly.

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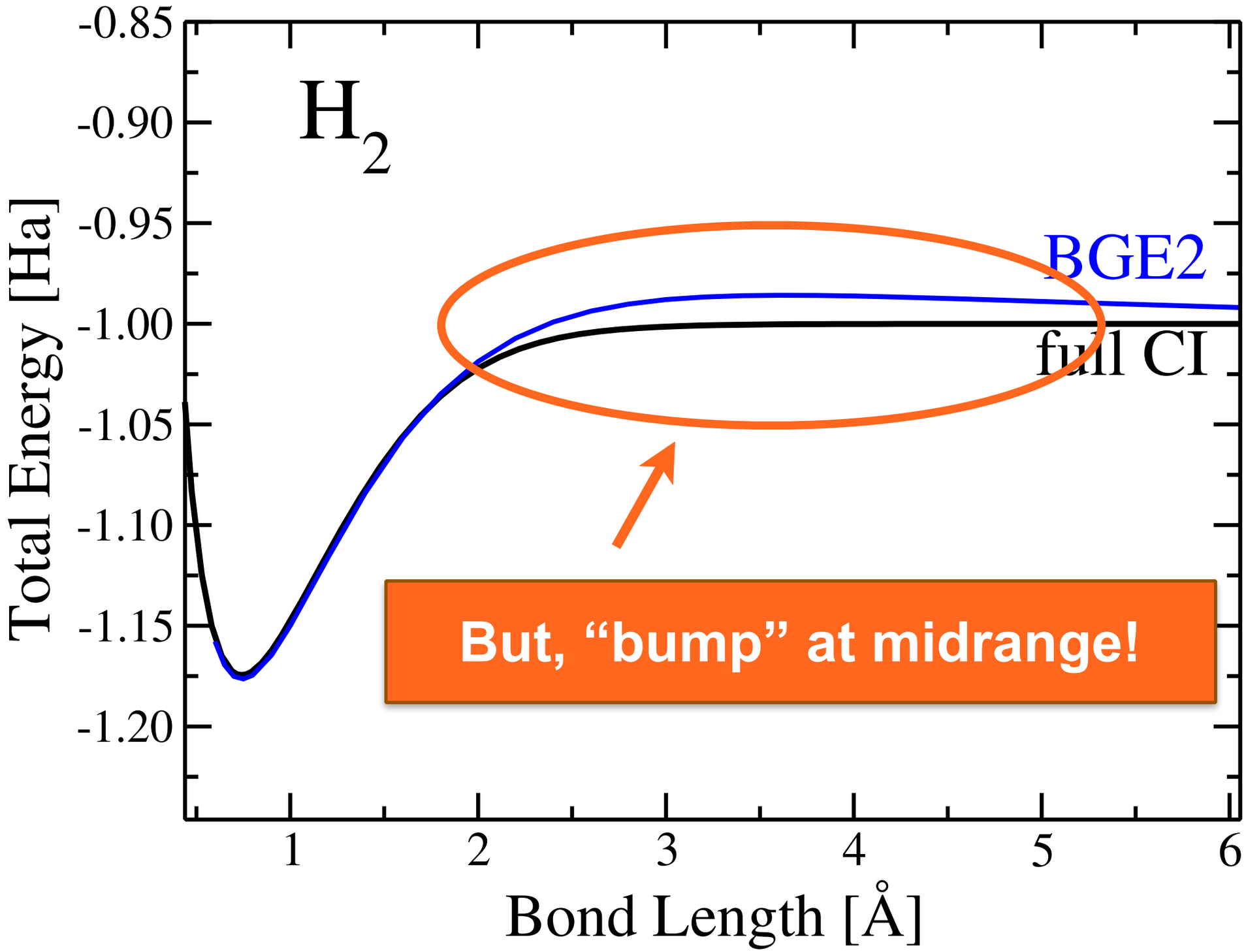

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Beyond BGE2

1: Additional diagrams (towards BGE) - not today

2: Screening factor s_{rs}^{ab} (sBGE2)

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

$$s_{rs}^{ab} = \mathrm{erfc}(\Delta\epsilon_{ab}^{rs})$$

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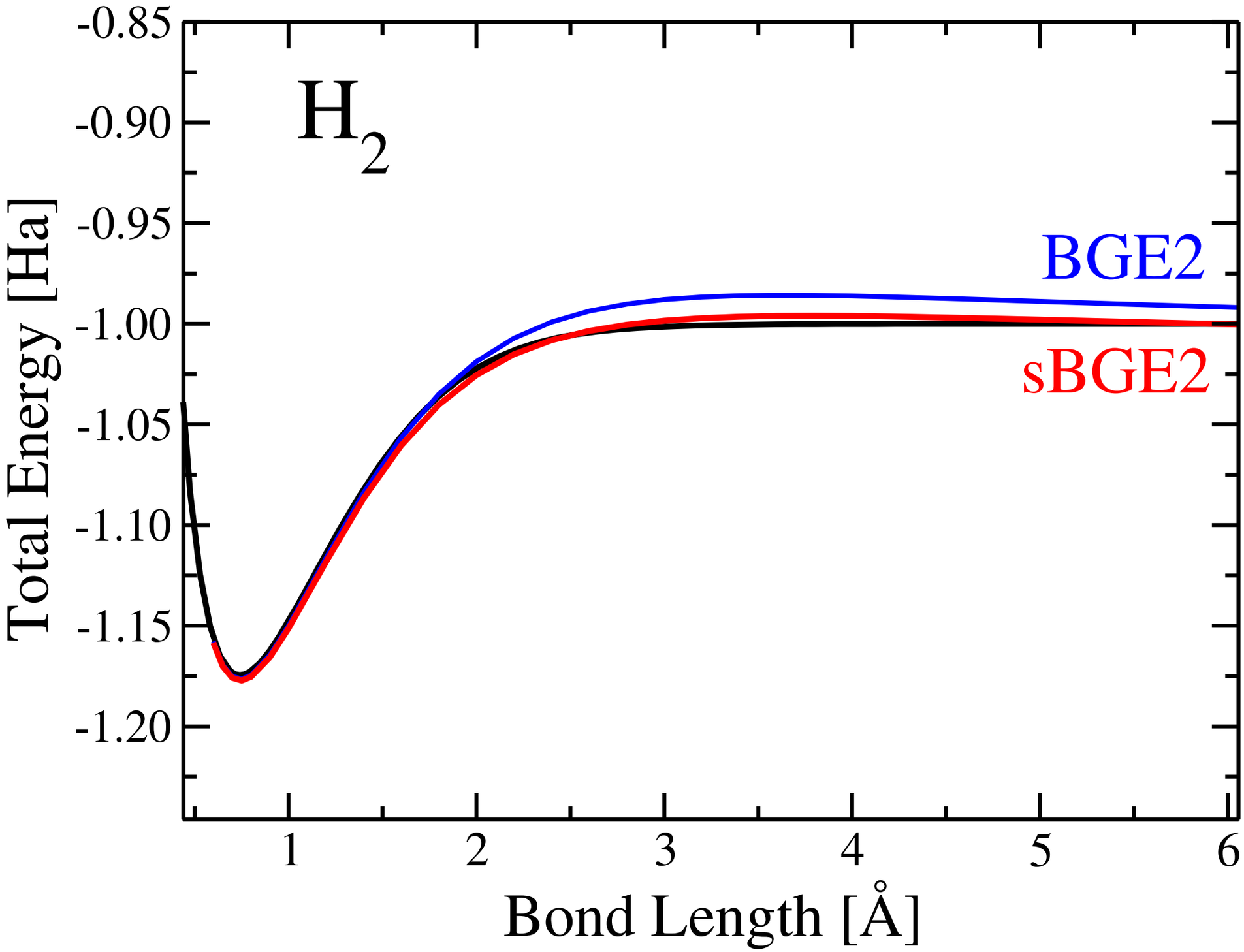
BGE2 applied to H_2 dissociation



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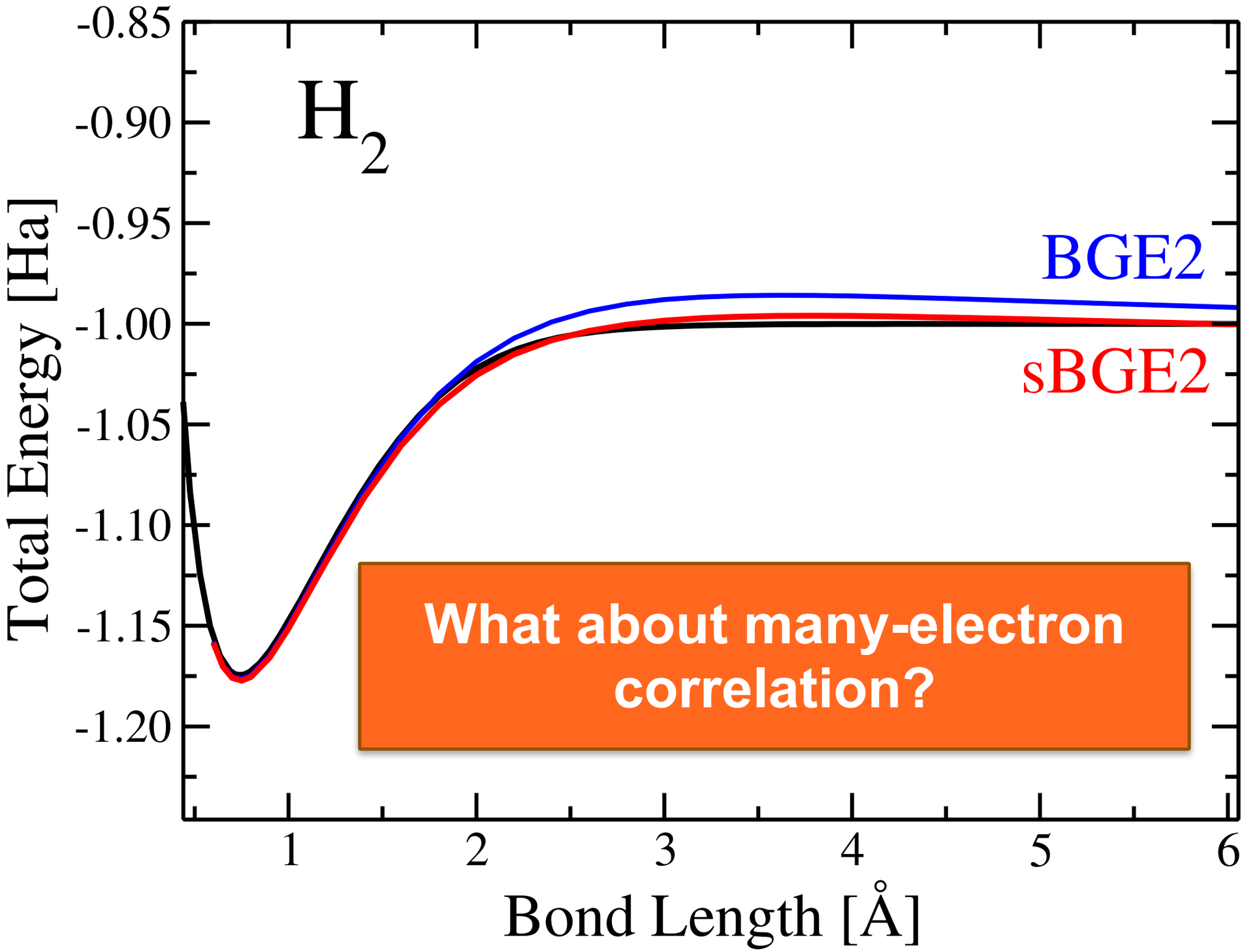

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New J. Phys. 18, 073026 (2016)

A new, parameter free level 5 DFT functional

DFT exchange-correlation functional

$$E_{xc}^{\mathrm{ZRPS}} = \frac{1}{2}E_x^{\mathrm{PBE}} + \frac{1}{2}E_x^{\mathrm{HF}} + \frac{3}{4}\left(E_c^{\mathrm{PBE}} + E_{vdw}^{\mathrm{TS}}\right) + \frac{1}{4}E_{c,os}^{\mathrm{sBGE2}}$$

- **Currently applied non-self-consistently.**
- **sBGE2 only applied to opposite spins.**

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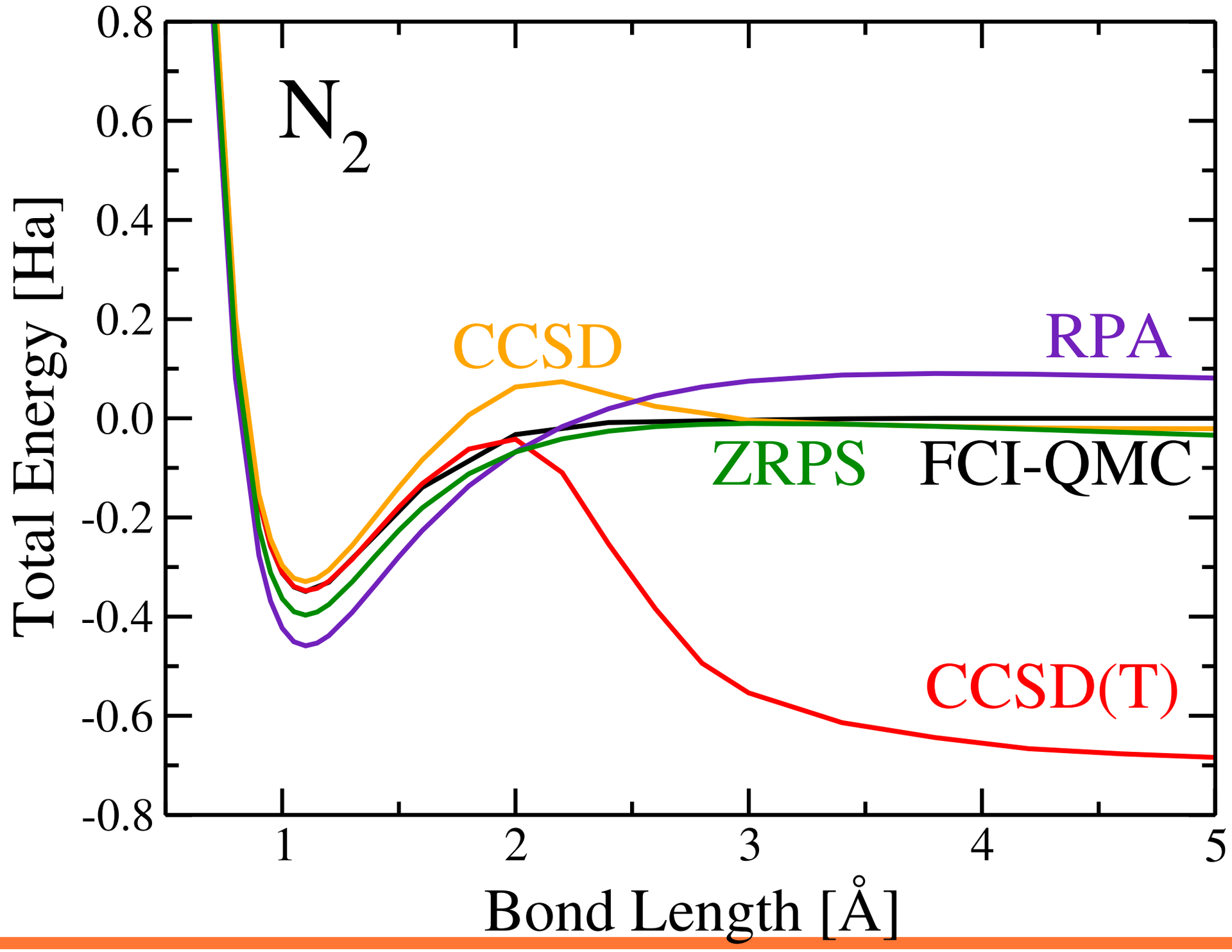
Phys. Rev. Lett. 117, 133002 (2016)

ZRPS applied to N_2 dissociation



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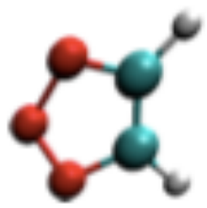
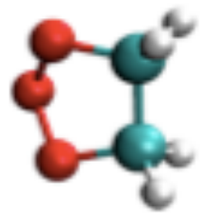
Phys. Rev. Lett. 117, 133002 (2016)

Singlet multi-reference problem

in meV	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: $O_3 + C_2H_4 \rightarrow$ 

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I. Y. Zhang, J. Perdew, P. Rinke, M. Scheffler,
Phys. Rev. Lett. 117, 133002 (2016)

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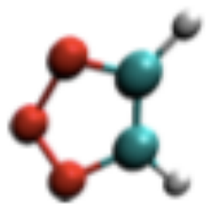
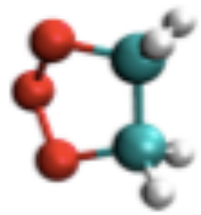
A: $O_3+C_2H_2 \rightarrow$ 

B: $O_3+C_2H_4 \rightarrow$ 

ZRPS also performs very well for weakly correlated systems.

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Phys. Rev. Lett. 117, 133002 (2016)

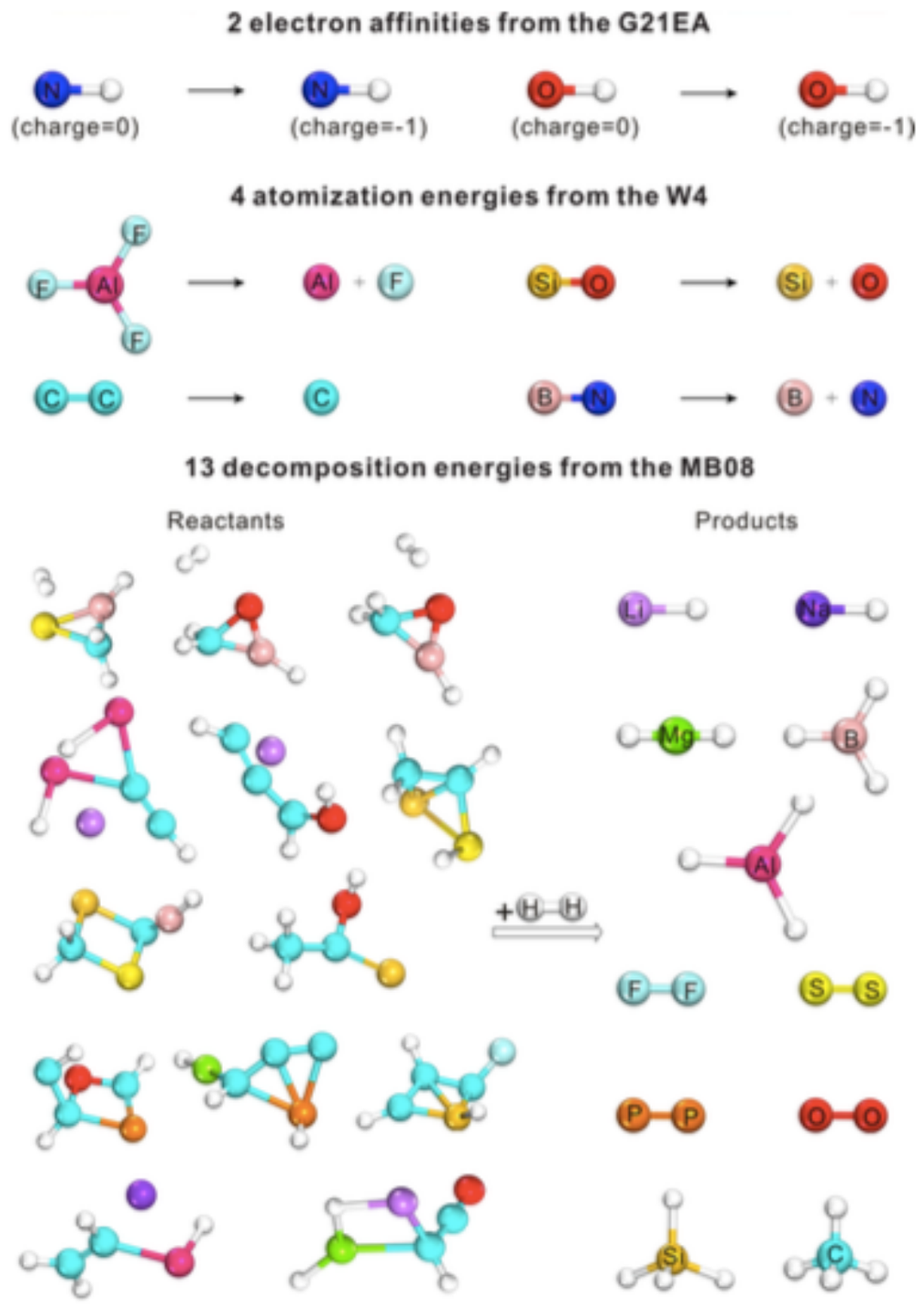
New benchmark set for strong correlation

GMTKN30 database

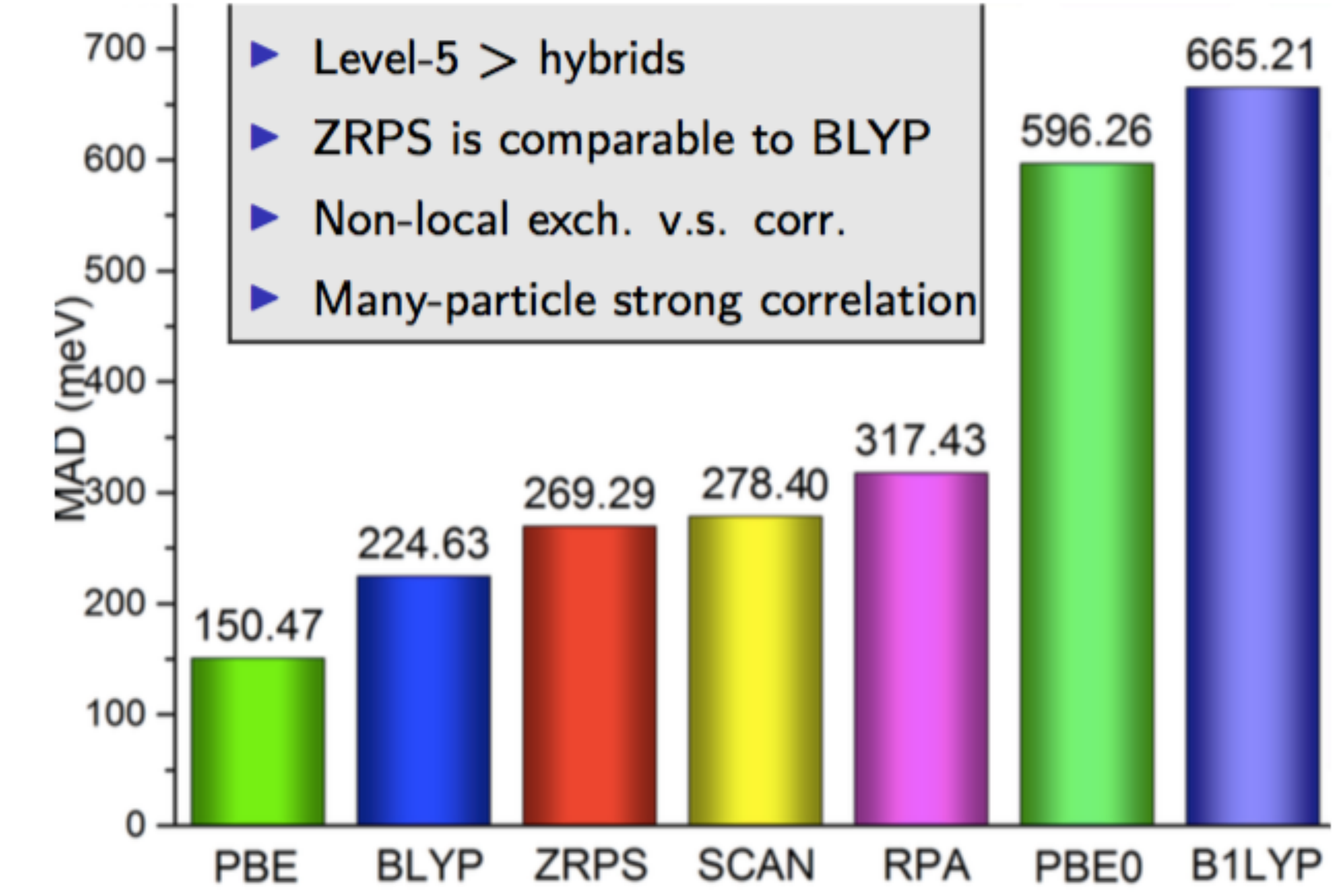
⇓ MR@DFT

MR19 test set

- 19 MR data points
- 2 EAs, 4 AEs, and 13 DEs
- REs $\in$ [0.36 eV, 18.68 eV]
- av. $|\mathrm{RE}|$=6.79 eV



New benchmark set for strong correlation

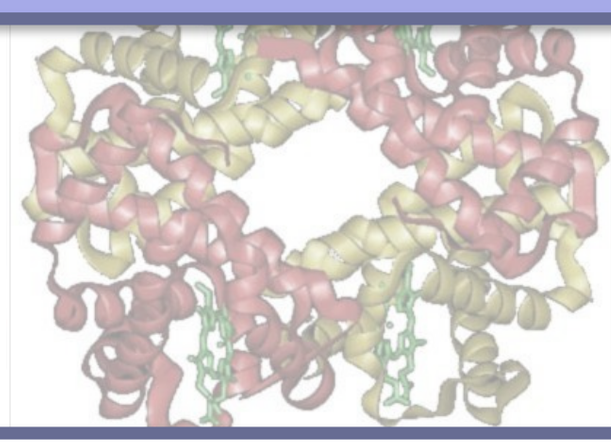


Wish list for electronic structure approaches

all dimensionalities (0D-3D)

efficient

free from pathologies, e.g.
- **self-interaction**
- **absence of van der Waals**
- **band-gap problem**



whole periodic table (including d/f)

ground+excited states

gradients+structure relaxation

Future work

Outlook

How to combine BGE2 and ZRPS with RPA and GW?

Bethe-Salpeter equation?

I. Y. Zhang, J. Perdew, P. Rinke, M. Scheffler,
Phys. Rev. Lett. 117, 133002 (2016)

Thank you!

J Mater Sci (2012) 47:7447–7471
DOI 10.1007/s10853-012-6570-4

FIRST PRINCIPLES COMPUTATIONS

Random-phase approximation and its applications in computational chemistry and materials science

Xinguo Ren · Patrick Rinke · Christian Joas · Matthias Scheffler

Aalto University
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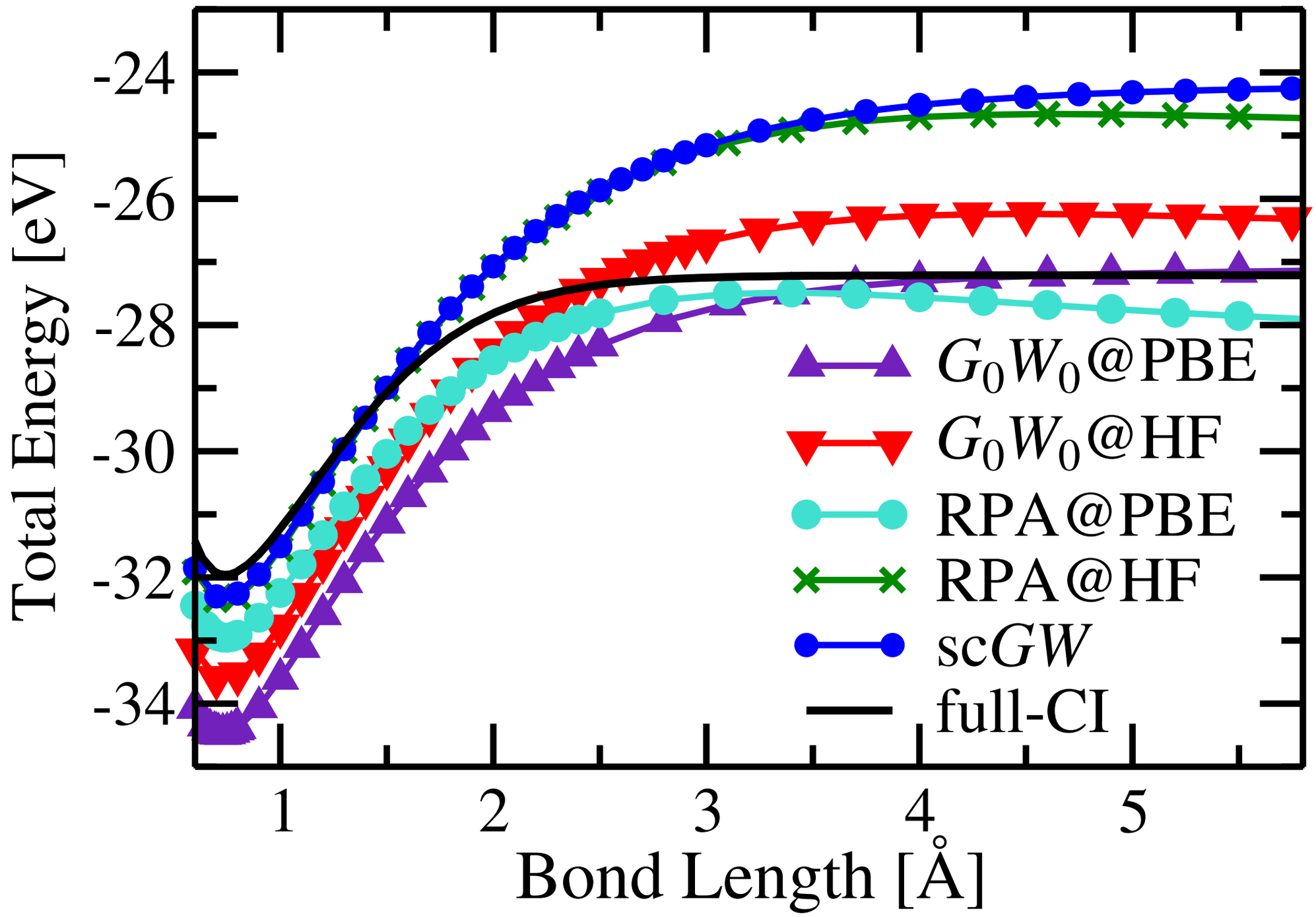
H_2 dissociation - performance of GW and RPA



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M. Hellgren, F. Caruso, D. R. Rohr, X. Ren, A. Rubio, M. Scheffler, P. Rinke, Phys. Rev. B 91, 165110 (2015)

ZRPS performance for weak correlation

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

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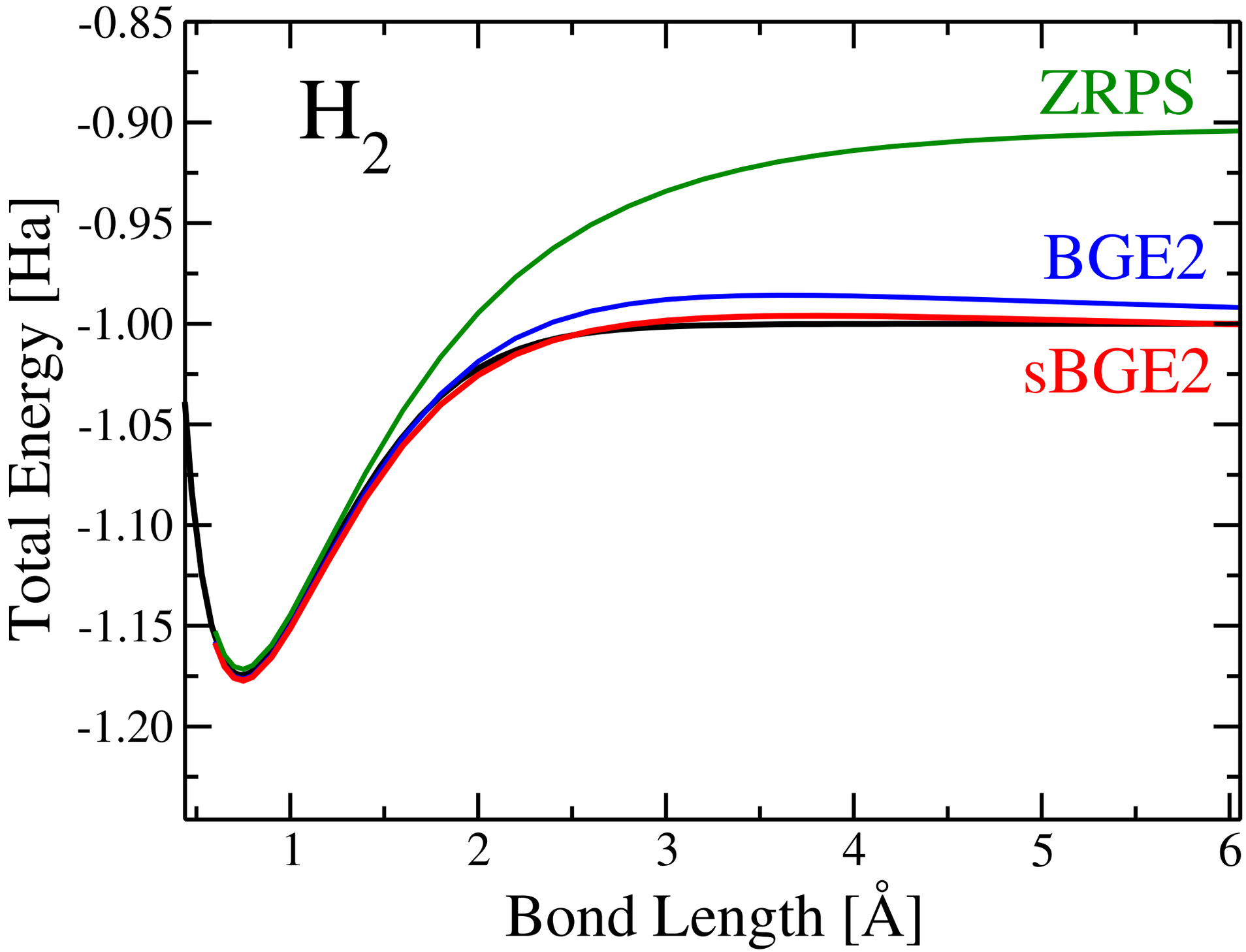
ZRPS applied to H_2 dissociation



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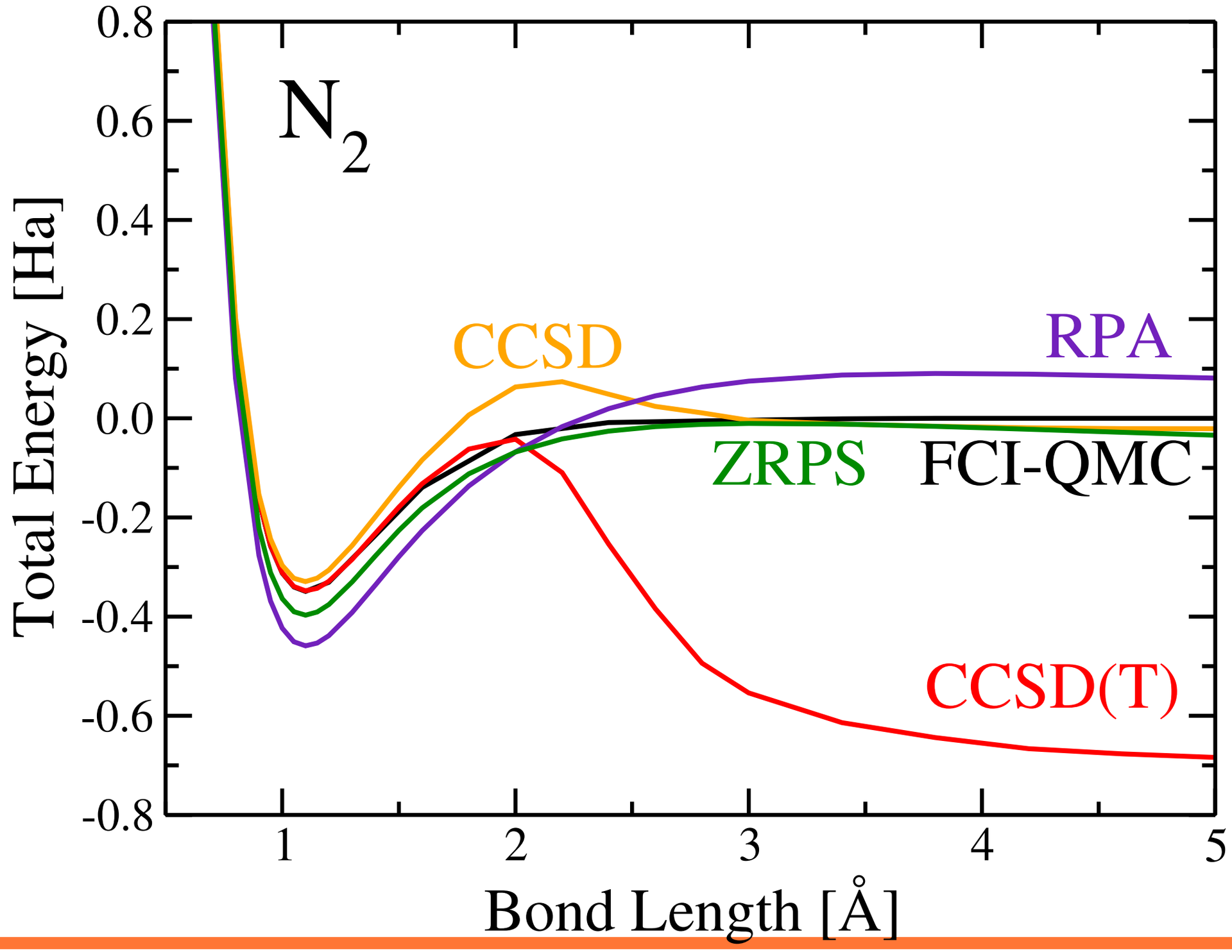
ZRPS applied to N_2 dissociation



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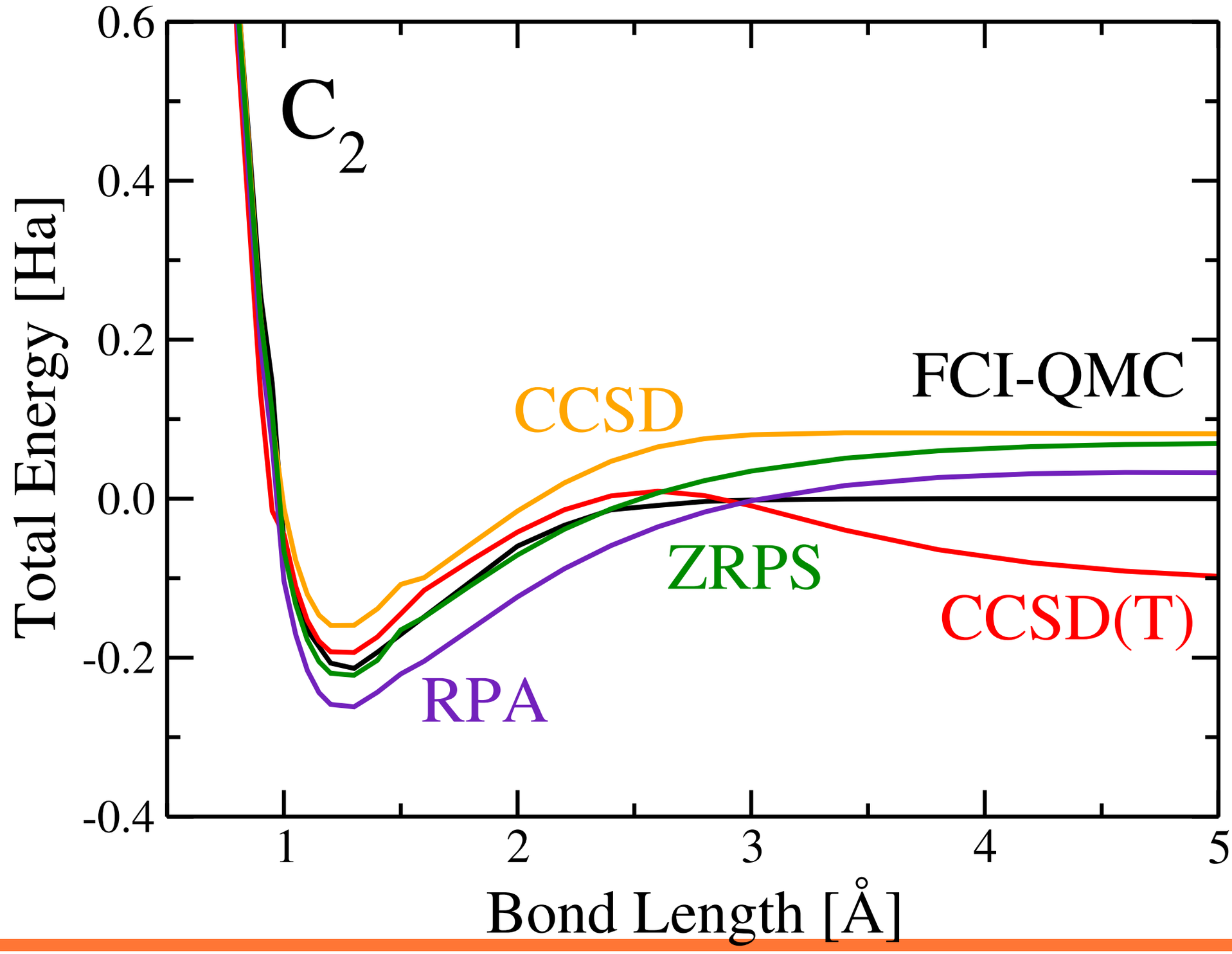
Phys. Rev. Lett. 117, 133002 (2016)

ZRPS applied to C_2 dissociation



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I. Y. Zhang, J. Perdew, P. Rinke, M. Scheffler,
Phys. Rev. Lett. 117, 133002 (2016)

Thank you!