Random Phase Approximation with Fractional Charge and Fractional Spin.

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Context and Motivation

We want to give ourselves a way to diagnos **systematic failures** of methods.

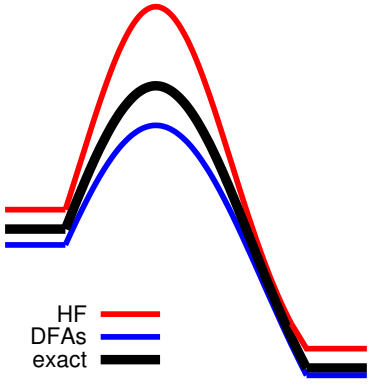
- Fractional charge
- Fractional spin

Fractional Charge and Fractional Spin : Motivation

We want a clear formulation to diagnos the **failures of methods** (HF and $E_{xc}[n]$)

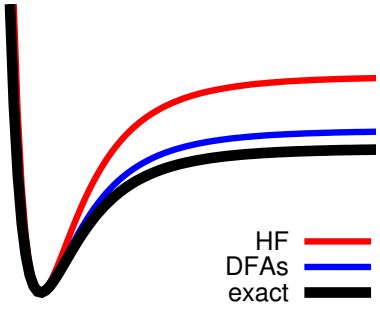
(De)localization Error (Self-Interaction Error ; interaction of the electron with itself)

Total energies
Charge-Transfert complexes
Barrier heights energies
Polarizabilities
...



Static Correlation Error (Strongly correlated systems ; (Near-)degeneracy)

Dissociation of molecules
...



Those are only **qualitative explanation**.

Fractional Charge and Fractional Spin : Occurences

These systems exist **as the dissociation limit** of real physical systems.

H_2^+ at dissociation :

Ensemble of the two pure states :

$\frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2)$, E

The **blue subsystem** is an hydrogen atom H[$1/2\uparrow$] with **half an electron** and **a density in ensemble form**.

H_2 at dissociation :

Ensemble of the two pure states :

$\frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2)$, E

The **blue subsystem** is an hydrogen atom H[$1/2\uparrow, 1/2\downarrow$] with integer charge but **half an electron up and half an electron down** and **a density in ensemble form**.

Exact conditions

What are the **exact properties** ruling the behavior of the exact energy ?

- Fractional charge
- Fractional spin
- Fractional occupation of orbitals

Fractional Charge

[Perdew,Parr,Levy,Balduz 1982] [Yang,Zhang,Ayers 2000]

The exact energy E is **piecewise linear** with respect to $\mathbf{N}$ and has a **derivative discontinuity** when passing at integer $\mathbf{N}$.

- Consider a system with a fractional number of electrons $\mathbf{N} = \mathbf{M} + \delta$. It's energy is :

$$E^{\mathbf{N}} = \min_{\hat{\Gamma} \to \mathbf{N}} \mathrm{Tr}\left[\hat{\Gamma}\hat{H}\right] \quad ; \quad \mathrm{Tr}\left[\hat{\Gamma}\hat{N}\right] = \mathbf{N}$$

- The minimizing $\hat{\Gamma}^{\mathbf{N}}$ is linear wrt $\mathbf{N}$ between two adjacent integer $\mathbf{M}$ and $\mathbf{M+1}$:

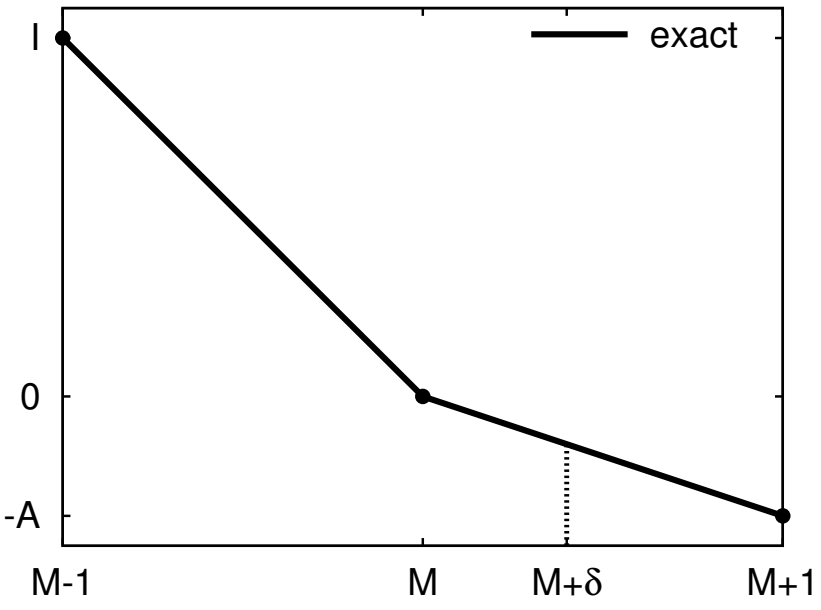
$$\hat{\Gamma}^{\mathbf{N}} = (1-\delta)\hat{\Gamma}^{\mathbf{M}} + (\delta)\hat{\Gamma}^{\mathbf{M+1}}$$

- The energy is linear wrt to δ :

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

- and so is the density :

$$\rho^{\mathbf{N}}(\mathbf{r}) = (1-\delta)\rho^{\mathbf{M}}(\mathbf{r}) + (\delta)\rho^{\mathbf{M+1}}(\mathbf{r})$$



Fractional Spin

[Yang,Zhang,Ayers 2000]

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

- Consider a system with fractional number of spin-up $\mathbf{N}^{\uparrow}$ and spin-down $\mathbf{N}^{\downarrow}$ electrons.
  This system has an integer total number of electrons $\mathbf{M} = \mathbf{N}^{\uparrow} + \mathbf{N}^{\downarrow} = \mathbf{M}^{\uparrow} + \mathbf{M}^{\downarrow} + \mathbf{1}$.

  It's corresponding $\hat{\Gamma}^{\mathbf{N}^{\uparrow}\mathbf{N}^{\downarrow}}$ is :

$$\hat{\Gamma}^{\mathbf{N}^{\uparrow}\mathbf{N}^{\downarrow}} = (1-\delta)\hat{\Gamma}^{\mathbf{M}^{\uparrow}+\mathbf{1},\mathbf{M}^{\downarrow}} + (\delta)\hat{\Gamma}^{\mathbf{M}^{\uparrow},\mathbf{M}^{\downarrow}+\mathbf{1}}$$

- This actually yields a constant energy :

$$E^{\mathbf{N}^{\uparrow}\mathbf{N}^{\downarrow}} = (1-\delta)E^{\mathbf{M}} + (\delta)E^{\mathbf{M}} = E^{\mathbf{M}}$$

- This is called the **constancy condition**.

Behavior of methods

How is the study of the behavior of **HF** and **DFAs** for fractional charges and fractional spins linked to the **Delocalization** and **Strong Correlation Errors**?

Implementation for Self-Consistent Field methods

In practice, the minimizing $\hat{\Gamma}^{N}$ **is not linear wrt** δ : $\hat{\Gamma}_s^{N} = (1-\delta)\hat{\Gamma}_s^{M,\delta} + (\delta)\hat{\Gamma}_s^{M+1,\delta}$

where the density matrices $\hat{\Gamma}^{M,\delta}$ and $\hat{\Gamma}^{M+1,\delta}$ are that of monodeterminantal wavefunctions $\Phi^{M,\delta}$ and $\Phi^{M+1,\delta}$ made **from a common set of orbitals** $\left\{\phi_p^N\right\}$.

The density matrix : $\rho(1,2) = \sum_i^{occ} \phi_i(1)\phi_i^*(2)$

is changed into : $\rho^{N}(1,2) = \sum_p^{all} n_p\, \phi_p^{N*}(1)\phi_p^{N}(2)$ $\quad n_p = \begin{cases} 1 & p \in \text{occ} \\ n_p & p \in \text{HOMOs} \\ 0 & p \in \text{unocc} \end{cases}$

Consider the **scaled** orbitals, that emerge at dissociation :

$$\Psi = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$$\rho(1,2) = \frac{1}{2}(\phi_1(1)\phi_1(2) + \phi_2(1)\phi_2(2))$$

$$= \left(\tfrac{1}{\sqrt{2}}\phi_1(1)\right)\left(\tfrac{1}{\sqrt{2}}\phi_1(2)\right) + \left(\tfrac{1}{\sqrt{2}}\phi_2(1)\right)\left(\tfrac{1}{\sqrt{2}}\phi_2(2)\right)$$

The density matrix then simply reads : $\rho^{N}(1,2) = \sum^{occ} \tilde{\phi}_i^{N*}(1)\tilde{\phi}_i^{N}(2)$ $\quad \tilde{\phi}_i^{N} = \sqrt{n_i}\phi_i^{N}$

Fractional Charge : Example of H_2^+

In the fractional charge calculations, we will be looking at **the deviation from the piecewise linearity**.

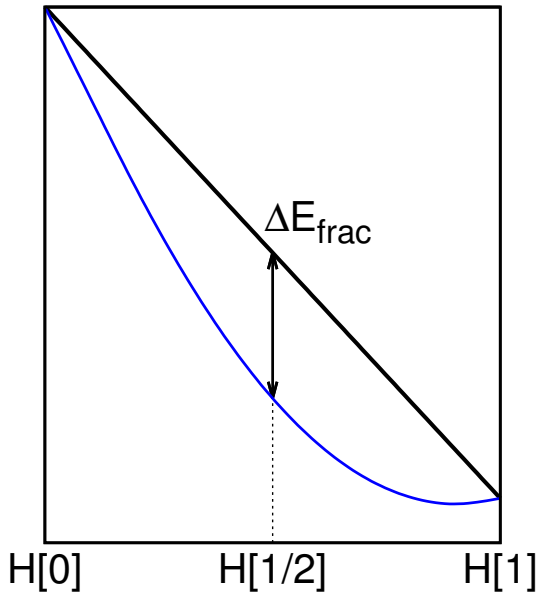
In other words, we want to plug

$$\rho^{N}(\mathbf{r}) = (1-\delta)\rho^{M}(\mathbf{r}) + (\delta)\rho^{M+1}(\mathbf{r})$$

in the approximate functional and compare $E[\rho^N]$ to

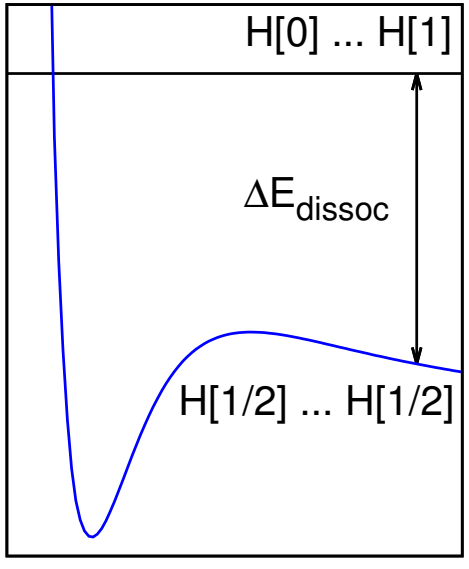
$$E^{N} = (1-\delta)E^{M} + (\delta)E^{M+1}$$

Both are simultaneously true for the exact density functional.

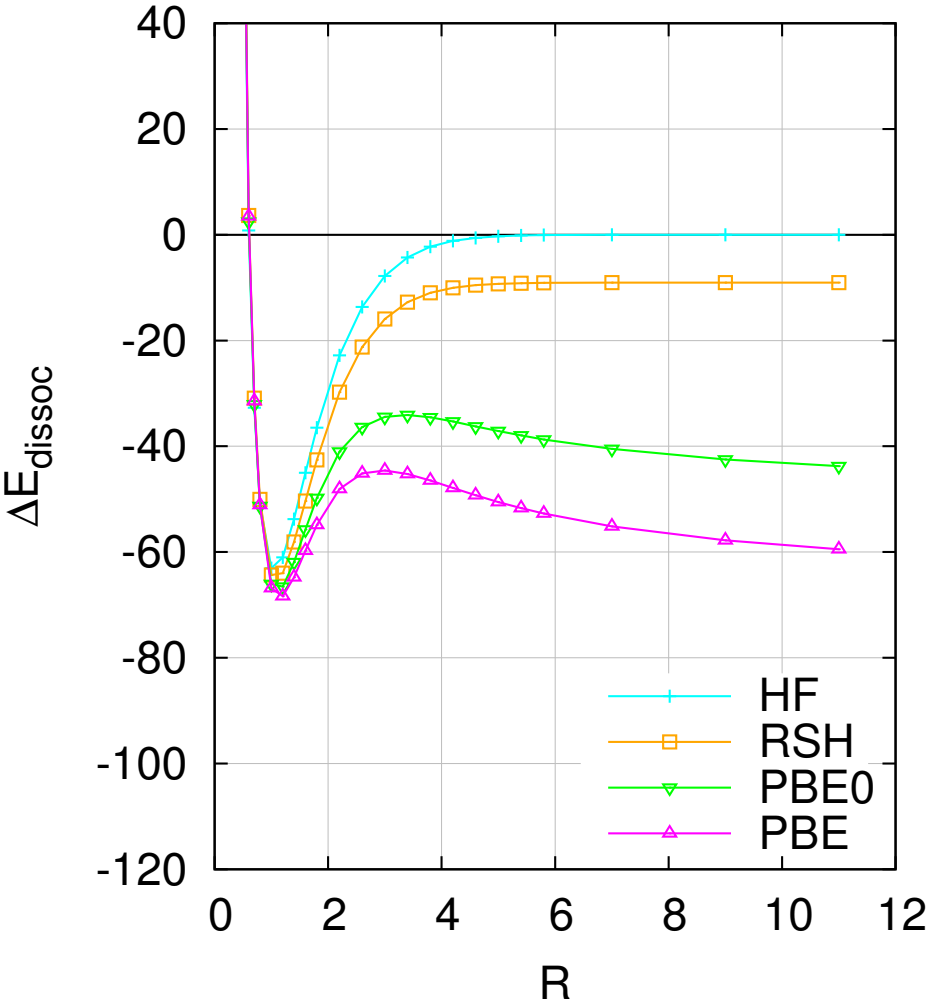


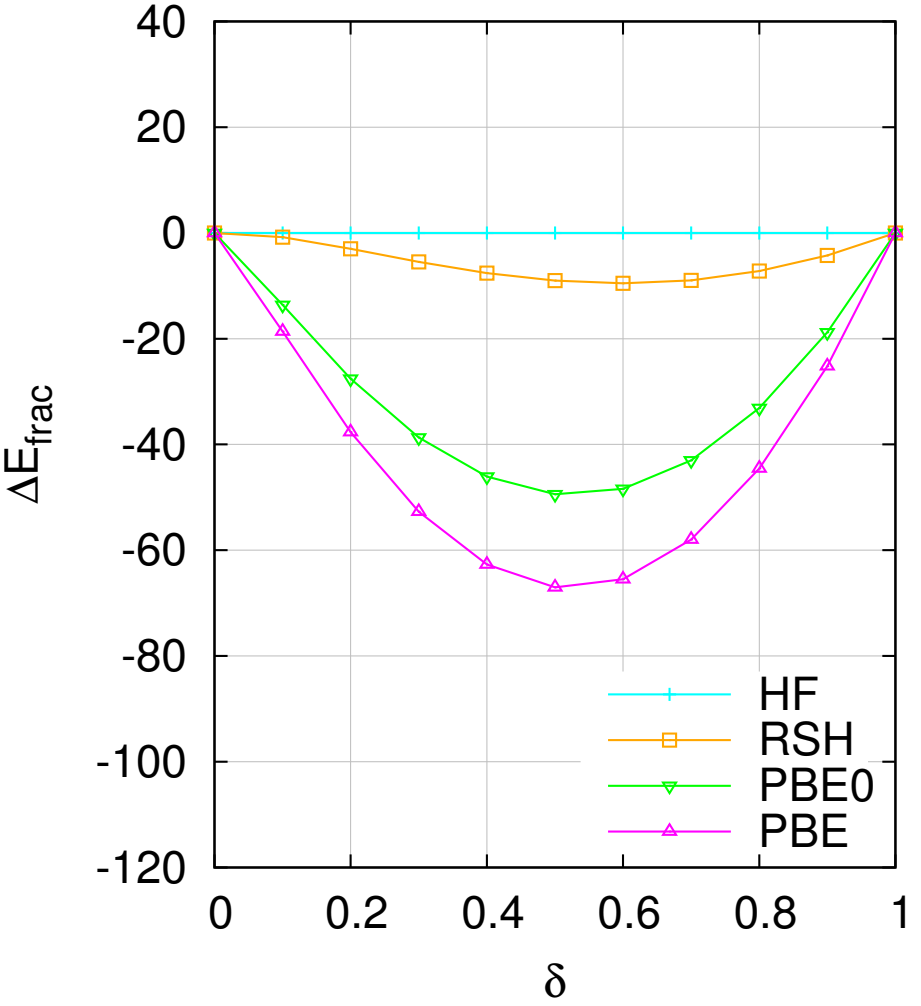
At dissociation, the methods describe the delocalized situation (H[1/2]...H[1/2]) which **should be equal to** (H[0] + H[1]) because of the piecewise linearity of the energy.

Hence, shifting dissociation curves by the method-dependant value of (H[0] + H[1]) allows one to **read the error made by the method wrt the piecewise linearity**.



Fractional Charge : Example of H_2^+





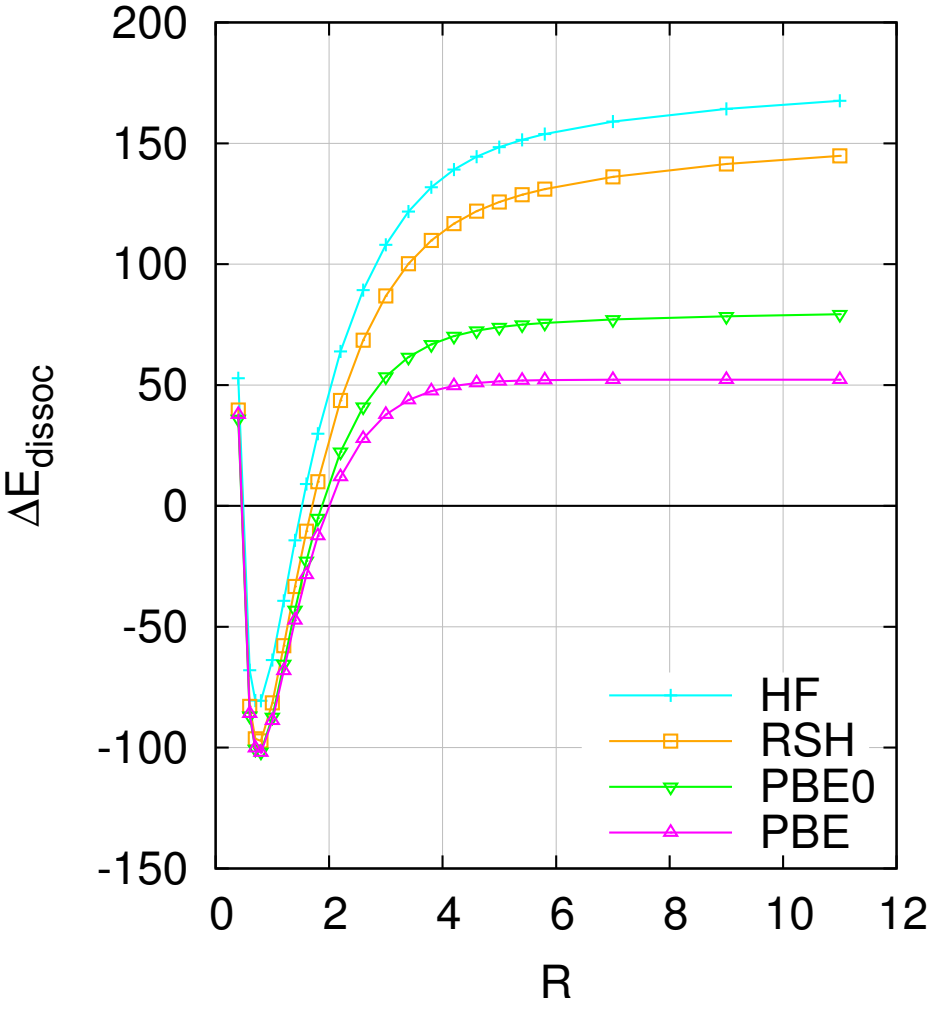
$$\Delta E_{\text{dissoc}} = E(H_2^+) - \left[E(H^+) + E(H)\right]$$

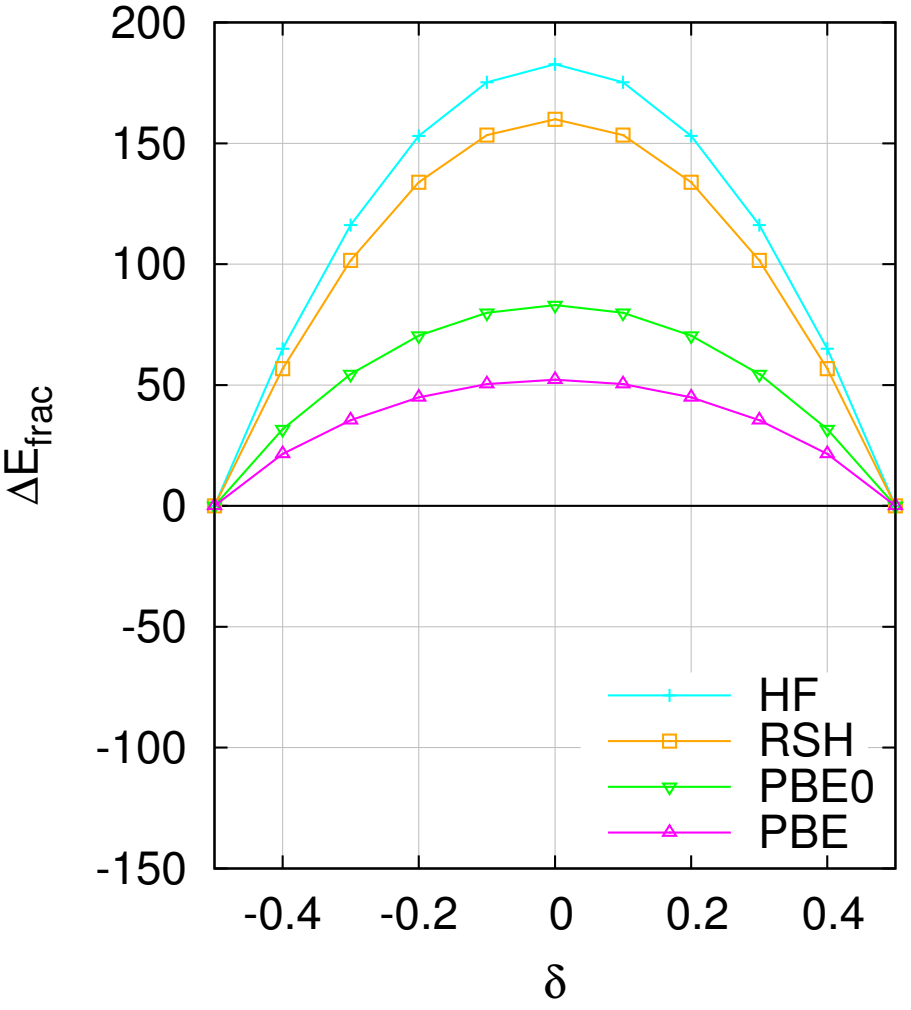
$$\Delta E_{\text{frac}} = 2E(H^{1+\delta}) - 2\left[(1-\delta)E(H^+) + \delta E(H)\right]$$

Exchange is good for Delocalization Error

(sr)Exchange is better than standard hybrids.

Fractional Spin : Example of H_2





$$\Delta E_{\text{dissoc}} = E(H_2) - 2\,[E(H)]$$

$$\Delta E_{\text{frac}} = 2E(H[\delta, 1-\delta]) - 2\,[E(H)]$$

Exchange is bad for Strong Correlation Error
(sr)Exchange isn't better.

Extension to RPA

We will give key points, but not go into to much details : the derivation is **an extension of the Fluctuation Dissipation Theorem to ensemble Green's Function**.

On the basic variable for RPA

Random Phase Approximation seen as $\mathbf{E}_c[G]$, a functional of the Green's function.

The basic variable to ensemble is the **one-electron Green's function of the non-interacting reference system**.

$$G^{0,\mathbf{M}}(1,2) = \sum_i^{\text{occ}} \frac{\phi_i(1)\phi_i^*(2)}{E - \epsilon_i - i\eta} + \sum_a^{\text{vir}} \frac{\phi_a(1)\phi_a^*(2)}{E - \epsilon_a + i\eta}$$

The ensemble is done on systems described by the same non-interacting reference hamiltonian. **The ensemble Green's Function reads :**

$$G^{0,\mathbf{N}}(1,2) = (1-\delta)G^{0,\mathbf{M}}(1,2) + (\delta)G^{0,\mathbf{M+1}}(1,2)$$

A fairly straigthforward derivation yields :

$$G^{0,\mathbf{N}}(1,2) = \sum_p^{\text{all}} \frac{\mathbf{n}_p\,\phi_p(1)\phi_p^*(2)}{E - \epsilon_p - i\eta} + \sum_p^{\text{all}} \frac{(1-\mathbf{n}_p)\phi_p(1)\phi_p^*(2)}{E - \epsilon_p + i\eta}$$

$$= \sum_i^{\text{part.+occ.}} \frac{\mathbf{n}_i\,\phi_i(1)\phi_i^*(2)}{E - \epsilon_i - i\eta} + \sum_a^{\text{part.+unocc.}} \frac{(1-\mathbf{n}_a)\phi_a(1)\phi_a^*(2)}{E - \epsilon_a + i\eta}$$

With scaled orbitals

Remember : $$G^{0,\mathbf{N}}(1,2) = \sum_{i}^{\text{part.+occ.}} \frac{\mathbf{n}_i\, \phi_i(1)\phi_i^*(2)}{E - \epsilon_i - i\eta} + \sum_{a}^{\text{part.+unocc.}} \frac{(1-\mathbf{n}_a)\phi_a(1)\phi_a^*(2)}{E - \epsilon_a + i\eta}$$

Rewritten with scaled orbitals, it yields :

$$G^{0,\mathbf{N}}(1,2) = \sum_{i} \frac{\tilde{\phi}_i(1)\tilde{\phi}_i^*(2)}{E - \epsilon_i - i\eta} + \sum_{a} \frac{\tilde{\phi}_a(1)\tilde{\phi}_a^*(2)}{E - \epsilon_a + i\eta}$$

where :

- the orbitals are **scaled**
  $$\tilde{\phi}_i = \sqrt{\mathbf{n}_i}\phi_i$$
  $$\tilde{\phi}_a = \sqrt{1-\mathbf{n}_a}\phi_a$$
- "a" runs through "**partial+unoccupied**" orbitals
- "i" runs through "**full+partial**" orbitals

Vocabulary

From :

N_o **occupied**
N_v **virtual** orbitals,

to :

N_f **fully occupied**,
$\mathbf{N}_p$ **partially occupied**, $\mathrm{N}_f + \mathbf{N}_p = \mathrm{N}_o$
N_u **unoccupied orbitals**. $\mathrm{N}_u = \mathrm{N}_v$

RPA equations

The RPA equations derived as **linear response equations** are :

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \mathbf{\Omega}$$

The extension to fractional occupations is easy if one simply considers :

- the scaled orbitals
- "a" runs through "partial+unoccupied" orbitals
- "i" runs through "full+partial" orbitals

In details, the matrix elements read :

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \sqrt{n_i n_j (1-n_a)(1-n_b)}\langle ib|aj\rangle$$

$$B_{ia,jb} = \sqrt{n_i n_j (1-n_a)(1-n_b)}\langle ij|ab\rangle$$

Two variants of the RPA energies

$$E_c^{\text{dRPA-I}} = \frac{1}{2}\sum_{ia,jb} \langle ij|ab\rangle \, T_{ia,jb} \qquad E_c^{\text{SOSEX}} = \frac{1}{2}\sum_{ia,jb} \langle ij||ab\rangle \, T_{ia,jb} \qquad (\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1})$$

Dimensions of the RPA problem

One has to be aware that the dimensions go from : $N_o.N_v$ to : $\underbrace{(N_f + N_p)}_{N_o}.(N_p + \underbrace{N_u}_{N_v})$

Two different ways to extend RPA to fractional occupations

What I presented

An extension of the **usual linear response equations**, fulled by a ensemble Green's function describing frational occupation. The fundamental equations **are the same** but are "evaluated" at a different Green's function.

$$\frac{\partial^2 \mathbf{E}}{\partial v \partial v}[\mathbf{G}_{\text{frac}}]$$

This is the extension that makes sense in the context of the comparison with dissociation ; this is the extension that allows diagnostics on Delocalization and Static Correlation Errors.

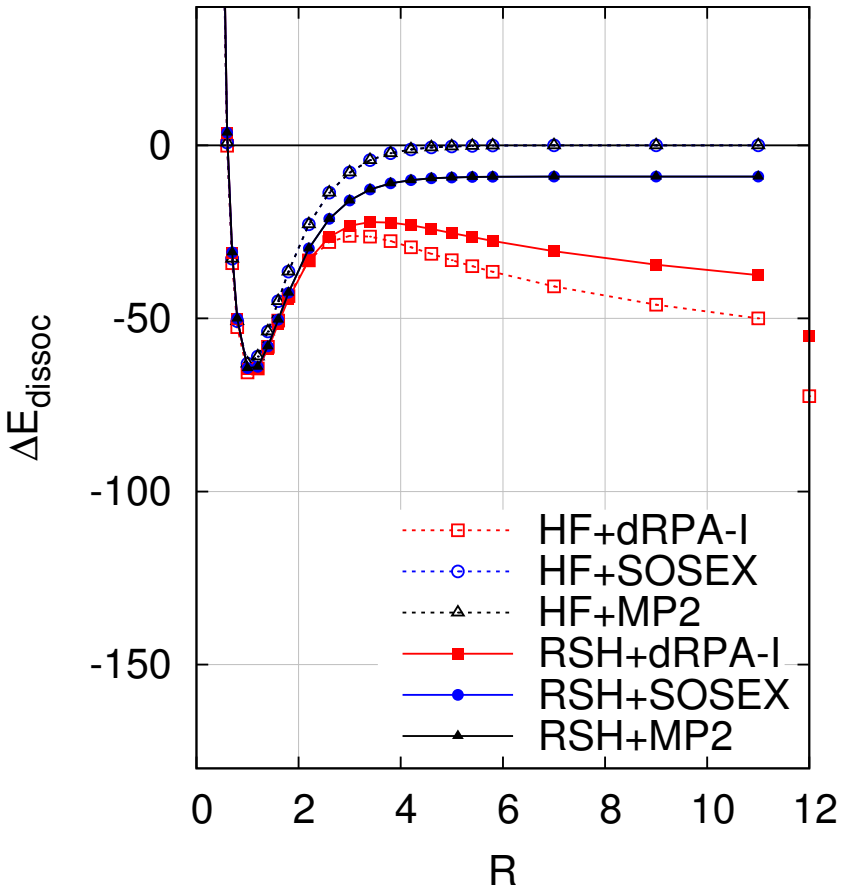
What could also be done

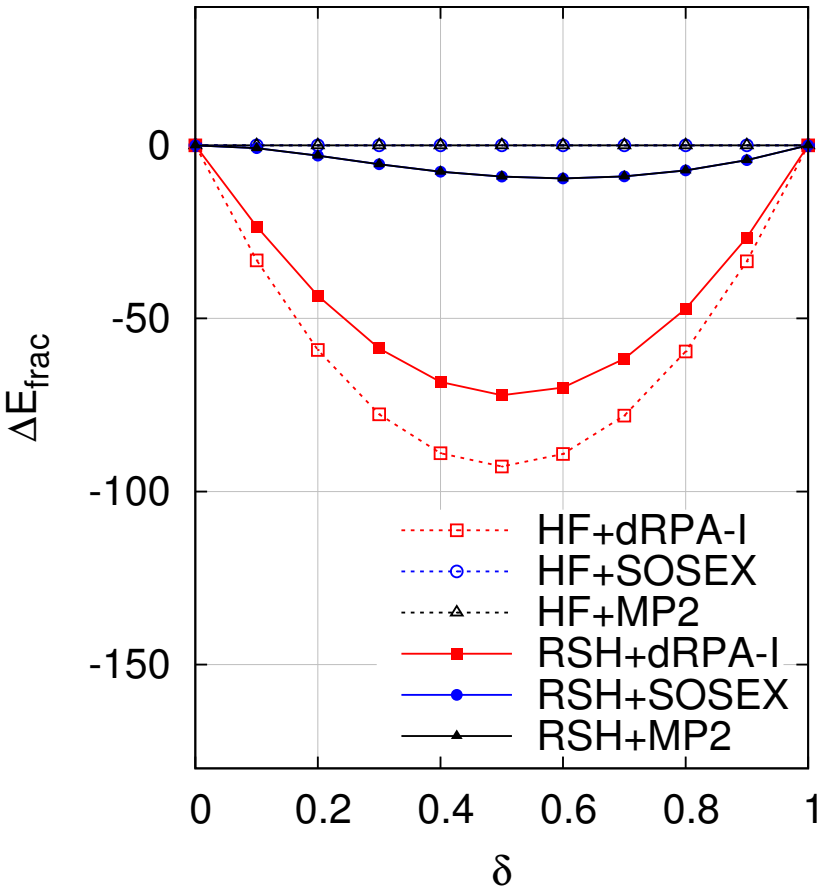
A different extension would consist in deriving the **linear response of a fractionally occupied system**. The underlying equations **are different**.

$$\frac{\partial^2 \mathbf{E}_{\text{frac}}}{\partial v \partial v}[\mathbf{G}_{\text{frac}}]$$

This is the extension that would be used to describe system that have inherent degenerescences (heavy atoms, ...).

Fractional Charge : Example of H_2^+





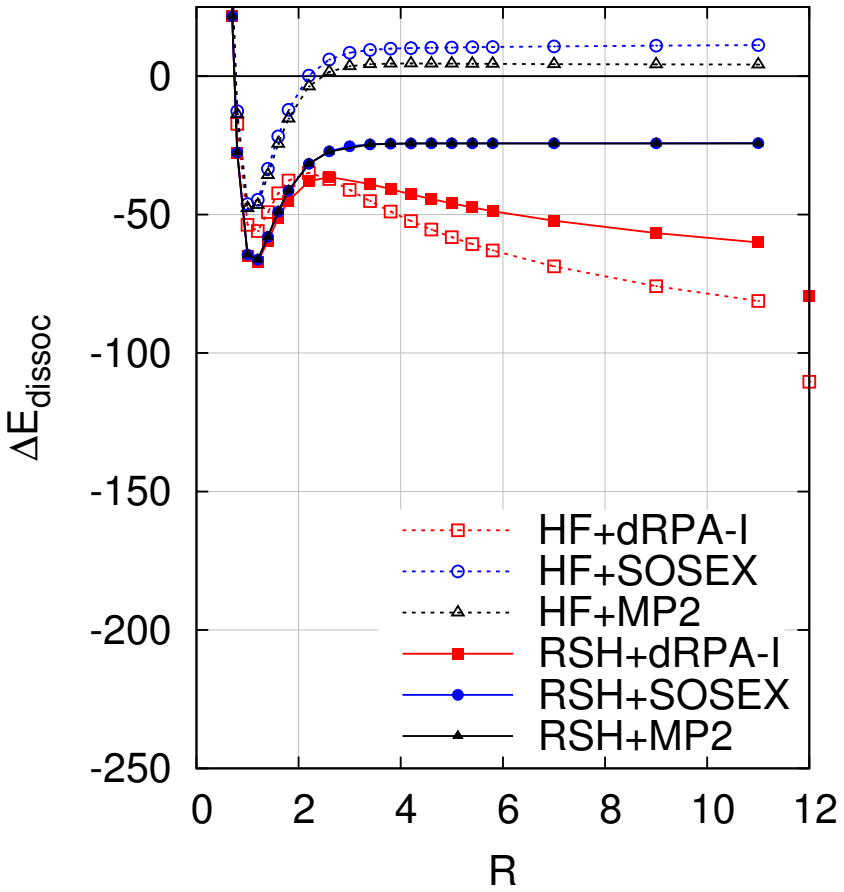
dRPA-I does not include exchange at all, and performs poorly.

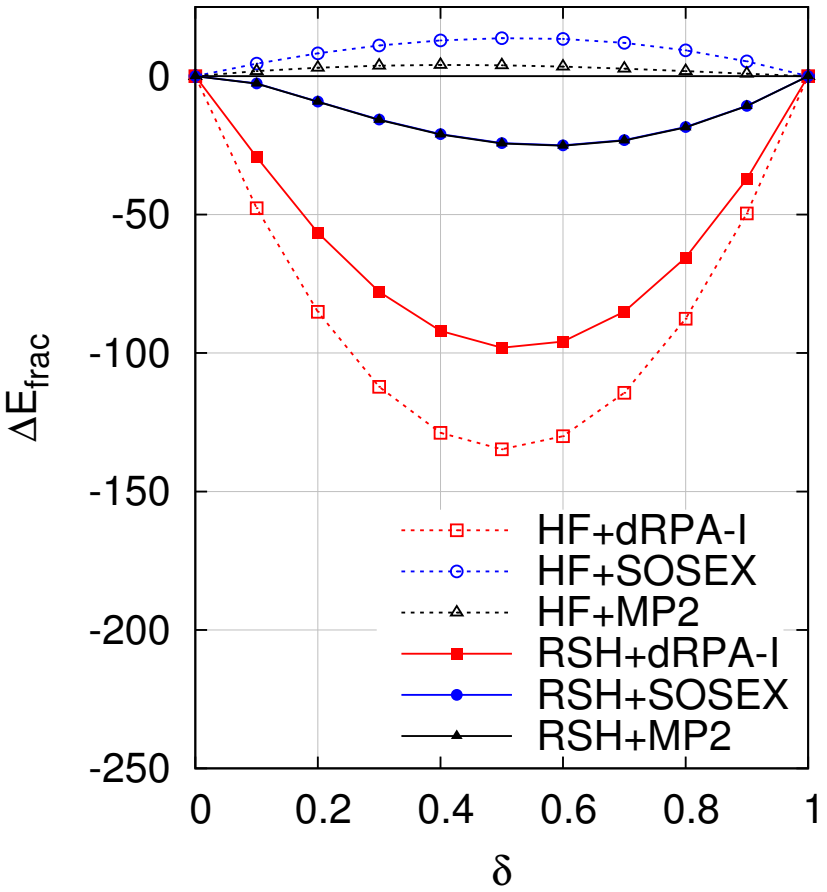
HF+MP2 performs well.

HF+SOSEX is less efficient (exchange diagrams included up to 2nd Order).

RSH+MP2 and RSH+SOSEX both suffer
from the convex error of the (sr)functional.

Fractional Charge : Example of He_2^+





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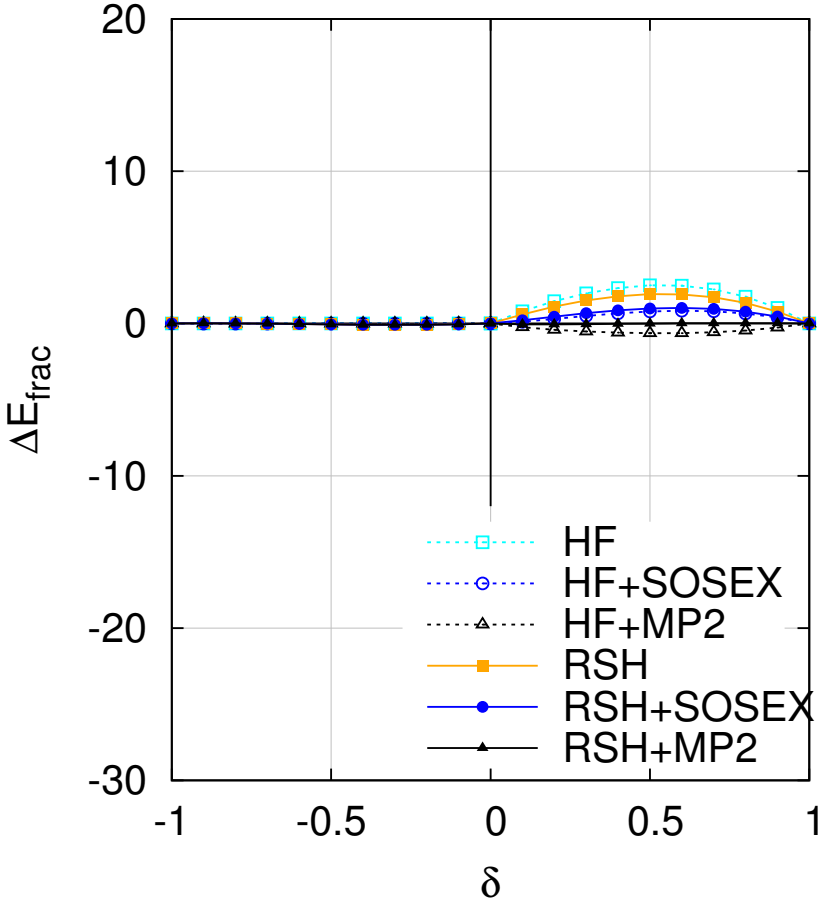
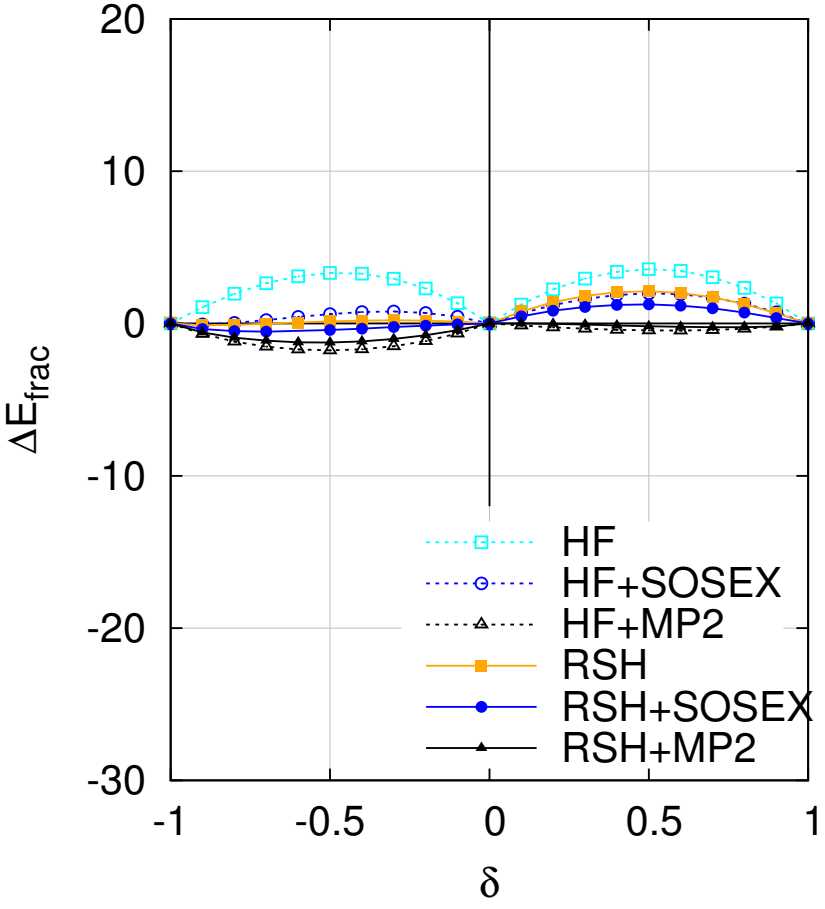
Fractional Charge : More examples (Li and Be)



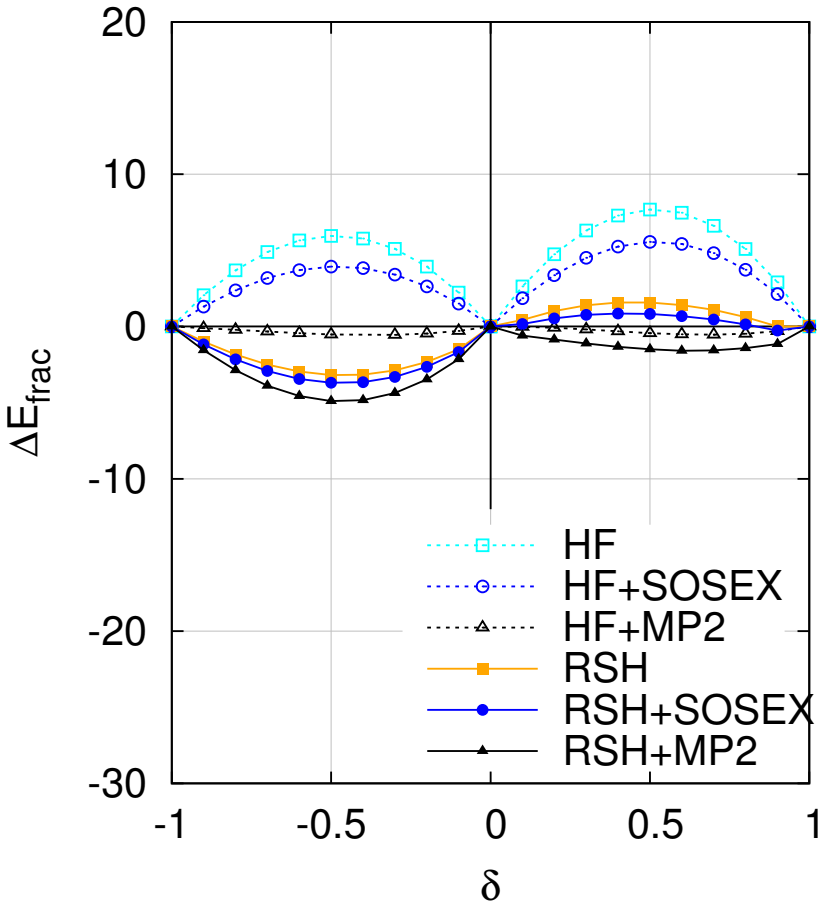


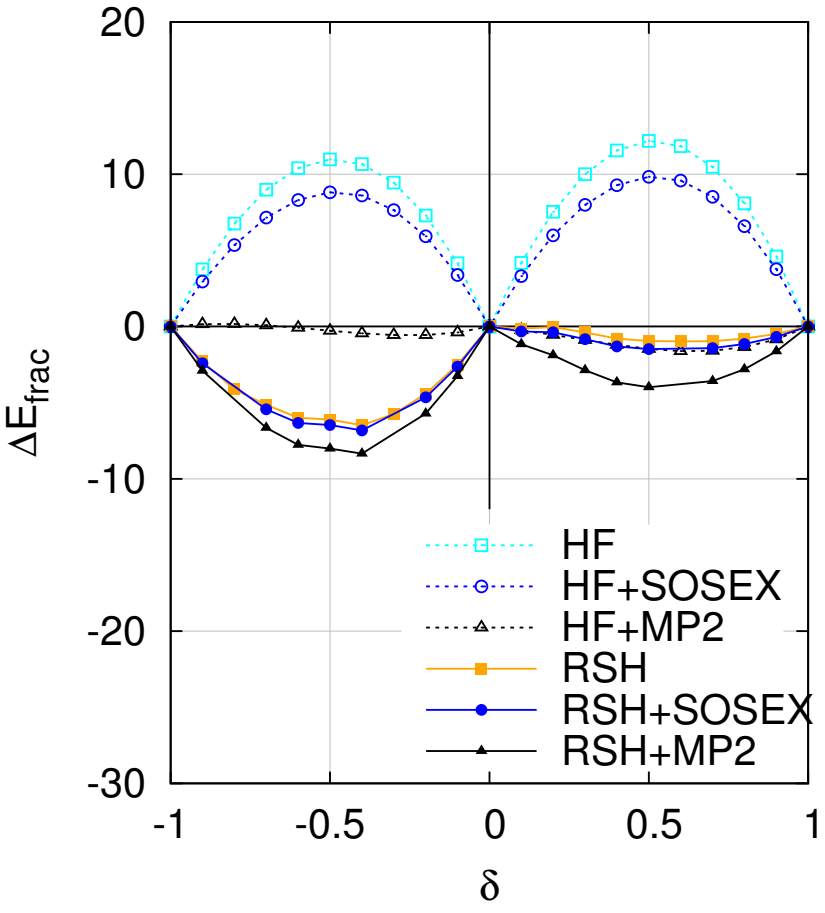
HF has a (large) concave error.
RSH has mixed behavior (concave/convex).
This is due to the relative magnitude of (sr)error.

dRPA-I is too bad (not shown) ; **MP2** is good, and worsen by RSH.

SOSEX has much better results when used with RSH.

Fractional Charge : More examples (B and C)





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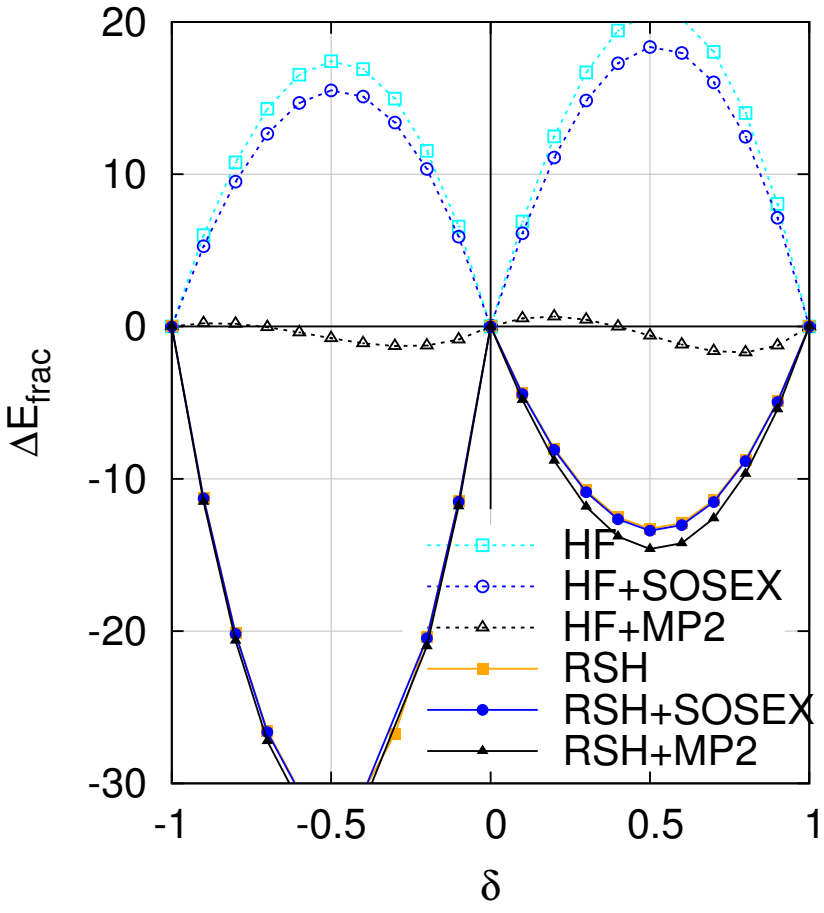
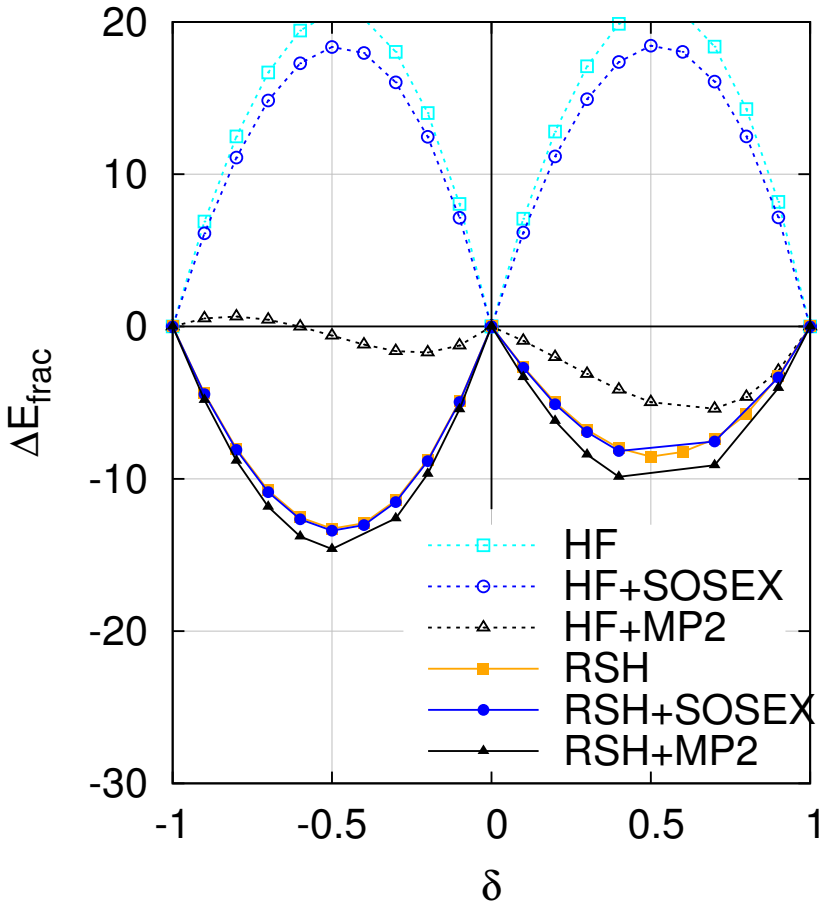
Fractional Charge : More examples (N and O)





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Conclusion

Fractional charge (and fractional spin) did give us a way to **diagnos systematic failures** of method.

Inclusion of **exchange** is important for the treatment of the Delocalization Error.

Use of range-separation introduces (sr) convex error that can be damaging.

The methods presented here cannot be free from **both the Delocalization Error and the Static Correlation Error**.

- Other inclusion of exchange (other variants of RPA) seem promising for the treatment of the Delocalization Error.
- In this context, very interesting questions on the **stability of the RPA equations** arise.