Range-Separated Random Phase Approximations

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Density Functional Theory and Approximations (DFAs)

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

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.

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

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.

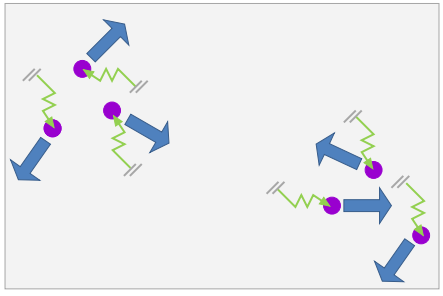
$$E = \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{Hx}}^{\mathrm{HF}}[\Phi] + E_{\mathrm{c}}^{\mathrm{RPA}}$$

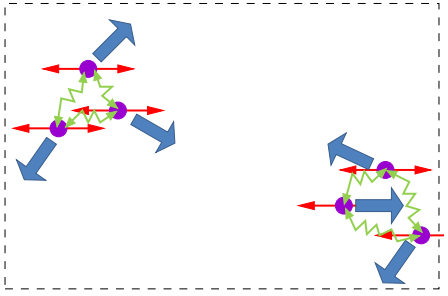
In practice, we do not use RPA in an hybrid functional context.
We do use it, as will be seen, in a range-separated context.

Random Phase Approximation

The original idea [Bohm,Pines PR **82** 625 (1951)]
is to decouple the particule 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 $\hat{H}^{\text{RPA}} = \hat{H}_{\text{part.}} + \hat{H}_{\text{oscillations}} + \hat{H}^{\text{sr}}_{\text{part./part.}}$





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

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

Consider the EOM for $Q^\dagger |0\rangle = |q\rangle$ —> $\langle 0| \left[\delta Q, \left[H, Q^\dagger\right]\right] |0\rangle = \epsilon_{q0} \langle 0| \left[\delta Q, Q^\dagger\right] |0\rangle$.
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 $Q^\dagger = \sum \left[X_a \zeta_a - Y_a \zeta_a^\dagger\right]$ 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**.

RPA from ACFDT [Langreth,Perdew PRB **15** 2884 (1977)]

[we track what is missing in the reference system]

Adiabatic connection formula for E_c

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

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

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

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

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

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

$$E_c = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \mathrm{Tr}\left(\mathbb{W}_{ee}.\left[\mathbb{\Pi}_\alpha^{RPA}(i\omega) - \mathbb{\Pi}_0(i\omega)\right]\right)$$

where $\mathbb{\Pi}_\alpha^{RPA}$ 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

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

- Analytical integration on the **frequency**

density matrix formulation $\quad E_c = \frac{1}{2}\int_0^1 d\alpha\, \mathrm{Tr}\left(\mathbb{W}_{ee}.\mathbb{P}_{c,\alpha}^{RPA}\right)$

- **Both** analytical integration

plasmon formulation $\quad E_c = \frac{1}{2}\mathrm{tr}\left(\mathbf{\Omega}^{RPA} - \mathbf{\Omega}^{TDA}\right)$

- which is **equivalent** to the

rCCD formulation $\quad E_c = \frac{1}{2}\mathrm{tr}\left(\mathbf{B}.\mathbf{T}\right)$

where $\mathbf{T}$ are solutions of the **Riccati** 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 $\quad E_c = \frac{1}{2}\int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \mathrm{tr}\left(\log\left[\mathbf{1} - \mathbf{\Pi}_0\mathbf{B}\right] + \mathbf{\Pi}_0\mathbf{B}\right)$

[Jansen,BM,Rocca,Ángyán (in prep.)]

RPA: different flavors

$E_c = \frac{1}{2}\mathrm{tr}\,(\mathbf{B}.\mathbf{T})$ where $\mathbf{B} + \mathbf{AT} + \mathbf{TA} + \mathbf{TBT} = \mathbf{0}$

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

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 $\longrightarrow$ $\mathbb{f}_{xc} = 0$ $\longrightarrow$

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

$E_c^{\text{dRPA-I}} = \frac{1}{2}\mathrm{tr}\,(\mathbf{B}^{\mathrm{I}}.\mathbf{T}^{\mathrm{dRPA}})$ where $\mathbf{B}^{\mathrm{I}} + \mathbf{A}^{\mathrm{I}}\mathbf{T} + \mathbf{T}\mathbf{A}^{\mathrm{I}} + \mathbf{T}\mathbf{B}^{\mathrm{I}}\mathbf{T} = \mathbf{0}$

- **rCCD** variant $\longrightarrow$ $\mathbb{f}_{c} = 0$ $\longrightarrow$

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

$E_c^{\text{RPAx-II}} = \frac{1}{4}\mathrm{tr}\,(\mathbf{B}^{\mathrm{II}}.\mathbf{T}^{\mathrm{RPAx}})$ where $\mathbf{B}^{\mathrm{II}} + \mathbf{A}^{\mathrm{II}}\mathbf{T} + \mathbf{T}\mathbf{A}^{\mathrm{II}} + \mathbf{T}\mathbf{B}^{\mathrm{II}}\mathbf{T} = \mathbf{0}$

- **Additionnal flavors**

$E_c^{\mathrm{SOSEX}} = \frac{1}{2}\mathrm{tr}\,(\mathbf{B}^{\mathrm{II}}.\mathbf{T}^{\mathrm{dRPA}})$

$E_c^{\mathrm{SO2}} = \frac{1}{2}\mathrm{tr}\,(\mathbf{B}^{\mathrm{I}}.\mathbf{T}^{\mathrm{RPAx}})$

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

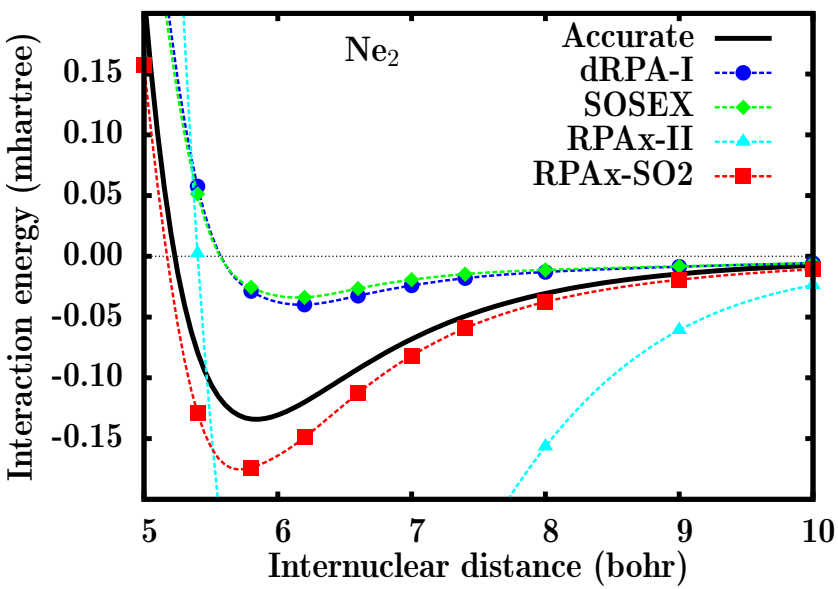
Full-range DFT + RPA

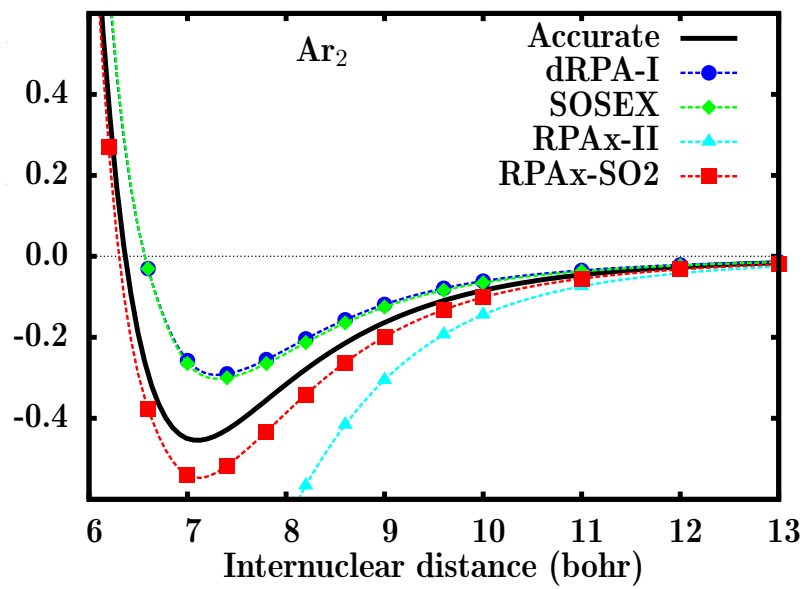
DFT calculation followed by an **RPA calculation using KS orbitals and energies**.

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

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

- 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





>PBE, aug-cc-pV6Z

[Toulouse,Zhu,Savin,Jansen,Ángyán **135** 084119 (2011)]

Range-Separated Hybrid + RPA

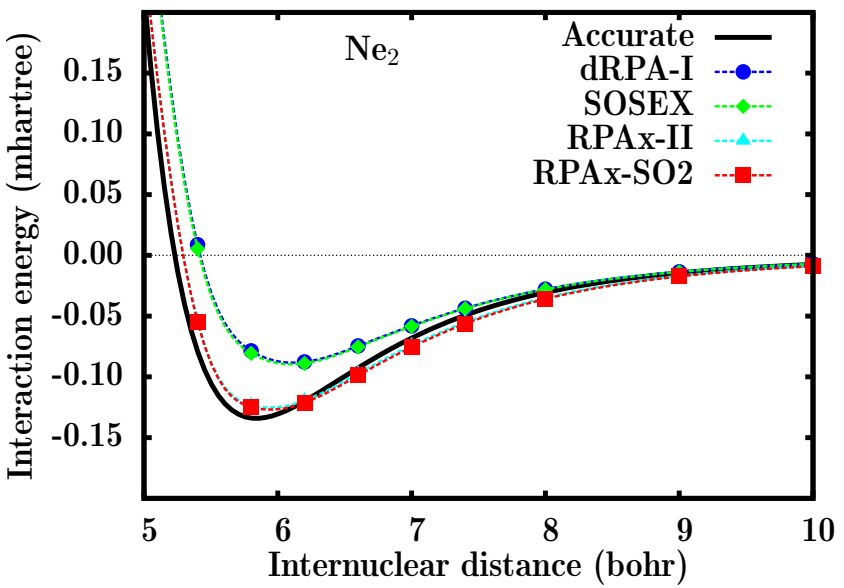
- The idea: split the e-e interaction into a **short-** and a **long-**range parts.

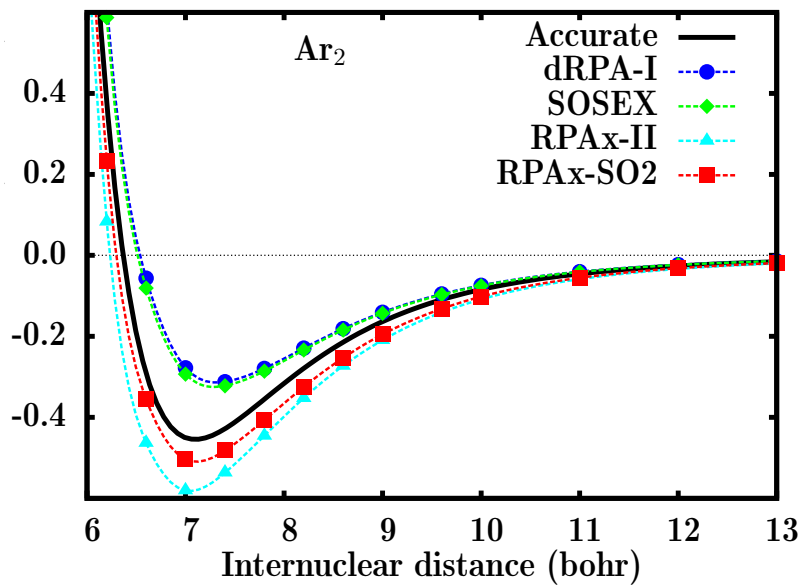
Hybrid **DFT** with exact HF exchange and RPA correlation, both at **long-range**:

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

[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)]

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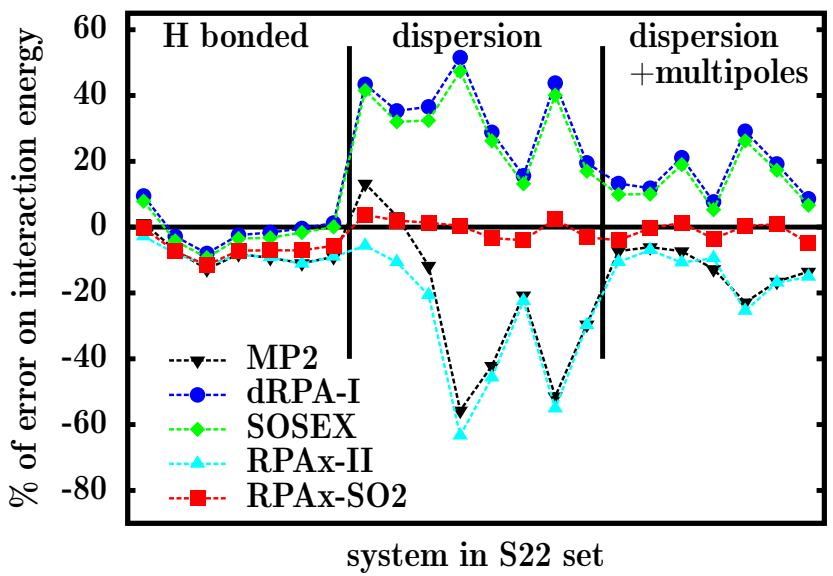
[Stoll,Savin (1985)][Savin IJQC **22** 59 (1988)][Savin, Rec.dev. 327 (1996)]

- 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**.

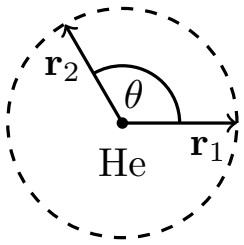


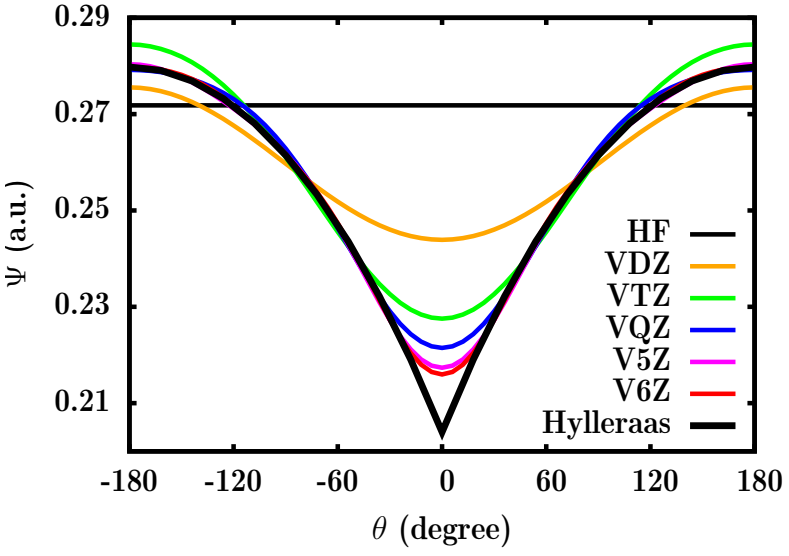
>srPBE, aug-cc-pVDZ, $\mu = 0.5$ [Toulouse,Zhu,Savin,Jansen,Ángyán **135** 084119 (2011)]

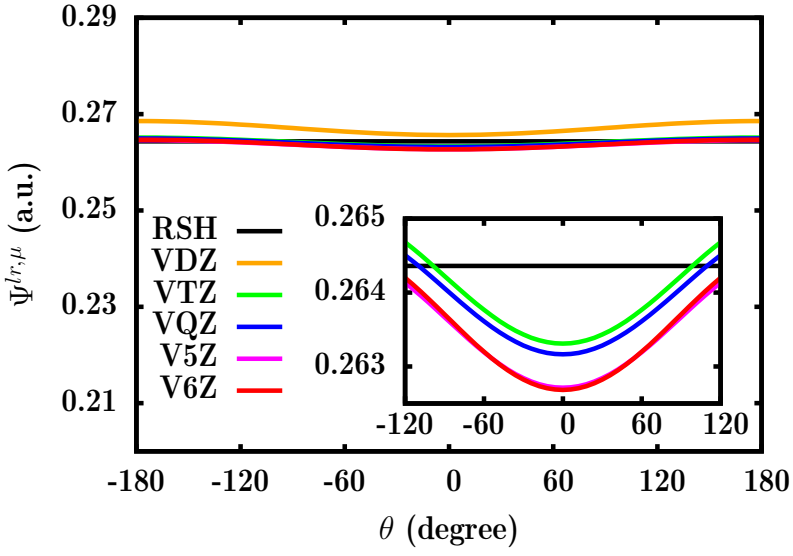
Wavefunction basis convergence

[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_2O
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

Spin-Unrestricted RPA [BM,Reinhardt,Ángyán,Toulouse JCP (2015)]

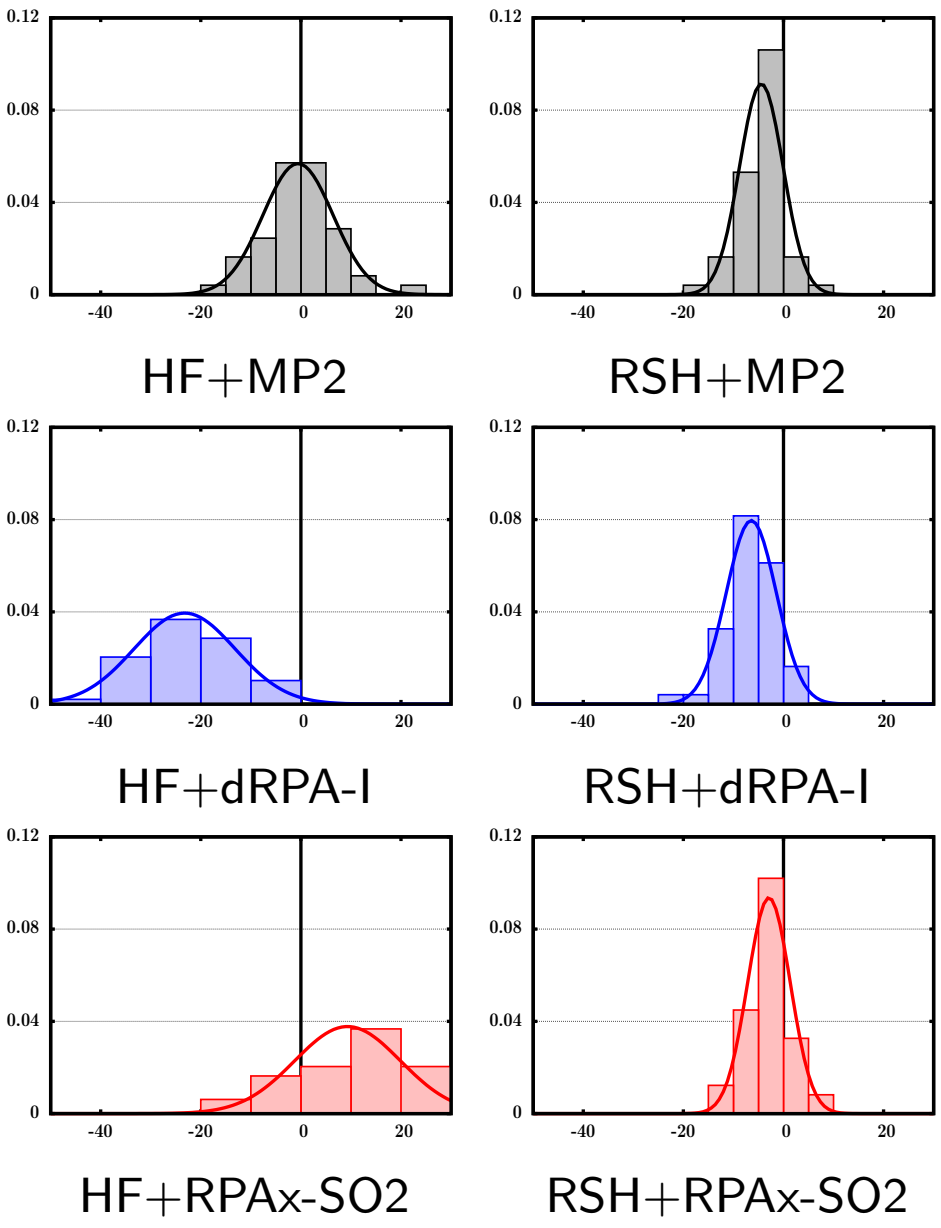
Implemented most of the variants with a nospinflip/spinflip block structure.

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.

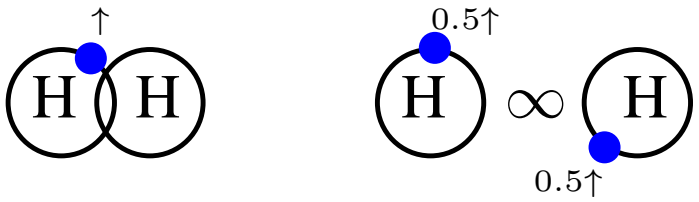
We argue that **RPAx-SO2** is a good method for a wide range of applications.



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

Fractional Occupation Numbers calculations [origins]

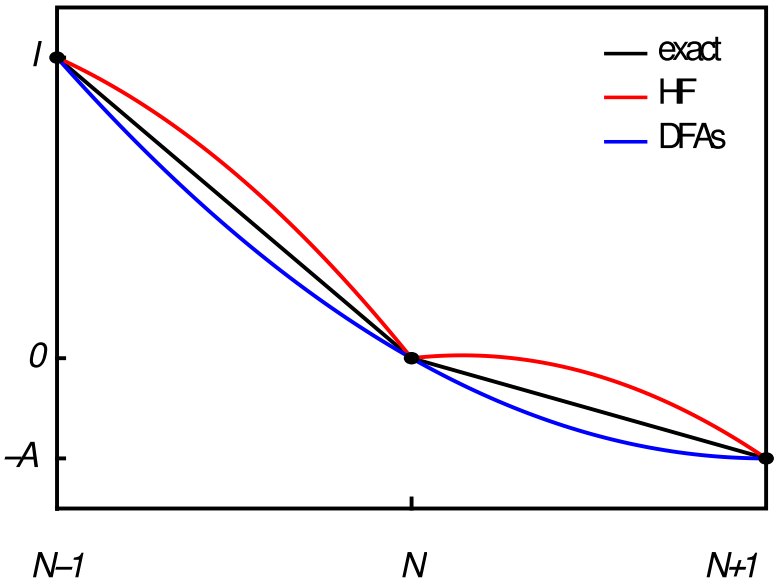
[Perdew,Parr,Levy,Balduz, PRL **49** 1982]



- Study of systems with a **non-integer charge**.
- $E^{N+\delta} = \min_{\hat{\Gamma}\to N+\delta} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T}+\hat{V}_{\mathrm{ext}}+\hat{V}_{\mathrm{ee}}\right)\right]$

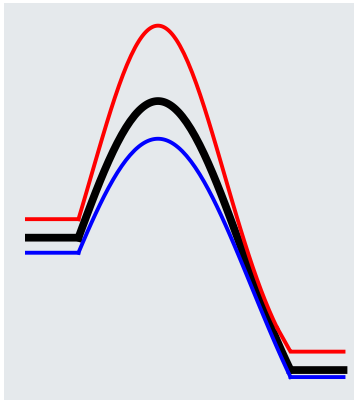
$$\hat{\Gamma}^{N+\delta} = (1-\delta)\hat{\Gamma}^{N} + (\delta)\hat{\Gamma}^{N+1}$$
$$E^{N+\delta} = (1-\delta)E^{N} + (\delta)E^{N+1}$$
$$n^{N+\delta} = (1-\delta)n^{N} + (\delta)n^{N+1}$$

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



- $E^{N+\delta} = \min_{\hat{\Gamma}\to N+\delta} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T}+\hat{V}_{\mathrm{ext}}\right)+E_{Hxc}[n_{\hat{\Gamma}}]\right]$

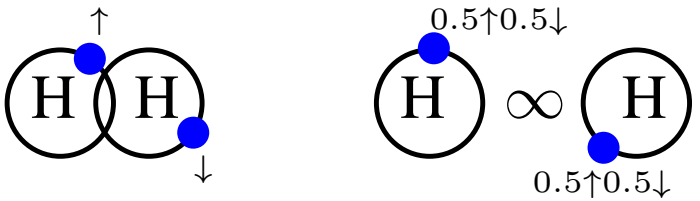
$$\hat{\Gamma}^{N+\delta} = (1-\delta)\hat{\Gamma}^{N,\delta} + (\delta)\hat{\Gamma}^{N+1,\delta}$$
$$n^{N+\delta}(\mathbf{r}) = \sum n_i \, |\phi_i^{N+\delta}(\mathbf{r})|^2$$



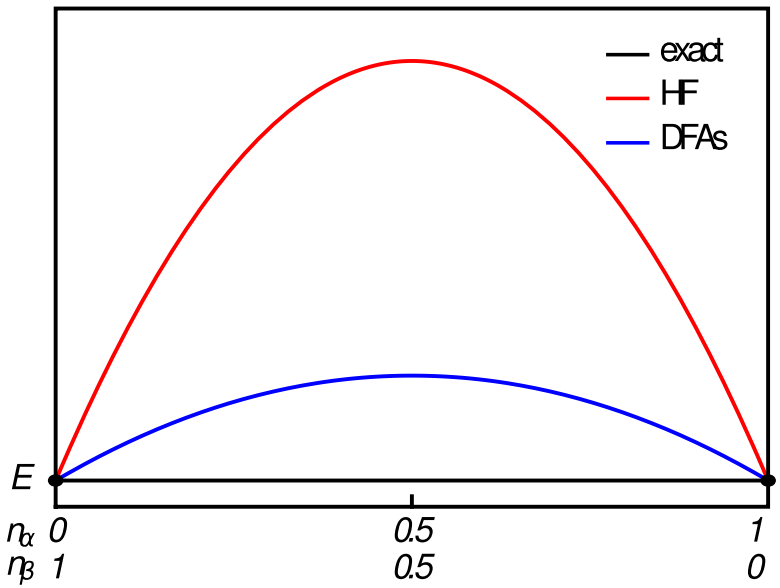
[Mori-Sánchez,Cohen,Yang JCP **125** 2006]

Fractional Occupation Numbers calculations [origins]

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

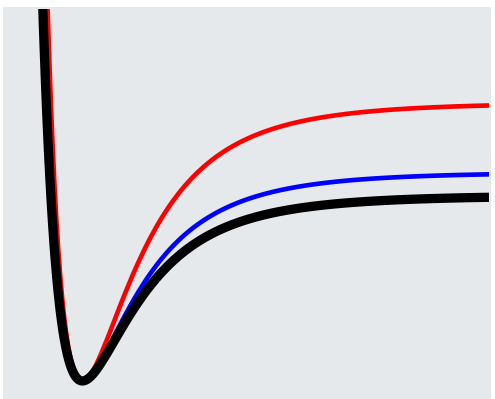


- Systems with fractional occupation of degenerate spin states should have the **same energy as the integer-spin states**.



- **Constancy condition**:

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



[Cohen,Mori-Sánchez,Yang JCP **129** 2008]

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 $ia = (\text{f+p}) \times (\text{p+u})$

The derivation is done by Green's function formalism.
It is comprehensive and useful, but somewhat involved.

$G_0^{N+\delta} = (1-\delta) G_0^N + \delta G_0^{N+1}$

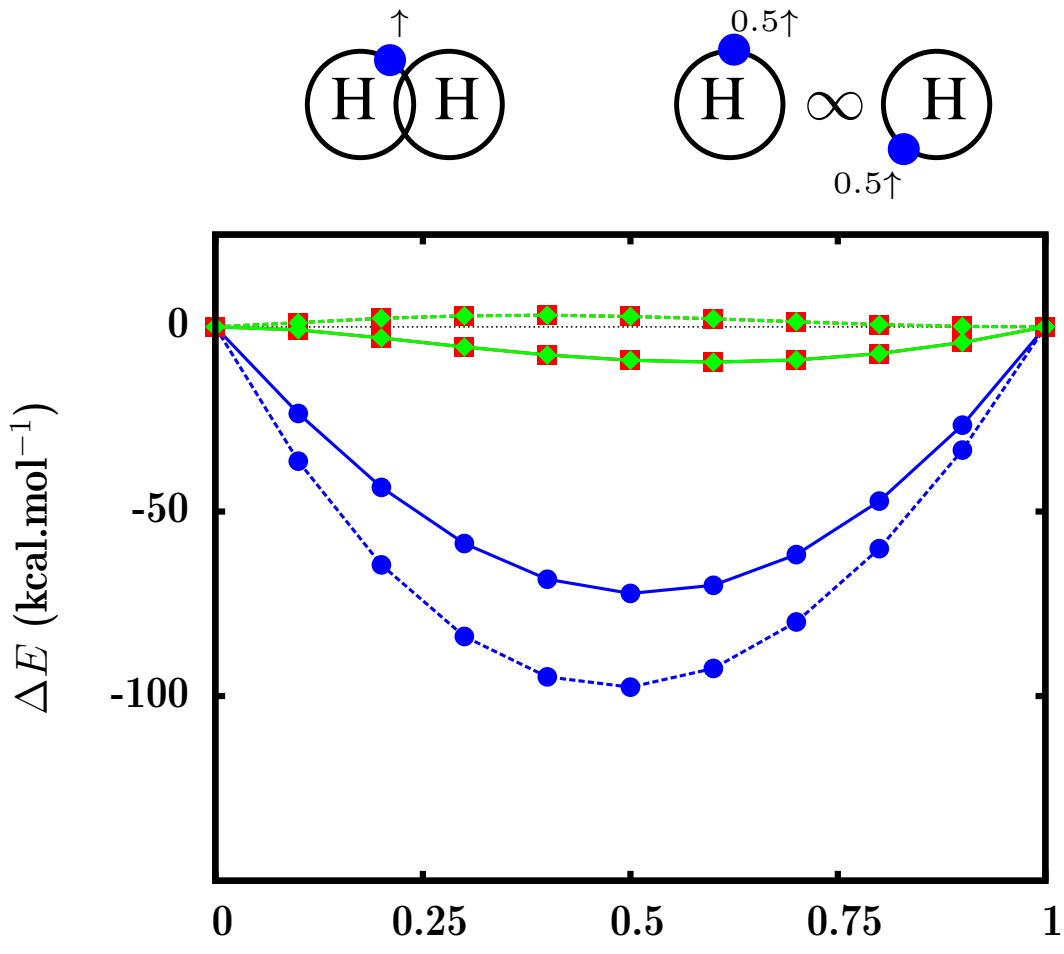
These changes appears from terms like $\theta(p - \text{FERMI})$ in the Green's functions.

Another way to see it:

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

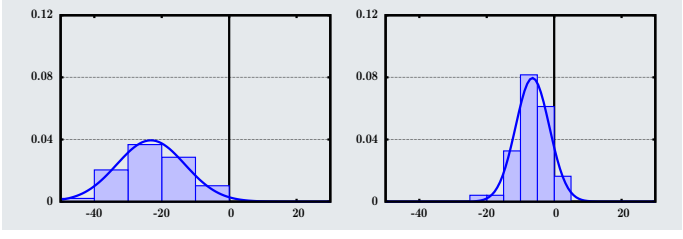
We believe that it is possible to propose an **alternate derivation** using the usual linear response derivation from $E = \sum_i n_i h_{ii} + \frac{1}{2}\sum_{ij} n_i n_j \langle ij||ij\rangle$

Fractional Occupation Numbers calculations [early results]



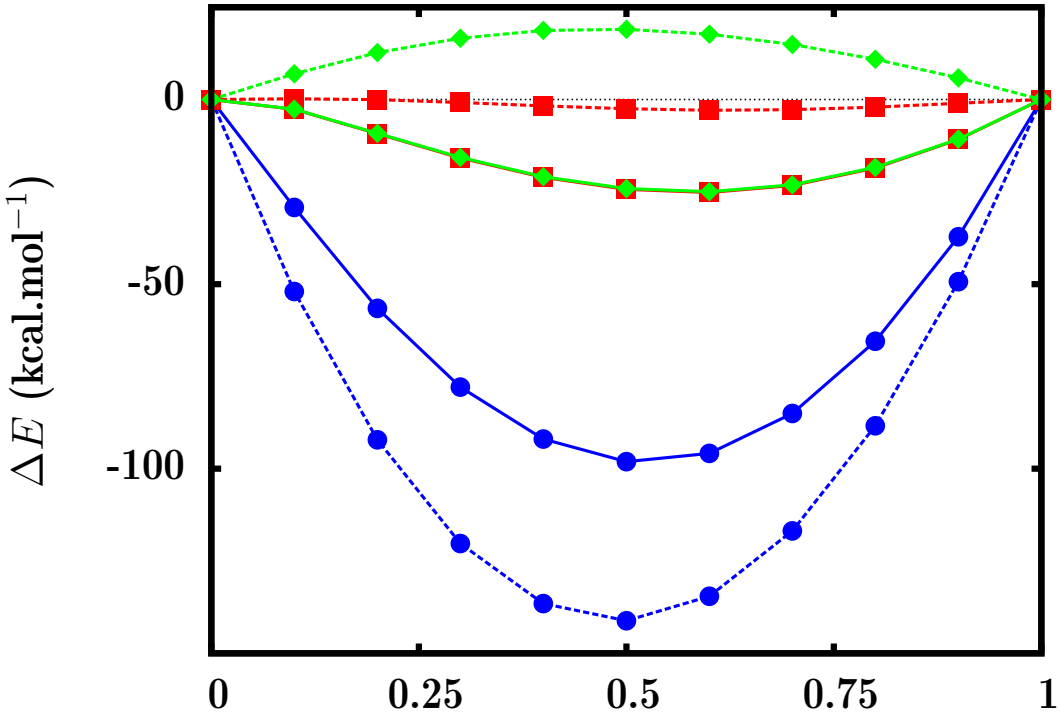
PBE+RPA
srPBE+lrRPA
PBE+SO2
srPBE+lrSO2
PBE+SOSEX
srPBE+lrSOSEX

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



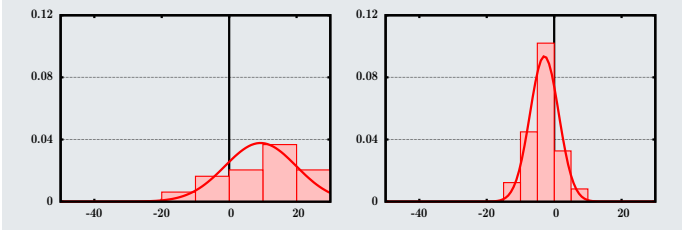
Fractional Occupation Numbers calculations [early results]

(same thing for He)

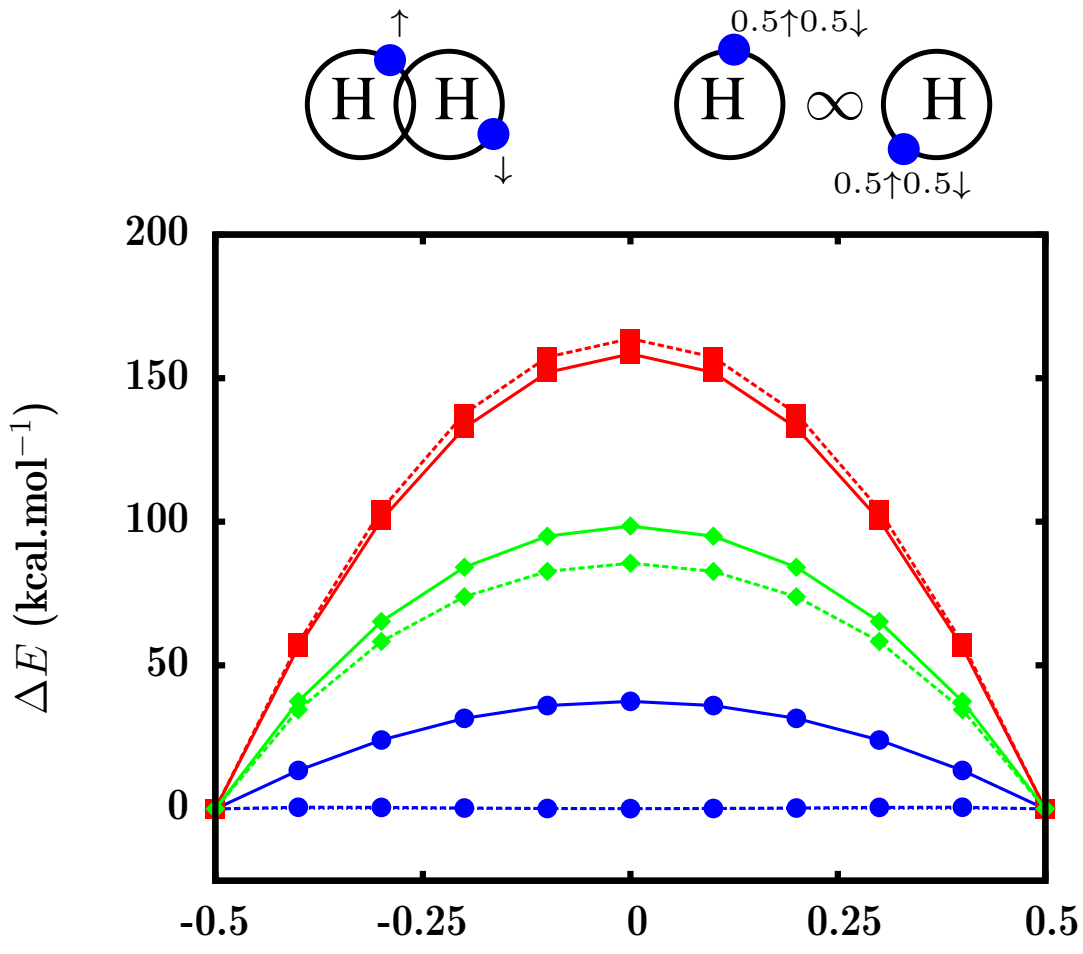


PBE+RPA
srPBE+lrRPA
PBE+SO2
srPBE+lrSO2
PBE+SOSEX
srPBE+lrSOSEX

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

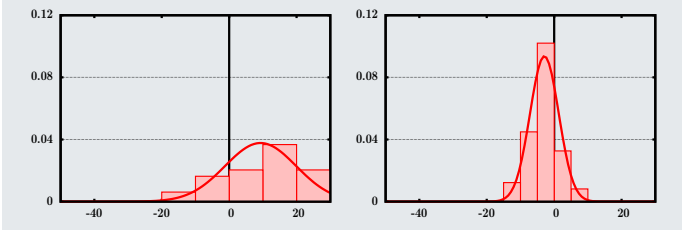


Fractional Occupation Numbers calculations [early results]



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

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