Correlation functionals from the Møller-Plesset adiabatic connection: Accurate description of noncovalent interactions

Timothy J. Daas, Eduardo Fabiano, Fabio Della Sala, Paola Gori-Giorgi, Stefan Vuckovic, Derk P. Kooi, Arthur J. A. F. Grooteman and Michael Seidl

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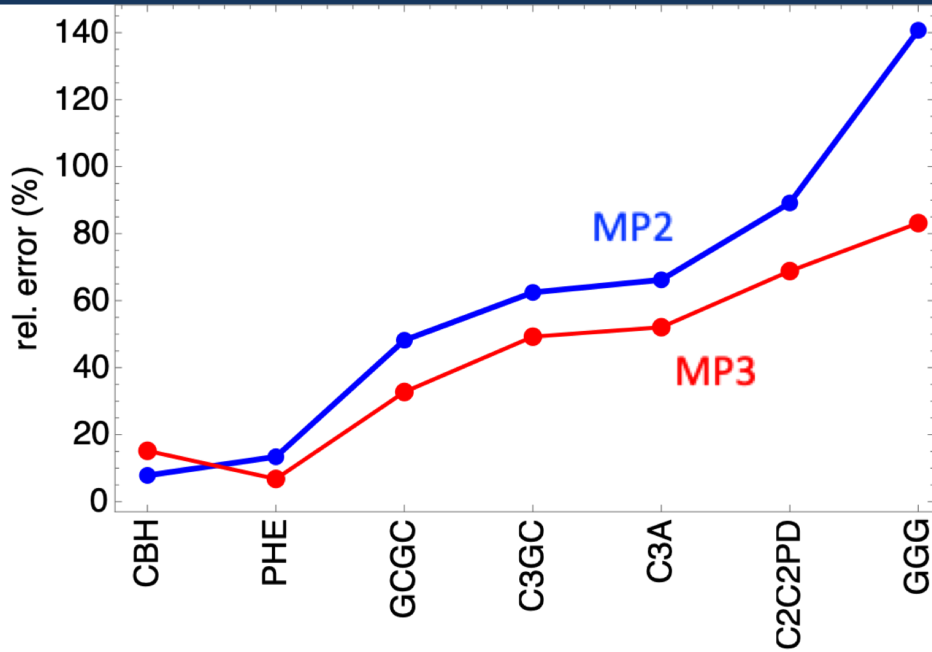
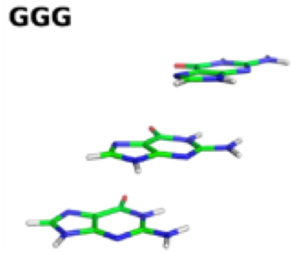
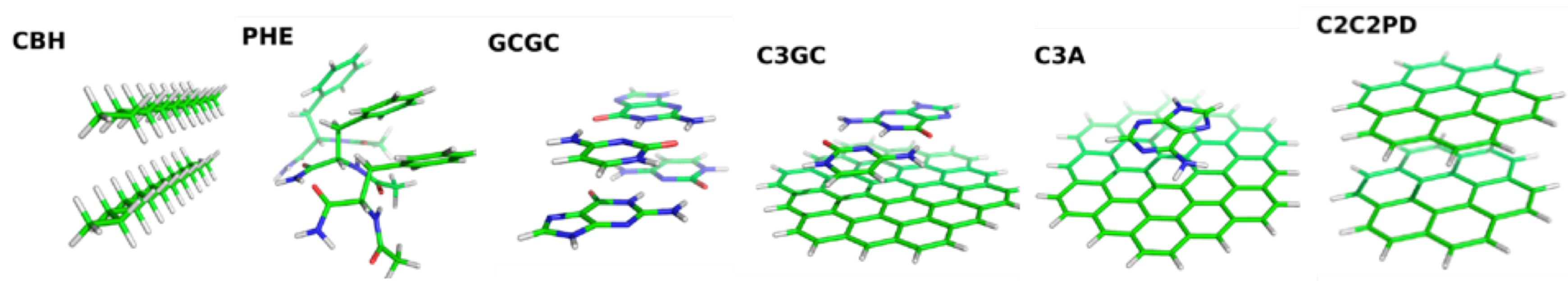
MP2 failure for large molecules: L7 dataset







Divergence of Many-Body Perturbation Theory for Noncovalent Interactions of Large Molecules

Brian D. Nguyen, Guo P. Chen, Matthew M. Agee, Asbjörn M. Burow, Matthew P. Tang, and Filipp Furche*

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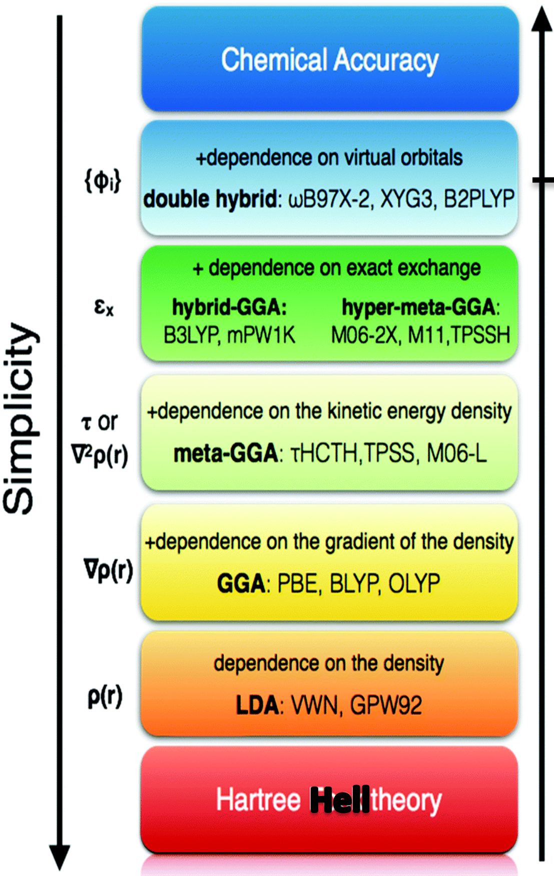
Jacob's Ladder of DFT

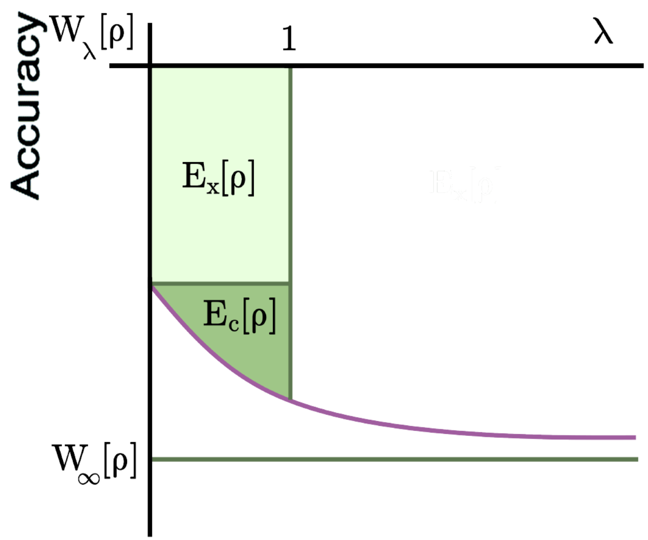
$$E_{xc}^{\mathrm{DH}}[\rho] = a_x E_x^{\mathrm{HF}} + (1 - a_x) E_x^{\mathrm{DFA}}[\rho] + (1 - a_c) E_c^{\mathrm{DFA}}[\rho] + a_c E_c^{\mathrm{MP2}}$$

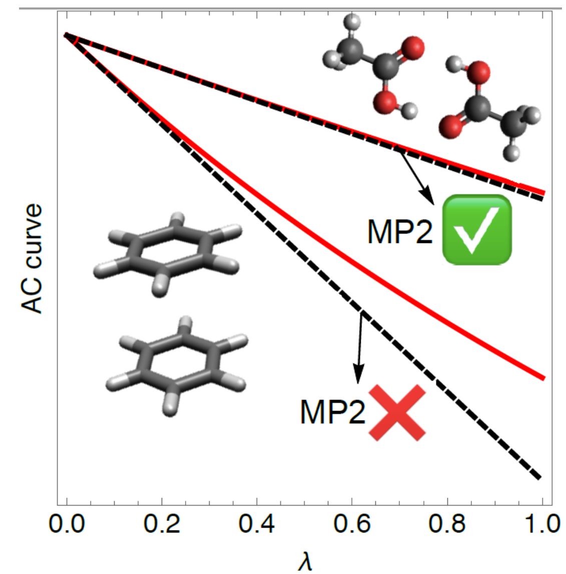


Same Cost

Full Ex and MP2

Møller Plesset Adiabatic Connection Functionals





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DFT AC vs HF AC/MPAC

DFT

$$\hat{H}_{\lambda}^{\rm DFT} = \hat{T} + \lambda\,\hat{V}_{ee} + \hat{V}_{\rm ext} + \hat{V}_{\lambda}[\rho]$$

$$\hat{V}_{\lambda}[\rho] \; : \; \rho_{\lambda} = \rho_1 = \rho \;\; \forall\lambda$$

$$W_{c,\lambda}^{\rm DFT} = \langle\Psi_{\lambda}|\hat{V}_{ee}|\Psi_{\lambda}\rangle - \langle\Psi_0|\hat{V}_{ee}|\Psi_0\rangle$$

$$E_c^{\rm DFT} = \int_0^1 W_{c,\lambda}^{\rm DFT}\, d\lambda$$

$\lambda \to 0$

$$W_{c,\lambda}^{\rm DFT} \to \sum_{n=2}^{\infty} n\, E_c^{{\rm GL}n}\, \lambda^{n-1}$$

$\lambda \to \infty$

$$W_{c,\lambda}^{\rm DFT} \to W_{c,\infty}^{\rm SCE} + \frac{W_{\frac{1}{2}}^{\rm SCE}}{\sqrt{\lambda}} + \ldots$$

Hartree-Fock/MP

$$\hat{H}_{\lambda}^{\rm HF} = \hat{T} + \hat{V}^{\rm HF} + \hat{V}_{\rm ext} + \lambda\,(\hat{V}_{ee} - \hat{V}^{\rm HF})$$

$$\hat{V}^{\rm HF} = \hat{J}[\rho^{\rm HF}] - \hat{K}[\{\phi_i^{\rm HF}\}] \quad \lambda\text{−independent}$$

$$\rho_{\lambda} \qquad \rho_{\lambda=0} = \rho^{\rm HF} \qquad \rho_{\lambda=1} = \rho$$

$$W_{c,\lambda}^{\rm HF} = \langle\Psi_{\lambda}|\hat{V}_{ee} - \hat{V}^{\rm HF}|\Psi_{\lambda}\rangle - \langle\Psi_0|\hat{V}_{ee} - \hat{V}^{\rm HF}|\Psi_0\rangle$$

$$E_c^{\rm HF} = \int_0^1 W_{c,\lambda}^{\rm HF}\, d\lambda$$

$\lambda \to 0$

$$W_{c,\lambda}^{\rm HF} \to \sum_{n=2}^{\infty} n\, E_c^{{\rm MP}n}\, \lambda^{n-1}$$

$\lambda \to \infty$

$$W_{c,\lambda}^{\rm HF} \to W_{c,\infty}^{\rm MP} + \frac{W_{\frac{1}{2}}^{\rm MP}}{\sqrt{\lambda}} + \frac{W_{\frac{3}{4}}^{\rm MP}}{\lambda^{3/4}} + \ldots$$

Daas, T. J.; Grossi, J.; Vuckovic, S.; Musslimani, Z. H.; Kooi, D. P.; Seidl, M.; Giesbertz, K. J. H.; Gori-Giorgi, P. Large coupling-strength expansion of the MøllerPlesset adiabatic connection: From paradigmatic cases to variational expressions for the leading terms. The Journal of Chemical Physics 2020, 153, 214112.

Strong coupling limit

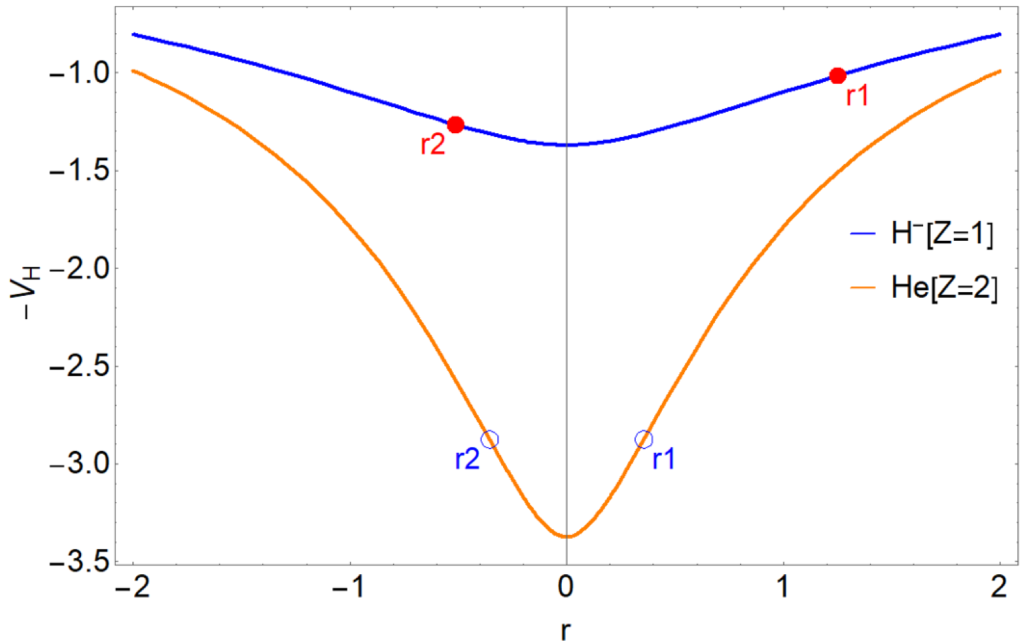
- Exact results on the strong-coupling expansion of the MPAC:

$$W^{\mathrm{HF}}_{c,\lambda\to\infty} = W^{\mathrm{HF}}_{c,\infty} + \frac{W^{\mathrm{HF}}_{\frac{1}{2}}}{\sqrt{\lambda}} + \frac{W^{\mathrm{HF}}_{\frac{3}{4}}}{\lambda^{\frac{3}{4}}} + \dots$$

$$W^{\mathrm{HF}}_{c,\infty} = E_{el}[\rho^{\mathrm{HF}}] + E_x$$

$$W^{\mathrm{HF}}_{\frac{1}{2}} \approx 2.8687 \sum_{i=1}^{N} \left(\rho^{\mathrm{HF}}(\mathbf{r}_i^{\min})\right)^{1/2}$$

$$W^{\mathrm{HF}}_{\frac{3}{4}} \approx -1.272 \sum_{\mathbf{r}_{Z_k}} Z_k \left(\rho^{\mathrm{HF}}(\mathbf{r}_{Z_k})\right)^{1/4}$$



$$E_{el}[\rho] = \min_{\{\mathbf{r}_1 \dots \mathbf{r}_N\}} \left\{ \sum_{\substack{i,j=1 \\ j>i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N} v_h(\mathbf{r}_i; [\rho]) + U[\rho] \right\}$$

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Strong Coupling Limit in Practice

- Our current functionals are crude approximations based on the DFT ones

$$W_{c,\infty}^{\alpha,\beta} = \alpha W_{\infty}^{\mathrm{DFT}}[\rho] + \beta E_x$$

$$W_{c,\infty}[\rho^{\mathrm{HF}}] \sim W_{c,\infty}^{\mathrm{DFT}}[\rho^{\mathrm{HF}}]$$

$$\approx \underbrace{\int \left[A\rho^{\mathrm{HF}}(\mathbf{r})^{4/3} + B\frac{|\nabla\rho^{\mathrm{HF}}(\mathbf{r})|^2}{\rho^{\mathrm{HF}}(\mathbf{r})^{4/3}} \right] d\mathbf{r}}_{W_{\infty}^{\mathrm{PC}}[\rho^{\mathrm{HF}}]}$$

$$- E_{\mathrm{x}}[\{\phi_i^{\mathrm{HF}}\}]$$

- What the future will hold:

$$W_{c,\lambda\to\infty}^{\mathrm{HF}} = W_{c,\infty}^{\mathrm{HF}} + \frac{W_{\frac{1}{2}}^{\mathrm{HF}}}{\sqrt{\lambda}} + \frac{W_{\frac{3}{4}}^{\mathrm{HF}}}{\lambda^{\frac{3}{4}}} + \cdots,$$

$$W_{c,\infty}^{\mathrm{HF}} = E_{el}[\rho^{\mathrm{HF}}] + E_x,$$

$$W_{\frac{1}{2}}^{\mathrm{HF}} \approx 2.8687 \sum_{i=1}^{N} \left(\rho^{\mathrm{HF}}(\mathbf{r}_i^{\min})\right)^{1/2},$$

build GGA's for these two functionals (so far approximated with DFT-like form)

$$W_{\frac{3}{4}}^{\mathrm{HF}} \approx -1.272 \sum_{\mathbf{r}_{Z_k}} Z_k \left(\rho^{\mathrm{HF}}(\mathbf{r}_{Z_k})\right)^{1/4},$$

Use this functional by making the approximation that there is 1e at the nucleus per atom

Daas, T. J.; Grossi, J.; Vuckovic, S.; Musslimani, Z. H.; Kooi, D. P.; Seidl, M.; Giesbertz, K. J. H.; Gori-Giorgi, P. Large coupling-strength expansion of the MøllerPlesset adiabatic connection: From paradigmatic cases to variational expressions for the leading terms. The Journal of Chemical Physics 2020, 153, 214112.

M. Seidl and J. P. Perdew, Size-dependent ionization energy of a metallic cluster: Resolution of the classical image-potential paradox, *Phys. Rev. B* 50, 5744 1994

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Interpolations along the MPAC

- Directly approximating the MPAC using information from both limits.

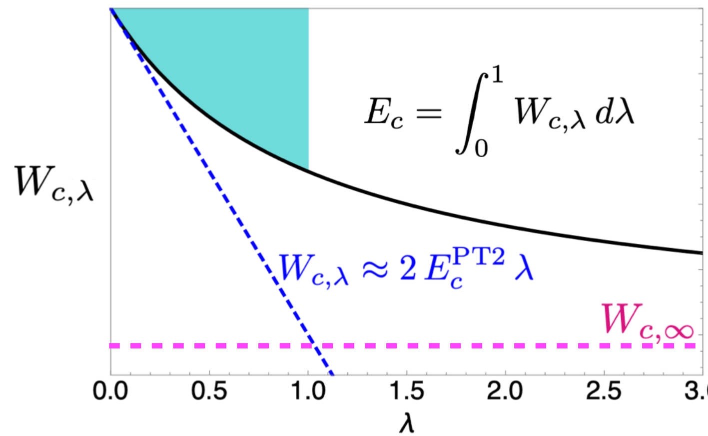
- SPL2: 4 fitted parameters on S22

$$W_\lambda^{\mathrm{SPL2}}(\mathbf{W}) = C - \frac{m_1}{\sqrt{1+b_1\lambda}} - \frac{m_2}{\sqrt{1+b_2\lambda}}$$

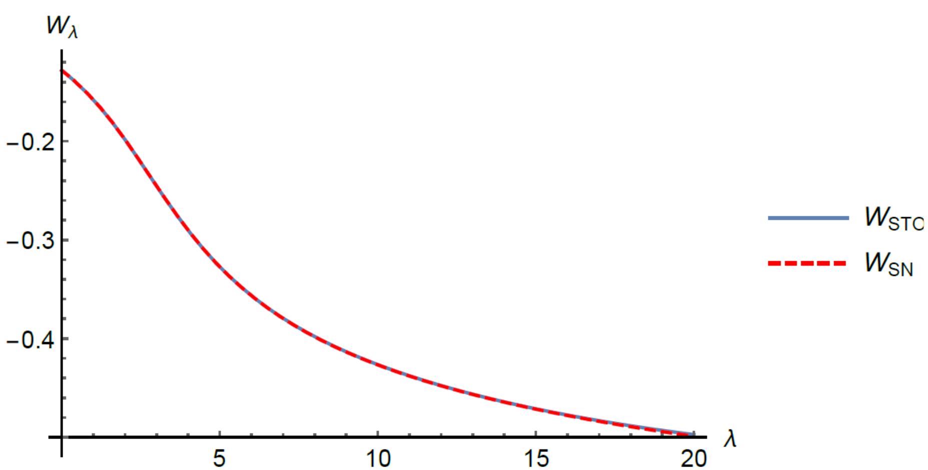
- MPACF-1: 2 fitted Parameters on S22

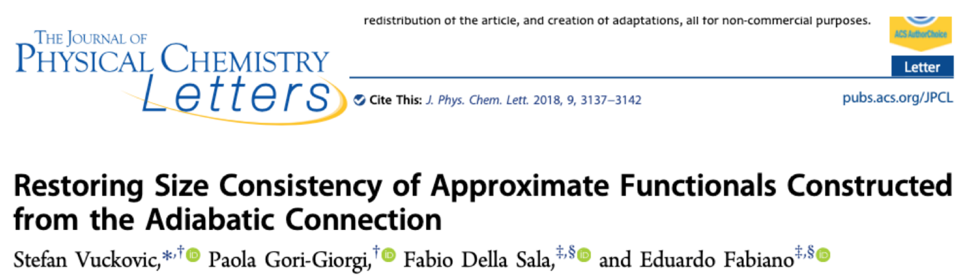
$$E_c(\lambda) = -a\lambda + \frac{a(c+1)\lambda}{\sqrt{b_1^2\lambda+1} + c\sqrt[4]{b_2^4\lambda+1}}$$

$$W_{c,\infty}^{\alpha,\beta} = \alpha W_\infty^{\mathrm{DFT}}[\rho] + \beta E_x$$



Interpolation in the DFT context was first proposed by Seidl, Perdew & Levy [PRA 1999]. The idea was abandoned because of lack of size consistency

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The Journal of Physical Chemistry Letters

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Restoring Size Consistency of Approximate Functionals Constructed from the Adiabatic Connection

Stefan Vuckovic,*,† Paola Gori-Giorgi,† Fabio Della Sala,‡,§ and Eduardo Fabiano‡,§

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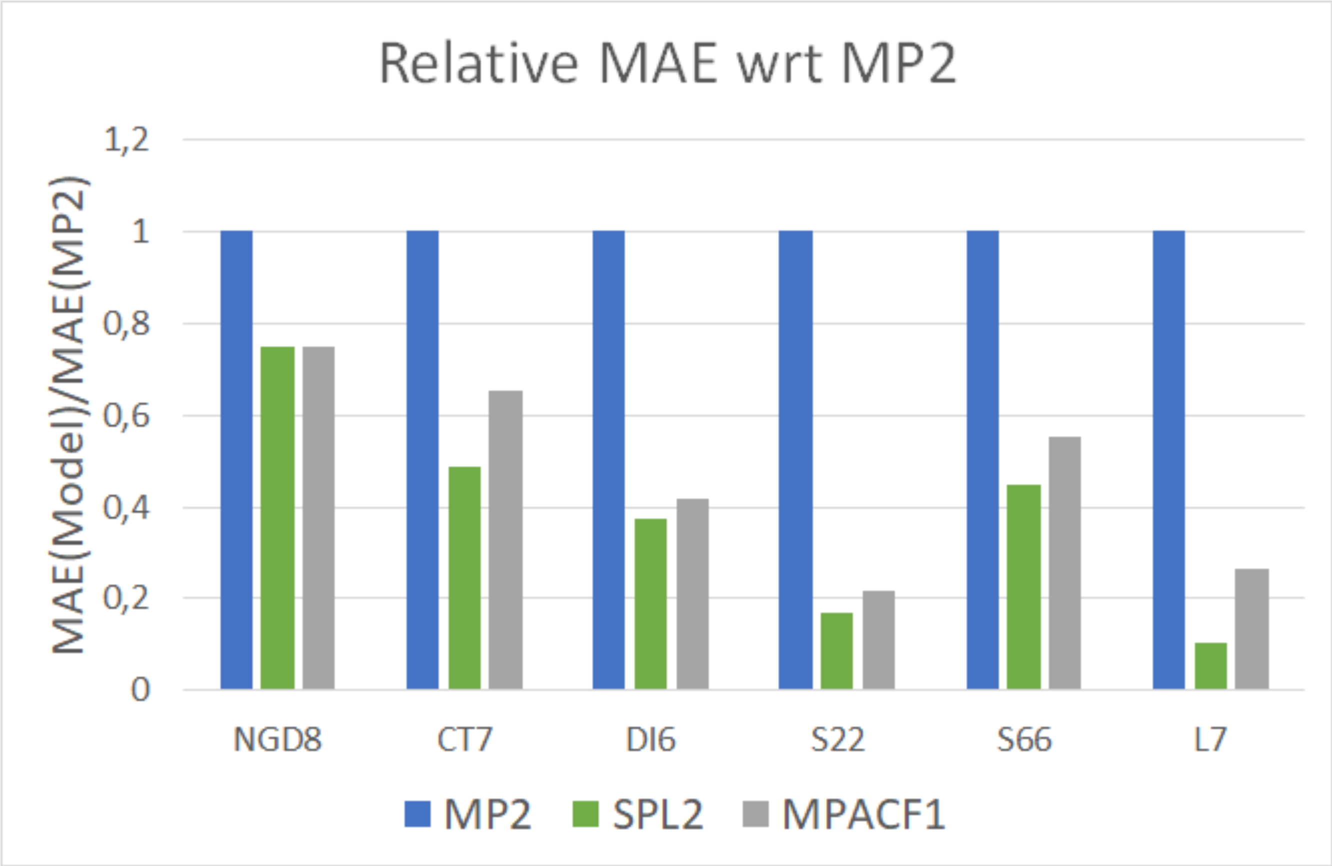
Explorative results: MAE for test-sets



Noncovalent Interactions from Models for the Møller–Plesset Adiabatic Connection

Timothy J. Daas, Eduardo Fabiano, Fabio Della Sala, Paola Gori-Giorgi, and Stefan Vuckovic*

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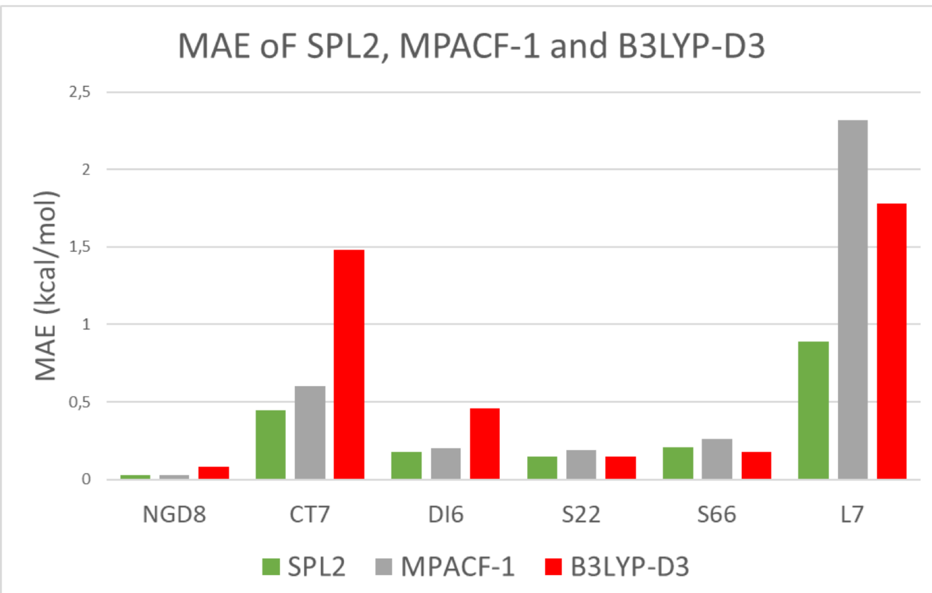

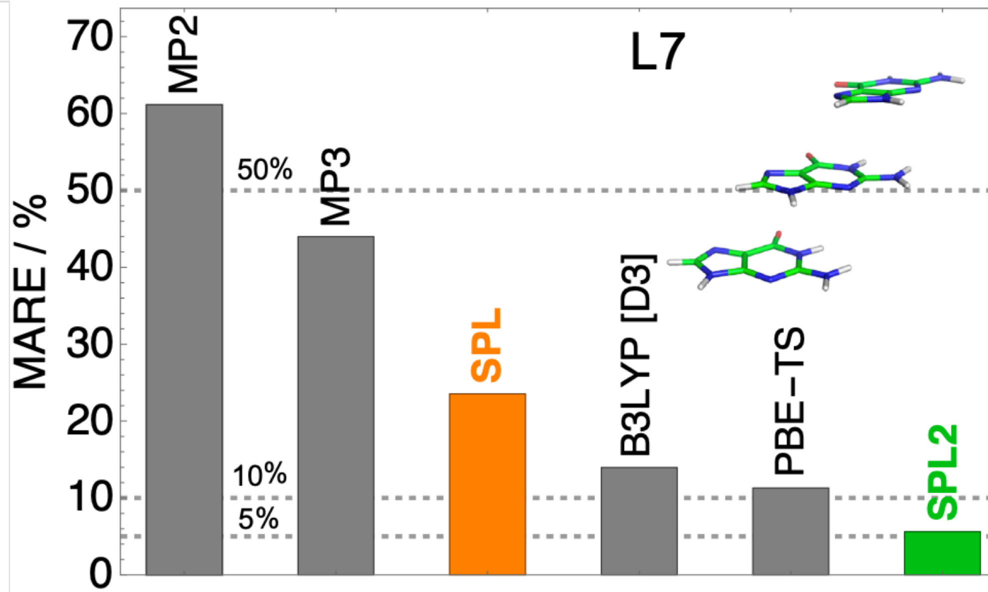

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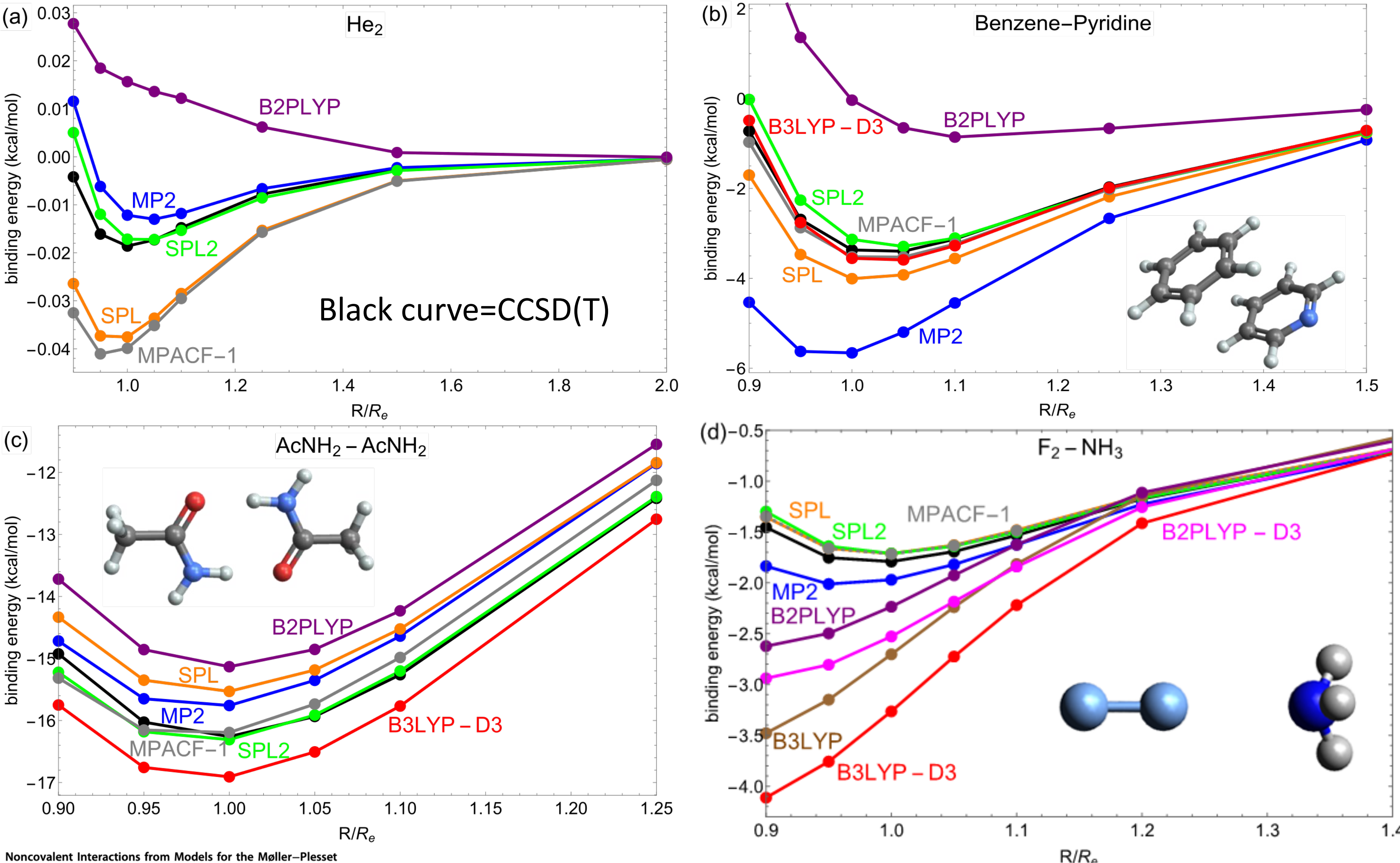
Explorative results: Dissociation Curves



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Advantages and Outlook

- No D3/D4 correction are needed for NCI

- Contains full exact exchange and MP2 for the same cost as DH.

- Improving our functionals so that they:

  – Are using exact properties from both limits fully

GEA/GGA for Eel

- Going back to GGA's

$$W_{c,\infty}^{\mathrm{HF}} = E_{el}[\rho^{\mathrm{HF}}] + E_x,$$

$$W_{\frac{1}{2}}^{\mathrm{HF}} \approx 2.8687 \sum_{i=1}^{N} \left(\rho^{\mathrm{HF}}(\mathbf{r}_i^{\min})\right)^{1/2},$$

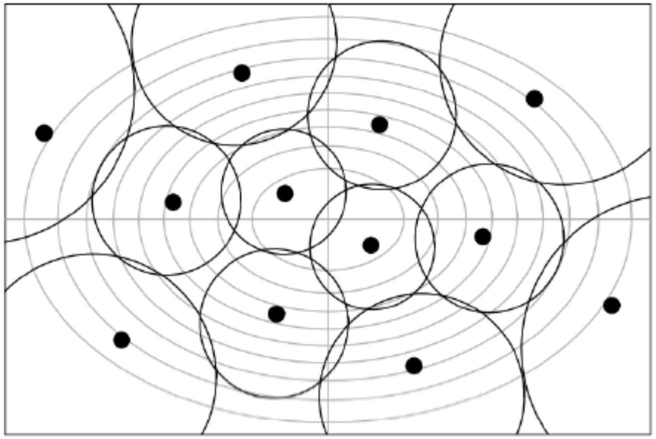
build GGA's for these two functionals
(so far approximated with DFT-like form)

- $E_{\mathrm{el}}[\rho]$ is bounded by $W_\infty^{\mathrm{DFT}}[\rho]$:

$$E_{\mathrm{el}}[\rho] \leq W_\infty^{\mathrm{DFT}}[\rho]$$

- Which has an accurate GEA (PC Model):

$$W_\infty^{\mathrm{PC}}[\rho] = A^{\mathrm{PC}} \int \rho(\mathbf{r})^{\frac{4}{3}}\, d\mathbf{r} + B^{\mathrm{PC}} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{\frac{4}{3}}}\, d\mathbf{r}$$



- GEA for $E_{\mathrm{el}}[\rho]$ will have the same LDA (Wigner crystal)

- And the same form, since it has the same scaling as $E_x^{\mathrm{HF}\Gamma}[\rho]$

$$E_{\mathrm{el}}[\rho_\gamma] = \gamma\, E_{\mathrm{el}}[\rho]$$

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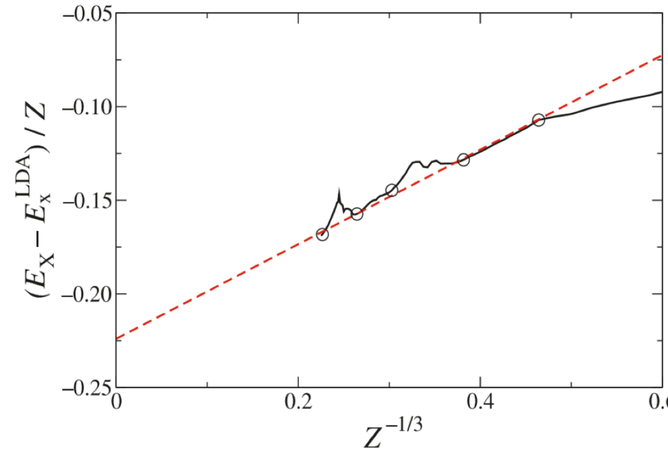
How to get the B: Semiclassics

- Burke derived Becke-88 of Ex using Thomas Fermi Scaling:

$$\Delta E_{\mathrm{x}}^{\mathrm{B88}}[n] = -\beta^{\mathrm{B88}} \int \mathrm{d}^3 r\, n^{4/3}(\mathbf{r}) \frac{x^2}{1 + 6x\beta^{\mathrm{B88}} \sinh^{-1}[2^{1/3}x]}$$



Elliott, P.; Burke, K. Non-empirical derivation of the parameter in the B88 exchange functional. Canadian Journal of Chemistry 2009, 87, 1485–1491.

- When $N \rightarrow \infty$ the bulk of the density of atoms becomes TF-like, which scales as:

$$\rho_\zeta(r) = \zeta^2 \rho(\zeta^{1/3} r) \qquad \zeta = N$$

- Where the reduced gradient gets smaller when N increases:

$$x(\boldsymbol{r}, [\rho_\zeta]) = \zeta^{-1/3} x(\zeta^{1/3} \boldsymbol{r}, [\rho]) \qquad x = \frac{|\nabla \rho|}{\rho^{4/3}}$$

- And the same can be applied to $E_{\mathrm{el}}[\rho]$

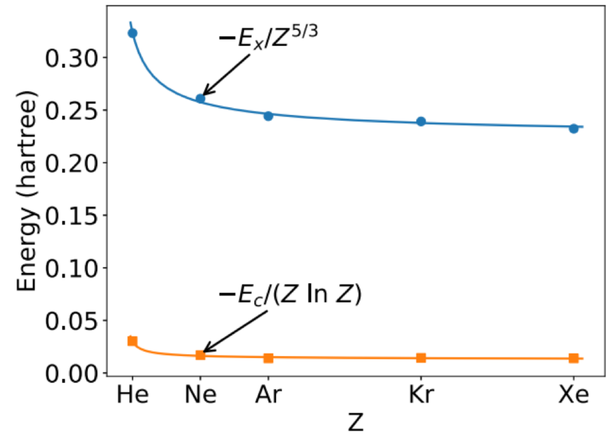
How to derive the B?

- One can prove that the GEA2 of $E_{\mathrm{el}}[\rho]$ scales as:

$$E_{\mathrm{el}}[\rho_\zeta] = a\,\zeta^{5/3} + b\,\zeta + \ldots$$

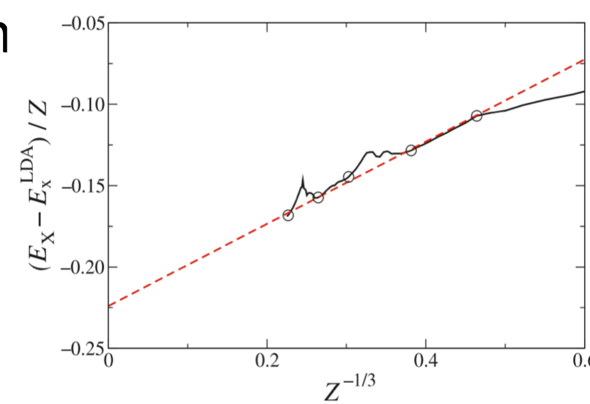
$$E_{\mathrm{el}}^{\mathrm{LDA}}[\rho_\zeta] = A\,\zeta^{5/3} \int \rho^{4/3}(\mathbf{t})\,d\mathbf{t} = A\,\sigma_a\,\zeta^{5/3}$$

$$E_{\mathrm{el}}^{\mathrm{GEA}}[\rho_\zeta] = B\,\zeta \int \frac{|\nabla\rho(t)|^2}{\rho(t)^{4/3}}\,d\mathbf{t} = B\,\sigma_b\,\zeta$$



- This only works for TF-scaled densities not for neutral atoms
- We will extract the B as a function of N with

$$\widetilde{B}(N) = \frac{E_{\mathrm{el}}[\bar\rho_N] \;-\; E_{\mathrm{el}}^{\mathrm{LDA}}[\bar\rho_N]}{\int d\mathbf{r}\,\frac{|\nabla\bar\rho_N(\mathbf{r})|^2}{\bar\rho_N(\mathbf{r})^{4/3}}}$$



- Notice that B is profile dependent!

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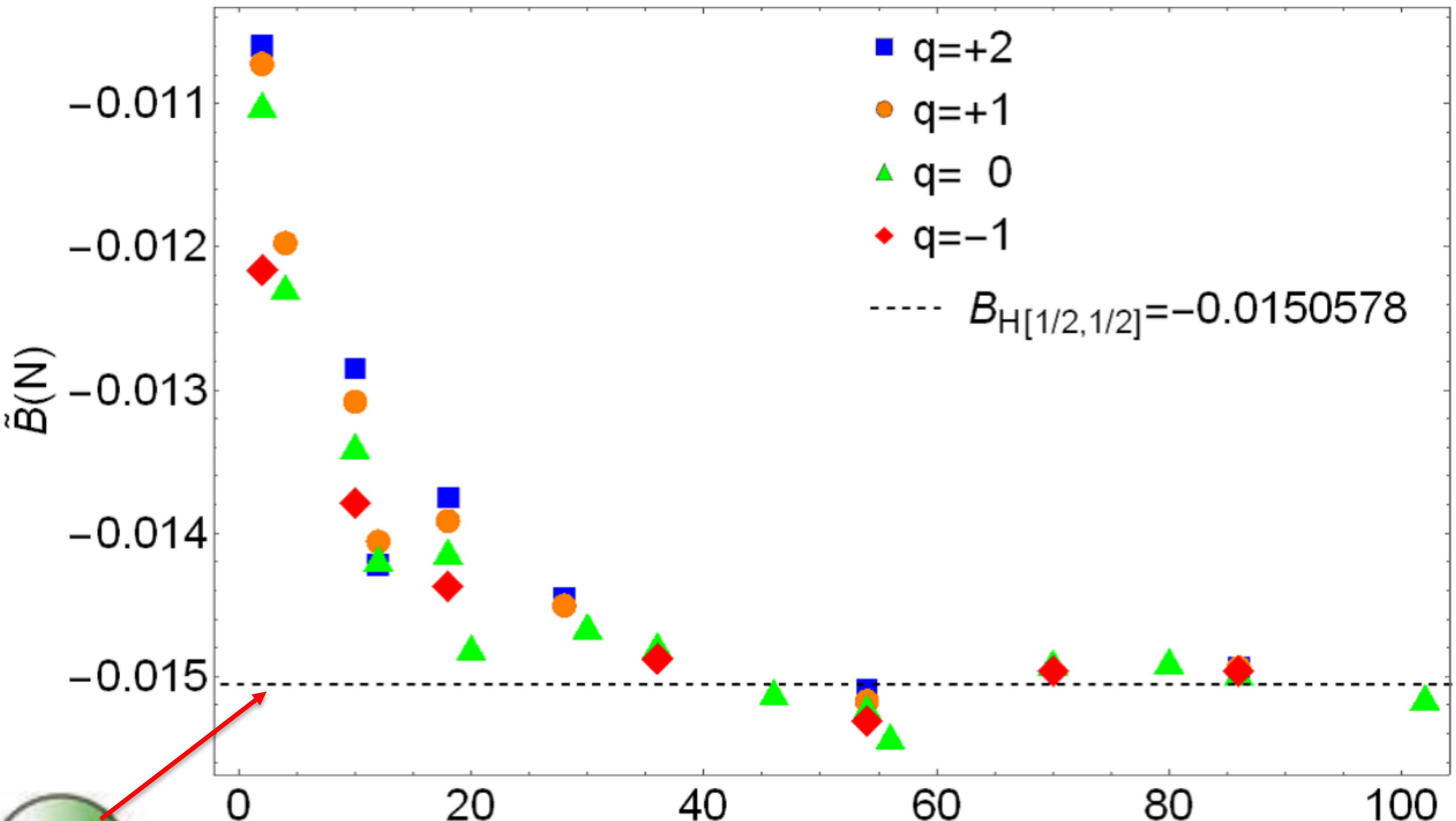
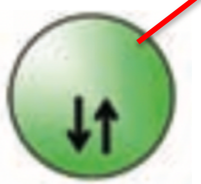
Relative Errors: Closed-shell atoms and ions





B=-0.0150578

Variations of the Hartree–Fock fractional-spin error for one electron

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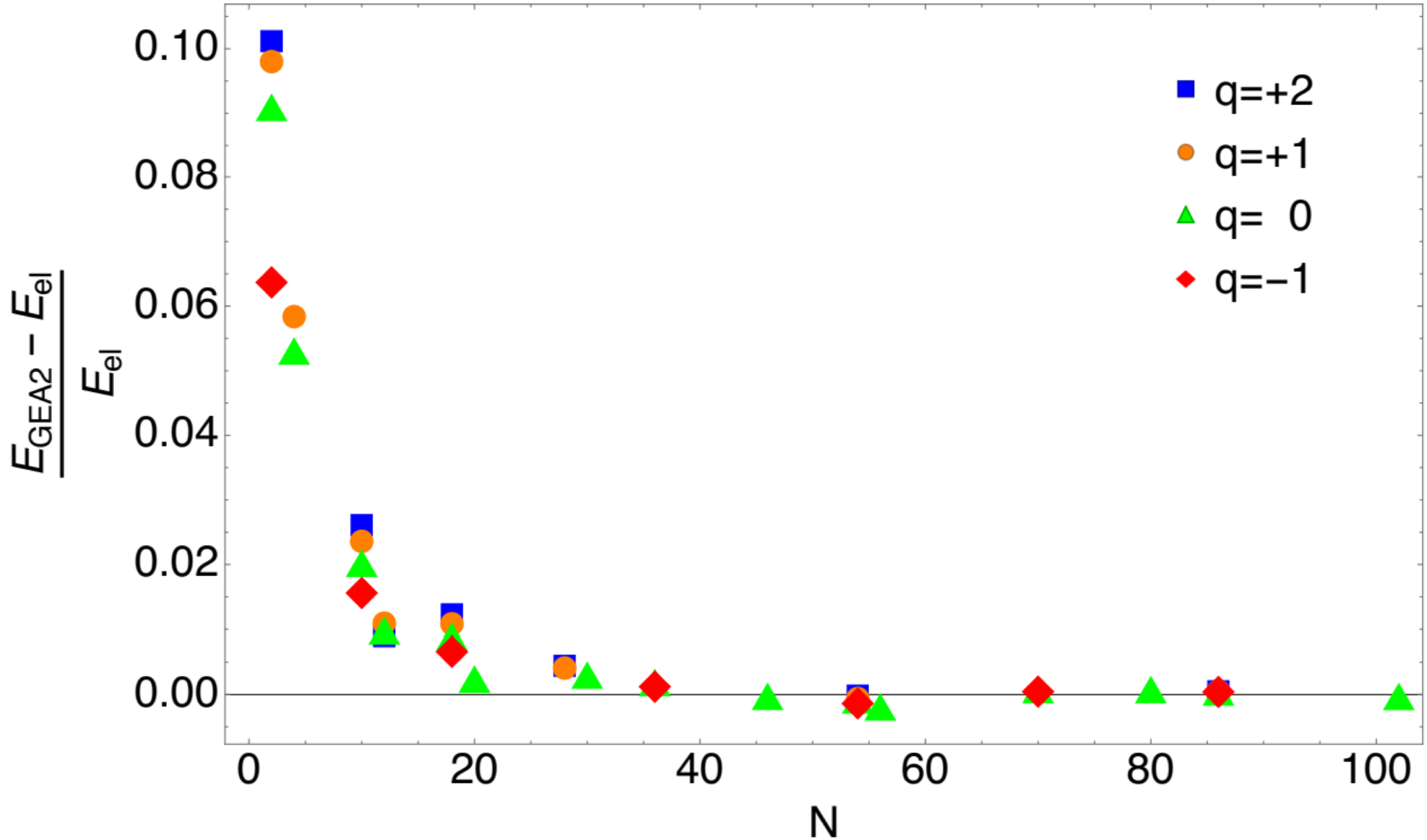

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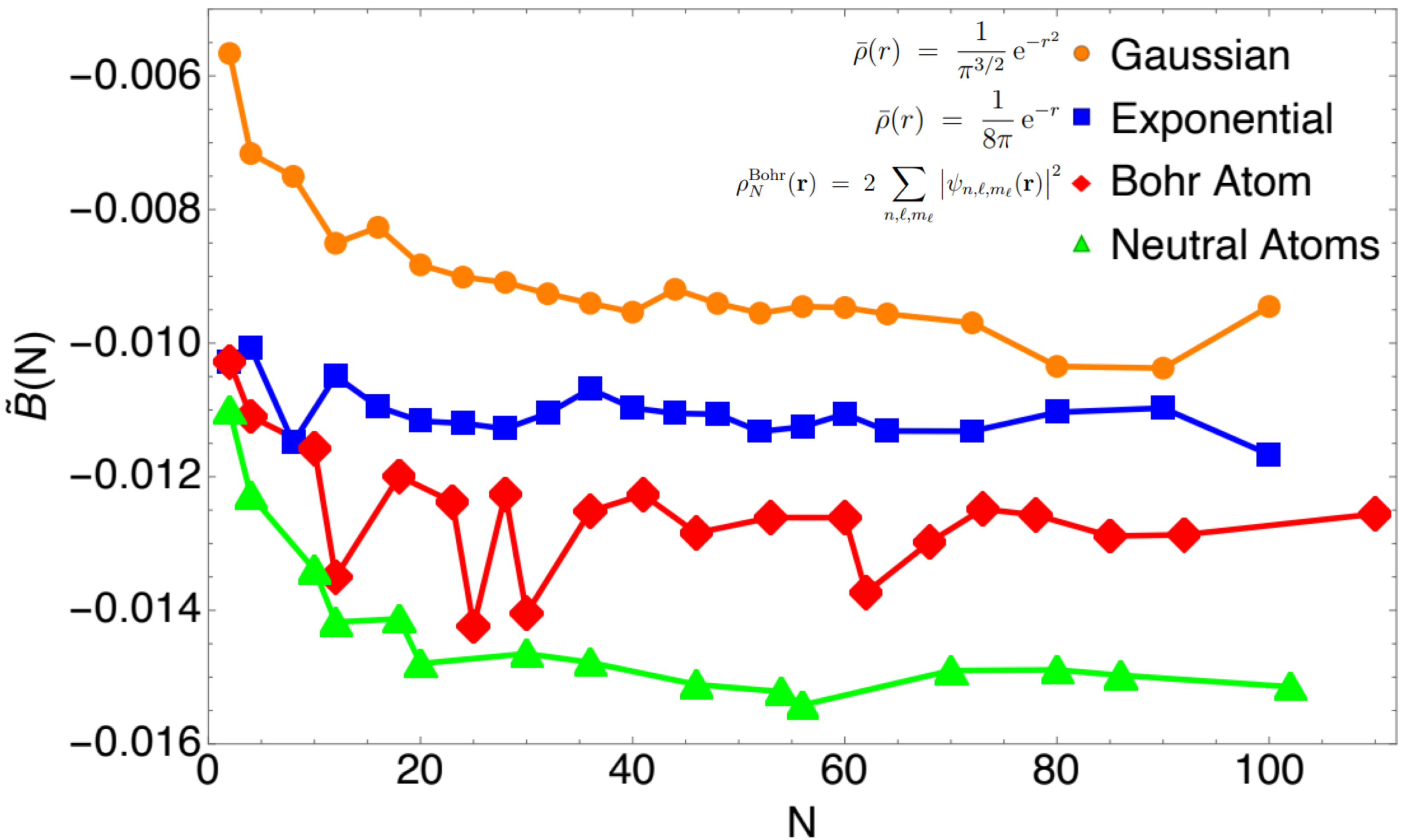
Profile Depedency B



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- Contains full exact exchange and MP2 for the same cost as DH.
- Improving our functionals so that they: 

  - Are using exact properties from both limits fully
  - Have less or no fitted parameters
  - Work for open-shell systems
  - Test for other NCI/bonds

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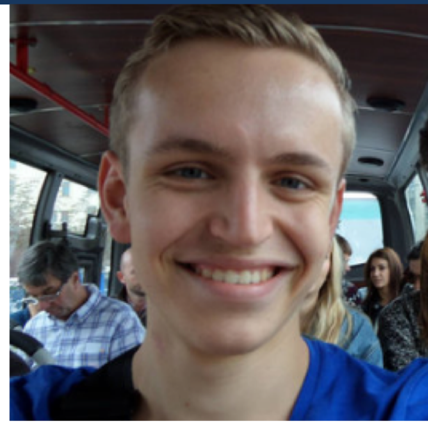
Acknowledgements

Paola Gori-Giorgi
VU Amsterdam



Derk Kooi
VU Amsterdam

Arthur Grooteman
VU Amsterdam

Micheal Seidl
VU Amsterdam

Stefan Vuckovic
UCI Irvine

Fabio Della Sala
CNR Lecce

Eduardo Fabiano
CNR Lecce

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Thank you for your attention!