

Range-Separated Random Phase Approximations

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$$E^{\text{DFT}} = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hxc}}[n_{\Phi}] \right\}$$

LDA, GGA, meta-GGA are semi-local exchange-correlation functionals that have good performances for a fair range of applications.

In the last years, **hybrid(H)** and **double hybrid(DH)** functionals increasingly became a standard both in development and in applications.

$$E_{\text{xc}}^{2\text{DH}} = a_x E_{\text{x}}^{\text{HF}} + (1 - a_x) E_{\text{x}}^{\text{DFA}} + (1 - a_c) E_{\text{c}}^{\text{DFA}} + a_c E_{\text{c}}^{\text{MP2}}$$

Double hybrids are an example of a class of functionals depending on **virtual orbitals**.

Another example of correlation functional depending on virtual orbitals and gathering interest in the community is **Random-Phase Approximation (RPA)**, which goes beyond second-order.

$$E = \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hx}}^{\text{HF}}[\Phi] + E_{\text{c}}^{\text{RPA}}$$

In practice, we do not use RPA in an hybrid functional context.

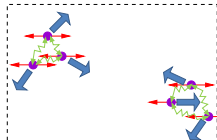
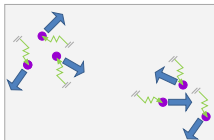
We do use it, as will be seen, in a range-separated context.

Random Phase Approximation

The original idea [Bohm,Pines PR 82 625 (1951)]

is to decouple the particle and field variables in the description of the UEG.

Go from $\hat{H} = \hat{H}_{\text{part.}} + \hat{H}_{\text{field}} + \hat{H}_{\text{part./field}}$ to $\hat{H}^{\text{RPA}} = \hat{H}_{\text{part.}} + \hat{H}_{\text{oscillations}} + \hat{H}_{\text{part./part.}}^{\text{sr}}$



Only the particles in phase with the oscillating field contribute to the oscillations the other particles, with a **random phase**, are neglected.

EOM derivation [Fetter,Walecka §59 (1971)]

Consider the EOM for $Q^\dagger |0\rangle = |q\rangle \rightarrow \langle 0| [\delta Q, [H, Q^\dagger]] |0\rangle = \epsilon_{q0} \langle 0| [\delta Q, Q^\dagger] |0\rangle$.

The RPA is an approximation of Q^\dagger on a basis $\{\zeta_a, \zeta_a^\dagger\}$ of operators of creation and destruction of p-h pairs, namely one writes $Q^\dagger = \sum [X_a \zeta_a - Y_a \zeta_a^\dagger]$ and the

EOM yields:
$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \epsilon_{q0} \begin{pmatrix} \mathbf{N} & \mathbf{0} \\ \mathbf{0} & -\mathbf{N} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

Also: **Adiabatic Connection Fluctuation Dissipation Theorem**, and **rCCD**.

[we track what is missing in the reference system]

Adiabatic connection formula for E_c

$$E_c = \frac{1}{2} \int_0^1 d\alpha \operatorname{Tr}(\mathbb{W}_{ee} \cdot \mathbb{P}_{c,\alpha}) = \int_0^1 d\alpha \left(\langle \Psi_\alpha | \hat{W}_{ee} | \Psi_\alpha \rangle - \langle \Phi_0 | \hat{W}_{ee} | \Phi_0 \rangle \right)$$

Fluctuation-dissipation theorem for $P_{c,\alpha}$

$$\mathbb{P}_{c,\alpha} = \int_{-\infty}^{\infty} \frac{-d\omega}{2\pi} [\mathbb{\Pi}_\alpha(i\omega) - \mathbb{\Pi}_0(i\omega)]$$

Linear response equations for $\mathbb{\Pi}_\alpha(i\omega)$

$$\mathbb{\Pi}_\alpha(i\omega)^{-1} = \mathbb{\Pi}_0(i\omega)^{-1} - \mathbb{f}_{\text{Hxc},\alpha}(i\omega) \quad \leftarrow \text{kernel}$$

RPA correlation energy $\mathbb{f}_{\text{xc},\alpha} = 0$ or $\mathbb{f}_{c,\alpha} = 0$

$$E_c = \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \operatorname{Tr}(\mathbb{W}_{ee} \cdot [\mathbb{\Pi}_\alpha^{\text{RPA}}(i\omega) - \mathbb{\Pi}_0(i\omega)])$$

where $\mathbb{\Pi}_\alpha^{\text{RPA}}$ is obtained from the eigenvectors of $\begin{pmatrix} \mathbf{A}_\alpha & \mathbf{B}_\alpha \\ -\mathbf{B}_\alpha & -\mathbf{A}_\alpha \end{pmatrix}$

RPA: different formalisms

$$E_c = \frac{1}{2} \int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr} (\mathbb{W}_{ee} \cdot [\mathbb{\Pi}_\alpha^{\text{RPA}}(i\omega) - \mathbb{\Pi}_0(i\omega)]) \quad \begin{aligned} (\mathbf{B})_{ia,jb} &= \langle ab|ij\rangle \\ (\mathbf{A})_{ia,jb} &= \Delta\epsilon_{ia,jb} + \langle ib|aj\rangle \end{aligned}$$

- ▶ Analytical integration on the **frequency**

density matrix formulation

$$E_c = \frac{1}{2} \int_0^1 d\alpha \text{Tr} (\mathbb{W}_{ee} \cdot \mathbb{P}_{c,\alpha}^{\text{RPA}})$$

- ▶ **Both** analytical integration

plasmon formulation

$$E_c = \frac{1}{2} \text{tr} (\mathbf{\Omega}^{\text{RPA}} - \mathbf{\Omega}^{\text{TDA}})$$

- ▶ which is **equivalent** to the

rCCD formulation

$$E_c = \frac{1}{2} \text{tr} (\mathbf{B} \cdot \mathbf{T})$$

where **T** are solutions of the **Riccatti** equations

$$\mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} = \mathbf{0}$$

[Scuseria,Henderson,Sorensen JCP **129** 231101 (2008)]

- ▶ Analytical integration on the **coupling constant**

dielectric matrix formulation

$$E_c = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} (\log [\mathbf{1} - \mathbf{\Pi}_0 \mathbf{B}] + \mathbf{\Pi}_0 \mathbf{B})$$

[Jansen,BM,Rocca,Ángyán (in prep.)]

RPA: different flavors

$$E_c = \frac{1}{2} \text{tr}(\mathbf{B} \cdot \mathbf{T})$$

$$\text{where } \mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = \mathbf{0}$$

$$(\mathbf{B})_{ia,jb} = \langle ab|ij \rangle$$

$$(\mathbf{A})_{ia,jb} = \Delta\epsilon_{ia,jb} + \langle ib|aj \rangle$$

The Riccati equations, in this context, are derived from $\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix}$

which depend on a kernel \mathbb{f} that **does not or does include exchange**.

► **drCCD** variant $\longrightarrow \mathbb{f}_{xc} = 0 \longrightarrow$

$$\begin{aligned} (\mathbf{B}^I)_{ia,jb} &= \langle ab|ij \rangle \\ (\mathbf{A}^I)_{ia,jb} &= \Delta\epsilon_{ia,jb} + \langle ib|aj \rangle \end{aligned}$$

$$E_c^{\text{drRPA-I}} = \frac{1}{2} \text{tr}(\mathbf{B}^I \cdot \mathbf{T}^{\text{drRPA}})$$

$$\text{where } \mathbf{B}^I + \mathbf{A}^I\mathbf{T} + \mathbf{T}\mathbf{A}^I + \mathbf{T}\mathbf{B}^I\mathbf{T} = \mathbf{0}$$

► **rCCD** variant $\longrightarrow \mathbb{f}_c = 0 \longrightarrow$

$$\begin{aligned} (\mathbf{B}^{II})_{ia,jb} &= \langle ab||ij \rangle \\ (\mathbf{A}^{II})_{ia,jb} &= \Delta\epsilon_{ia,jb} + \langle ib||aj \rangle \end{aligned}$$

$$E_c^{\text{RPAx-II}} = \frac{1}{4} \text{tr}(\mathbf{B}^{II} \cdot \mathbf{T}^{\text{RPAx}})$$

$$\text{where } \mathbf{B}^{II} + \mathbf{A}^{II}\mathbf{T} + \mathbf{T}\mathbf{A}^{II} + \mathbf{T}\mathbf{B}^{II}\mathbf{T} = \mathbf{0}$$

► Additional flavors

$$E_c^{\text{SOSEX}} = \frac{1}{2} \text{tr}(\mathbf{B}^{II} \cdot \mathbf{T}^{\text{drRPA}})$$

$$E_c^{\text{SO2}} = \frac{1}{2} \text{tr}(\mathbf{B}^I \cdot \mathbf{T}^{\text{RPAx}})$$

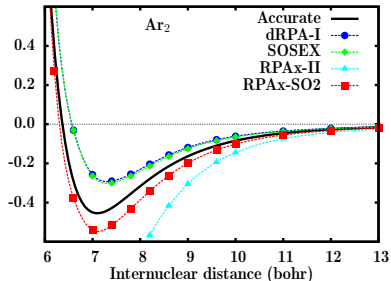
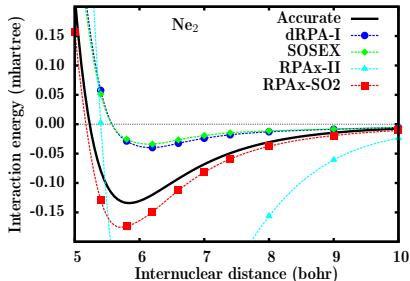
Note that comparable additional flavors also exist in the **density matrix** formulation (they have been explored in the literature) and in the **dielectric matrix** formulation.

DFT calculation followed by an **RPA calculation using KS orbitals and energies.**

$$E^{\text{DFT}} = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hxc}}[n_{\Phi}] \right\}$$

$$E = \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hx}}^{\text{HF}}[\Phi] + E_{\text{c}}^{\text{RPA}}$$

- ▶ DFT (LDA/GGA/...) do not describe well the **long-range dispersion forces**, while RPA does.
- ▶ Still problems with: **short-range correlation energies** (far too negative)
strong dependence on basis size
simple van der Waals dimers



Range-Separated Hybrid + RPA

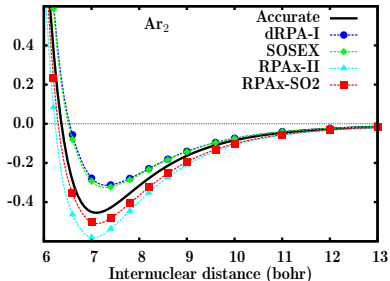
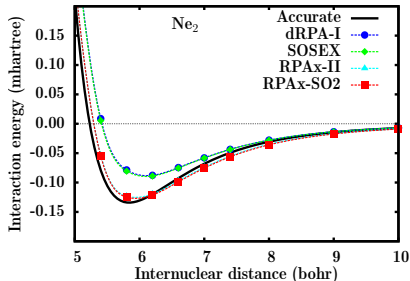
- ▶ The idea: split the e-e interaction into a **short-** and a **long-range** parts.

Hybrid **DFT** with exact HF exchange and RPA correlation, both at **long-range**:

$$E = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{lr} | \Phi \rangle + E_{Hxc}^{sr}[n_{\Phi}] \right\} + E_c^{lr,RPA}$$

[Stoll,Savin (1985)][Savin IJQC 22 59 (1988)][Savin, Rec.dev. 327 (1996)]

- ▶ range separation greatly **improves RPA** (see **srPBE+RPAx-SO2**).
- ▶ basis dependence is reduced.



>srPBE, aug-cc-pV6Z, $\mu = 0.5$ [Toulouse,Zhu,Savin,Jansen,Ángyán 135 084119 (2011)]

Range-Separated Hybrid + RPA

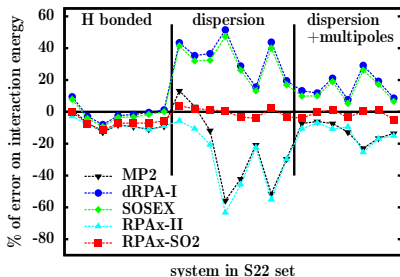
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[Stoll,Savin (1985)][Savin IJQC 22 59 (1988)][Savin, Rec.dev. 327 (1996)]

- ▶ range separation greatly **improves RPA** (see **srPBE+RPAx-SO2**).
- ▶ basis dependence is reduced.
- ▶ for ex.: performance on the S22 dataset is very good for **srPBE+RPAx-SO2**.

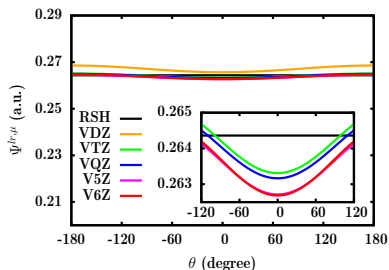
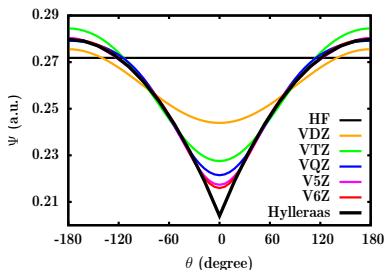
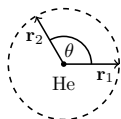


>srPBE, aug-cc-pVDZ, $\mu = 0.5$ [Toulouse,Zhu,Savin,Jansen,Ángyán 135 084119 (2011)]

Wavefunction basis convergence

[Gori-Giorgi, Savin PRA 73 032506 (2006)]

both **partial wave** and **principal number** expansions
lead to **exponential convergence** of the wavefunction.



Extrapolation formula for total energies

We propose a **three-point extrapolation scheme** for total RSH+correlation energies (fitting $E_X = E_\infty + B \exp(-\beta X)$).

$$E_\infty = E_{XYZ} = \frac{E_Y^2 - E_X E_Z}{2E_Y - E_X - E_Z}$$

>errors (mHartree) wrt. cc-pV6Z

	He	Ne	N ₂	H ₂ O
ΔE_D	8.488	74.523	51.581	55.850
ΔE_T	0.781	20.337	13.406	14.736
ΔE_Q	0.245	5.763	4.090	4.499
ΔE_5	0.078	0.751	0.810	0.726
ΔE_{DTQ}	0.205	0.401	1.083	1.105
ΔE_{TQ5}	0.002	-1.876	-0.972	-1.475

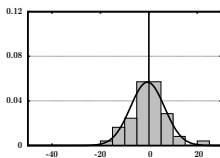
Implemented most of the variants with a nospinflip/spinflip block structure.

Normal distributions of errors
(kcal/mol) of calculations on **AE49**.

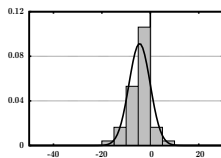
- ▶ mean errors of post-RSH calculation are better.
- ▶ post-RSH calculations dist. of errors have **sharper distributions**.

Similar results were obtained on the **DBH24/08** dataset.

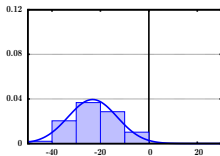
We argue that **RPax-SO2** is a good method for a wide range of applications.



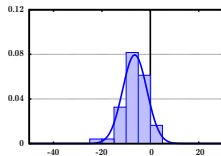
HF+MP2



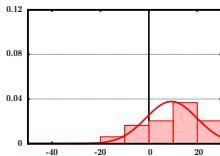
RSH+MP2



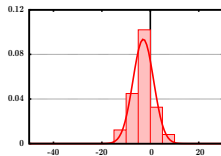
HF+dRPA-I



RSH+dRPA-I



HF+RPax-SO2



RSH+RPax-SO2

>cc-pVQZ (post-RSH: srPBE, $\mu = 0.5$)

Fractional Occupation Numbers calculations [origins]

[Perdew, Parr, Levy, Balduz, PRL **49** 1982]

► Study of systems with a **non-integer charge**.

$$\text{► } E^{N+\delta} = \min_{\hat{f} \rightarrow N+\delta} \text{Tr} \left[\hat{f} \left(\hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ee}} \right) \right]$$

$$\hat{f}^{N+\delta} = (1 - \delta) \hat{f}^N + (\delta) \hat{f}^{N+1}$$

$$E^{N+\delta} = (1 - \delta) E^N + (\delta) E^{N+1}$$

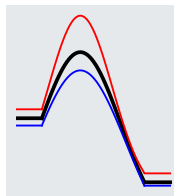
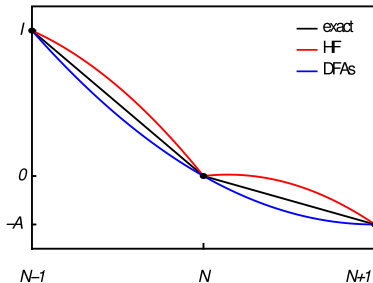
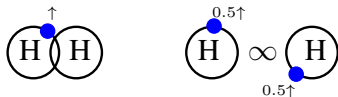
$$n^{N+\delta} = (1 - \delta) n^N + (\delta) n^{N+1}$$

E is **piecewise linear** wrt N and has a **derivative discontinuity** at integer N .

$$\text{► } E^{N+\delta} = \min_{\hat{f} \rightarrow N+\delta} \text{Tr} \left[\hat{f} \left(\hat{T} + \hat{V}_{\text{ext}} \right) + E_{\text{Hxc}}[n_{\hat{f}}] \right]$$

$$\hat{f}^{N+\delta} = (1 - \delta) \hat{f}^{N,\delta} + (\delta) \hat{f}^{N+1,\delta}$$

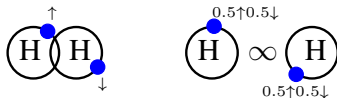
$$n^{N+\delta}(\mathbf{r}) = \sum n_i |\phi_i^{N+\delta}(\mathbf{r})|^2$$



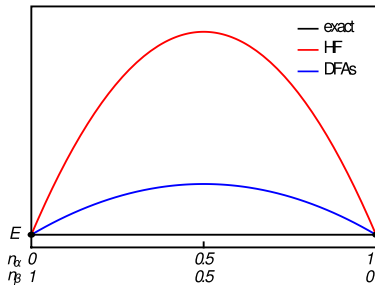
[Mori-Sánchez, Cohen, Yang JCP **125** 2006]

Fractional Occupation Numbers calculations [origins]

- ▶ Study of systems with a **non-integer spin**.

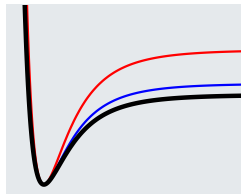


- ▶ Systems with fractional occupation of degenerate spin states should have the **same energy as the integer-spin states**.



- ▶ **Constancy condition:**

$$E \left[\sum c_i n_i \right] = E[n] = E(N)$$



Fractional Occupation Numbers calculations [in practice]

SCF: from $n(\mathbf{r}) = \sum_i^{\text{occ.}} |\phi_i(\mathbf{r})|^2$ to $n(\mathbf{r}) = \sum_i^{f+p} n_i |\phi_i(\mathbf{r})|^2$

We have now fully occupied (f) and **partially occupied** (p) orbitals.

RPA:

[Yang, Mori-Sánchez, Cohen JCP **139** 2013]

The fractional occupation numbers appear in the expressions of the matrices **A** and **B** and their dimension change from $ia = \text{occ.} \times \text{vir.}$ to $ia = (f+p) \times (p+u)$

The derivation is done by Green's function formalism.

It is comprehensive and useful, but somewhat involved.

$G_0^{N+\delta} = (1 - \delta)G_0^N + \delta G_0^{N+1}$ These changes appears from terms like $\theta(p - \text{FERMI})$ in the Green's functions.

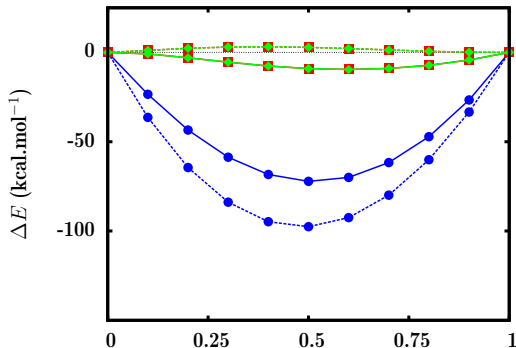
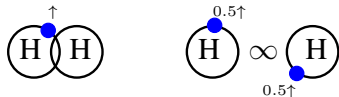
Another way to see it:

$\Gamma^{N+\delta} = (1 - \delta)\Gamma^N + \delta\Gamma^{N+1}$, $\Gamma^N = |\phi(\kappa^N)\rangle \langle \phi(\kappa^N)|$, $\hat{\kappa}^N = \sum_{ia} \kappa_{ai}^N a^\dagger i - \kappa_{ai}^N i^\dagger a$

We believe that it is possible to propose an **alternate derivation** using the usual

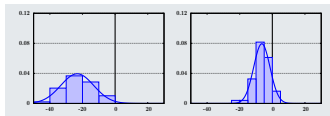
linear response derivation from $E = \sum_i n_i h_{ii} + \frac{1}{2} \sum_{ij} n_i n_j \langle ij || ij \rangle$

Fractional Occupation Numbers calculations [early results]

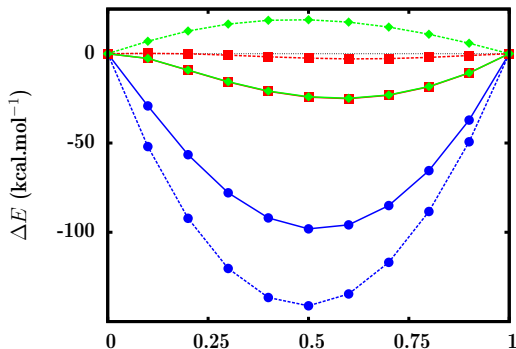


- PBE+RPA —●—
- srPBE+lrRPA —●—
- PBE+SO2 - -■- -
- srPBE+lrSO2 - -■- -
- PBE+SOSEX - -◆- -
- srPBE+lrSOSEX - -◆- -

> deviation from linear extrapolation for H
with δ electron, cc-pVDZ

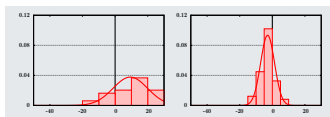


(same thing for He)

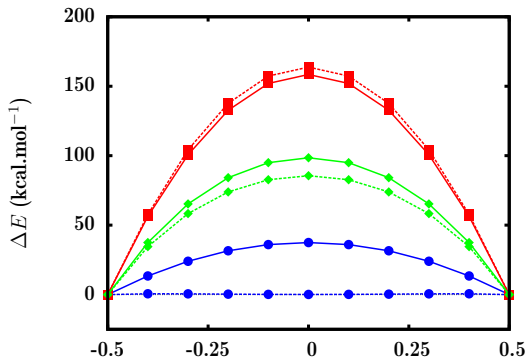
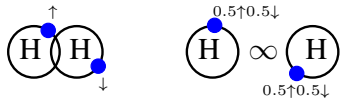


- PBE+RPA ● - - -
- srPBE+lrRPA ● —
- PBE+SO2 ■ - - -
- srPBE+lrSO2 ■ —
- PBE+SOSEX ◆ - - -
- srPBE+lrSOSEX ◆ —

> deviation from linear extrapolation for He with $1 + \delta$ electrons, cc-pVDZ

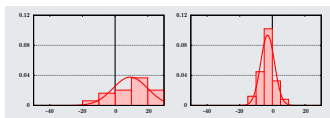


Fractional Occupation Numbers calculations [early results]



PBE+RPA --●--
srPBE+lrRPA —●—
PBE+SO2 --■--
srPBE+lrSO2 —■—
PBE+SOSEX --◇--
srPBE+lrSOSEX —◇—

>energy for H using cc-pVDZ
 with $(0.5 + \delta)$ α -electron and $(0.5 - \delta)$ β -electron



Conclusions (and future work)

- ▶ All (and more) is implemented in the **Quantum Chemistry Package MOLPRO**
Forces for (RSH+)RPA energies are available
and so are **geometry optimizations** at the (RSH+)RPA levels
[BM,Szalay,Ángyán JCTC **10** 1968 (2014)]
- ▶ Using the fractional occupations implementations
to get IP and AE with double-hybrids
- ▶ **Instabilities in the RPA problem**
- ▶ at the Université Pierre et Marie Curie
Odile Franck
Eleanora Luppi
Peter Reinhardt
Julien Toulouse
and, at the Université de Lorraine
János Ángyán
Dario Rocca