

Fractional-charge and Fractional-spin errors in Range-Separated Density-Functional Theory with Random Phase Approximation.

Bastien Mussard, Julien Toulouse

Laboratoire de Chimie Théorique
Institut du Calcul et de la Simulation
Sorbonne Universités, Université Pierre et Marie Curie

bastien.mussard@upmc.fr
www.lct.jussieu.fr/pagesperso/mussard/

Motivation

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

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

- Self-Interaction Error (interaction of the electron with itself, (de)localization)

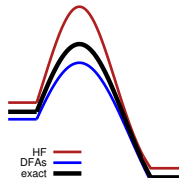
Total energies

Charge-Transfer complexes

Barrier heights energies

Polarizabilities

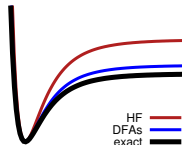
...



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

Dissociation of molecules

...



Those are only **qualitative explanation**.

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

- H₂⁺ at dissociation (two protons, one electron up) :

Ensemble of the two pure states :



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

- H₂ at dissociation (two protons, one electron up, one electron down) :

Ensemble of the two pure states :



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

Properties that rule the **behavior of the exact energy** (piecewise linearity and constancy condition).

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

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

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

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

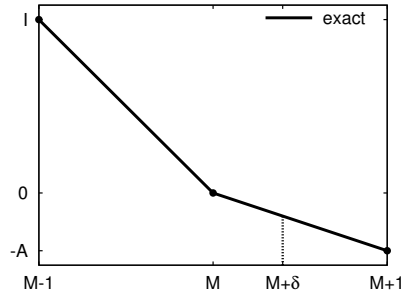
$$\hat{r}^N = (1 - \delta)\hat{r}^M + (\delta)\hat{r}^{M+1}$$

- The energy is linear wrt to δ :

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

- and so is the density :

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



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

- Consider a system with fractional numbers of spin-up $N^\uparrow = M^\uparrow + 1 - \delta$ and spin-down $N^\downarrow = M^\downarrow + \delta$ electrons.

This system has an integer total number of electrons $M = N^\uparrow + N^\downarrow = M^\uparrow + M^\downarrow + 1$.

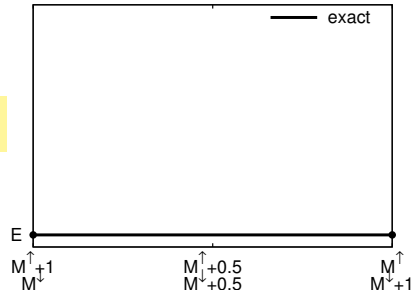
- It's corresponding $\hat{I}^{N^\uparrow N^\downarrow}$ is :

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

- This actually yields a constant energy :

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

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



Behavior of methods

The behavior of approximate theories with respect to **fractional charges** and **fractional spins** is linked to the Self-Interaction and Strong Correlation errors.

- In practical calculations, the **explicit e-e interaction is replaced by** $E_{\text{Hxc}}[n]$:

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

- The minimizing $\hat{\Gamma}^{\mathbf{N}}$ is **not linear wrt** δ : $\hat{\Gamma}_s^{\mathbf{N}} = (1 - \delta)\hat{\Gamma}_s^{\mathbf{M},\delta} + (\delta)\hat{\Gamma}_s^{\mathbf{M}+1,\delta}$
 where the density matrices $\hat{\Gamma}^{\mathbf{M},\delta}$ and $\hat{\Gamma}^{\mathbf{M}+1,\delta}$ are that of monodeterminantal wavefunctions $\Phi^{\mathbf{M},\delta}$ and $\Phi^{\mathbf{M}+1,\delta}$ made **from a common set of orbitals** $\{\phi_p^{\mathbf{N}}\}$.

- The density is $n^{\mathbf{N}}(\mathbf{r}_1, \mathbf{r}_2) = \sum_p^{\text{all}} n_p \phi_p^{\mathbf{N}*}(\mathbf{r}_1) \phi_p^{\mathbf{N}}(\mathbf{r}_2)$ $n_p = \begin{cases} 1 & p \in \text{valence} \\ n_p & p \in \text{HOMOs} \\ 0 & p \in \text{conduction} \end{cases}$

- Considering the **scaled orbitals** $\tilde{\phi}_i^{\mathbf{N}} = \sqrt{n_i} \phi_i^{\mathbf{N}}$ that emerge at dissociation :

$$\begin{array}{c} \text{1/2} \uparrow \qquad \qquad \qquad \text{1/2} \uparrow \\ \text{---} \qquad \qquad \qquad \text{---} \\ \psi = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2) \end{array} \quad \begin{aligned} n(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{2} (\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2)) \\ &= \left(\frac{1}{\sqrt{2}} \phi_1(\mathbf{r}_1) \right) \left(\frac{1}{\sqrt{2}} \phi_1(\mathbf{r}_2) \right) + \left(\frac{1}{\sqrt{2}} \phi_2(\mathbf{r}_1) \right) \left(\frac{1}{\sqrt{2}} \phi_2(\mathbf{r}_2) \right) \end{aligned}$$

The density then simply reads : $n^{\mathbf{N}}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i^{\text{val}} \tilde{\phi}_i^{\mathbf{N}*}(\mathbf{r}_1) \tilde{\phi}_i^{\mathbf{N}}(\mathbf{r}_2)$

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

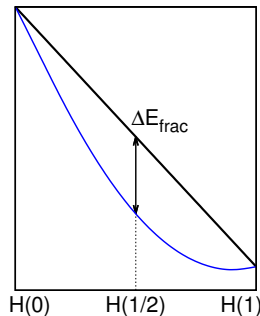
In other words, we want to plug

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

in the approximate functional and compare $E[n^{\mathbf{N}}]$ to

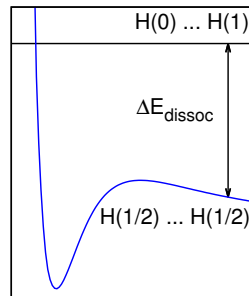
$$E^{\mathbf{N}} = (1 - \delta)E^{\mathbf{M}} + (\delta)E^{\mathbf{M}+1}$$

Both are true together for the exact density functional.



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

Hence, shifting dissociation curves by the method-dependant value of ($H(0) \dots H(1)$) allows to **read the error made by the method wrt the piecewise linearity**.



$$E^X = \langle \Phi^X | \hat{T} + \hat{V}_{ne} | \Phi^X \rangle + E_H[\Phi^X] + E_{xc}^X[\Phi^X]$$

Hartree-Fock (HF)

$$E_{xc}^{HF} = E_x^{HF}[\Phi^{HF}]$$

Density Functional Approximations (DFA : PBE, PBE0 ($\frac{1}{4}$ HF exch. $\frac{3}{4}$ PBE exch.))

$$E_{xc}^{DFA} = E_x^{DFA}[n_{\Phi^{DFA}}] + E_c^{DFA}[n_{\Phi^{DFA}}]$$

Range-Separated Hybrid (RSH)

$$E_{xc}^{RSH} = E_x^{sr,DFA}[n_{\Phi^{RSH}}] + E_c^{sr,DFA}[n_{\Phi^{RSH}}] + E_x^{lr,HF}[\Phi^{RSH}]$$

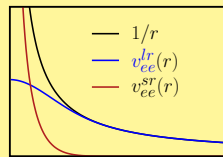
Random Phase Approximation (RPA)

$$E_{xc}^{HF+RPA} = E_x^{HF}[\Phi^{HF}] + E_c^{RPA}$$

$$E_{xc}^{DFA+RPA} = E_x^{HF}[\Phi^{DFA}] + E_c^{RPA}$$

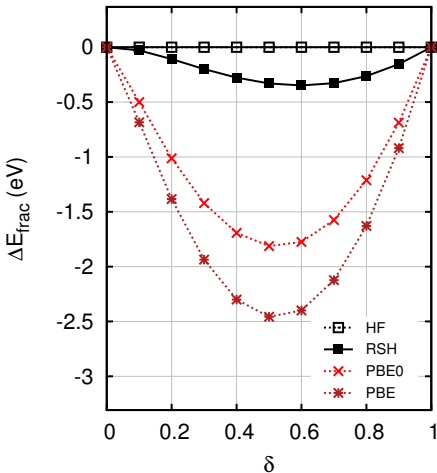
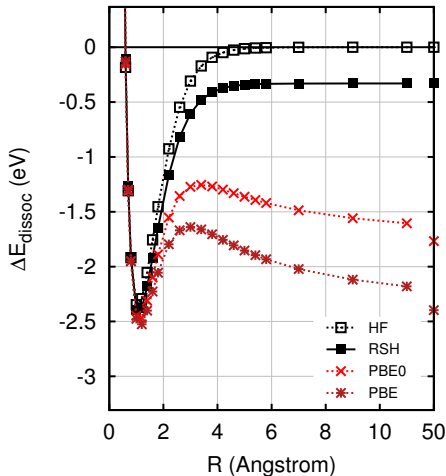
$$E_{xc}^{RSH+RPA} = E_x^{sr,DFA}[n_{\Phi^{RSH}}] + E_c^{sr,DFA}[n_{\Phi^{RSH}}] + E_x^{lr,HF}[\Phi^{RSH}] + E_c^{lr,RPA}$$

$$\frac{1}{r} = v_{ee}^{lr}(\mathbf{r}) + v_{ee}^{sr}(\mathbf{r})$$



> cc-pVTZ, RSH :srPBE, $\mu = 0.5$

$$\Delta E_{\text{dissoc}} = E(H_2^+) - [E(H^+) + E(H)] \quad \text{and} \quad \Delta E_{\text{frac}} = 2E(H^{+1-\delta}) - 2[(1-\delta)E(H^+) + \delta E(H)]$$



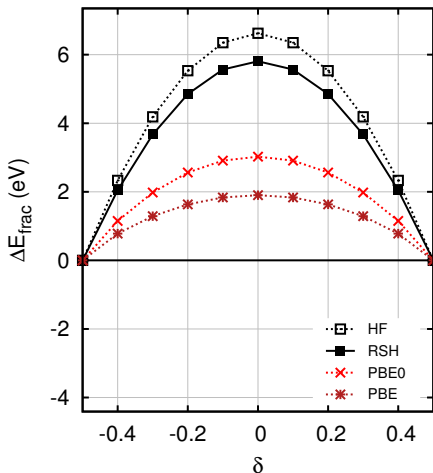
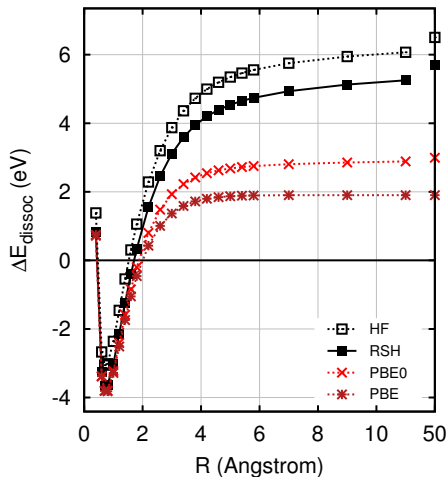
HF exchange is good for the treatment of the Self-Interaction Error
(sr)exchange is better than standard hybrids.

Remember :

$> \text{cc-pVTZ, RSH :srPBE, } \mu = 0.5$

$$\Delta E_{\text{dissoc}} = E(H_2) - 2E(H) \quad \text{and}$$

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



HF exchange is bad for the treatment of the Strong Correlation Error
(sr)exchange isn't much better (but see next slide for a more detailed analysis).

> cc-pVTZ, RSH : $\mu = 0.5$

Figure 1 is a plot showing the error of the RSH approximation for the exchange energy of the H_2 molecule as a function of the parameter δ . The plot compares the error of the RSH approximation (red lines) with the error of the srPBE approximation (black lines) for the exchange energy (E_x) and the correlation energy (E_c). The x-axis is δ (0 to 1) and the y-axis is the error in eV (-6 to 6). The RSH error for E_x (red dotted line with circles) is negative, reaching a minimum of about -4.5 eV at $\delta = 0.5$. The RSH error for E_c (red solid line with triangles) is positive, reaching a maximum of about 6 eV at $\delta = 0.5$. The srPBE error for E_x (black dotted line with circles) is near zero. The srPBE error for E_c (black dotted line with triangles) is positive, reaching a maximum of about 1.5 eV at $\delta = 0.5$. The srPBE error for E_{xc} (black dotted line with squares) is near zero.

Extension of Random Phase Approximation to fractional occupations

We will give key points (RPA derived as linear response equations).

(The detailed derivation is **an extension of the Fluctuation Dissipation Theorem to ensemble Green's Function**).

- The RPA is seen as $\mathbf{E}_c[G]$, a functional of the Green's function ; the basic variable to be ensembled is the **one-electron Green's function of the non-interacting reference system** : $G^{0,\mathbf{N}}(\mathbf{r}_1, \mathbf{r}_2) = (1 - \delta)G^{0,\mathbf{M}}(\mathbf{r}_1, \mathbf{r}_2) + (\delta)G^{0,\mathbf{M}+1}(\mathbf{r}_1, \mathbf{r}_2)$
- The RPA equations derived as **linear response equations** are :
$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \Omega$$

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

- > the orbitals are **scaled** : $\tilde{\phi}_i = \sqrt{n_i} \phi_i$ and $\tilde{\phi}_a = \sqrt{1 - n_a} \phi_a$
- > "i" now runs through "**fully occupied+partially occupied**" orbitals
- > "a" now runs through "**partially occupied+fully unoccupied**" orbitals

Be aware : the dimensions go from $N_v.N_c$ to : $(N_f + N_p).(N_p + N_u)$
(with N_v valence, N_c conduction, N_f fully occ., N_p partially occ., N_u fully unocc.)

The matrices read :

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

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

- What I presented : is an extension of the **usual linear response equations**, fuelled by **an ensemble Green's function describing fractional occupation**. The fundamental equations are the same but are “evaluated” at a different Green's function :

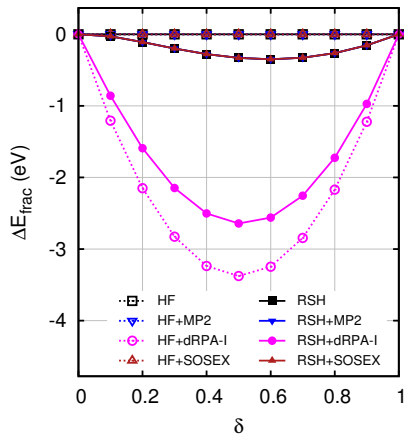
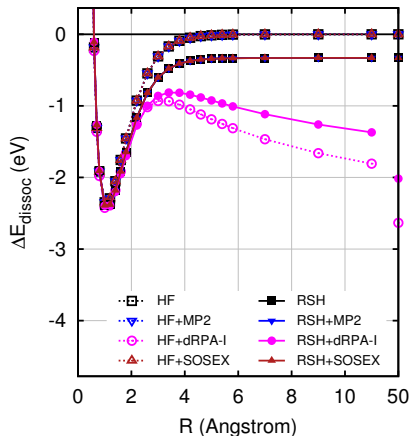
$$\frac{\partial^2 \mathbf{E}}{\partial v \partial v} [\mathbf{G}_{\text{frac}}]$$

This is the extension that makes sense in the context of the comparison with dissociation ; this is the extension that allows diagnostics on the Self-Interaction 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, ...).

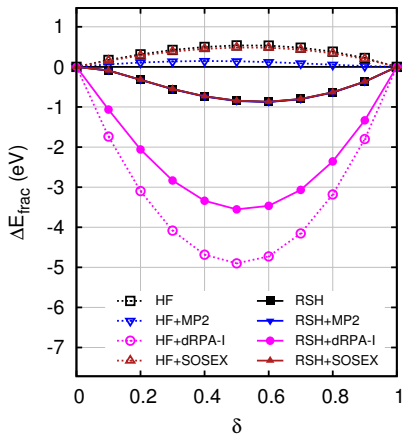
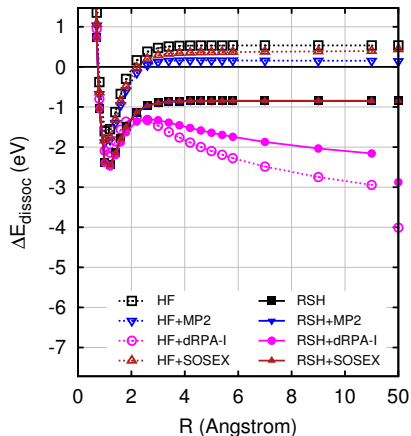
> cc-pVTZ, RSH :srPBE, $\mu = 0.5$ 

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

HF+MP2 performs well.

HF+SOSEX seems less efficient (include exchange diagrams up to 2nd order).

Post-**RSH** method seem to suffer from the convex error of the (sr)functional.

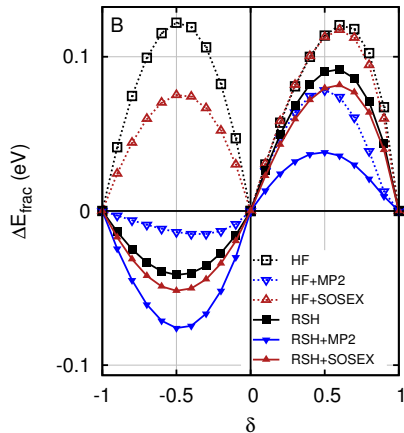
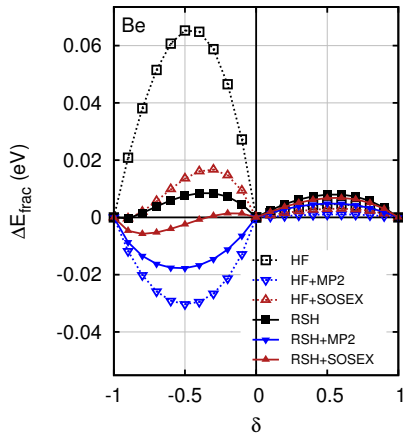
> cc-pVTZ, RSH :srPBE, $\mu = 0.5$ 

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

HF+MP2 performs well.

HF+SOSEX seems less efficient (include exchange diagrams up to 2nd order).

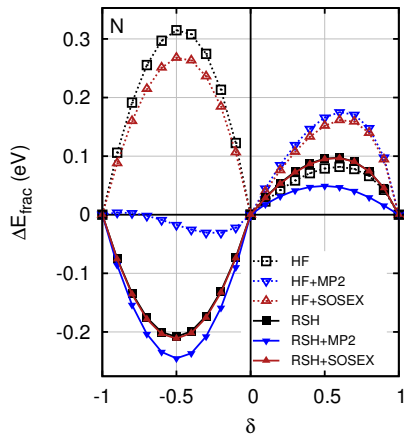
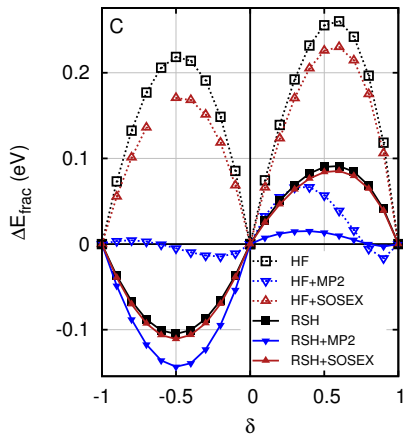
Post-**RSH** method seem to suffer from the convex error of the (sr)functional.

> aug-cc-pCVTZ, RSH :srPBE, $\mu = 0.5$ 

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

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

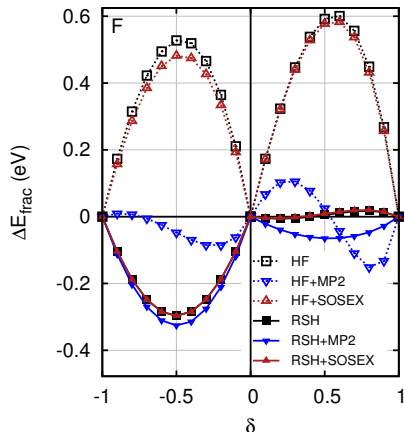
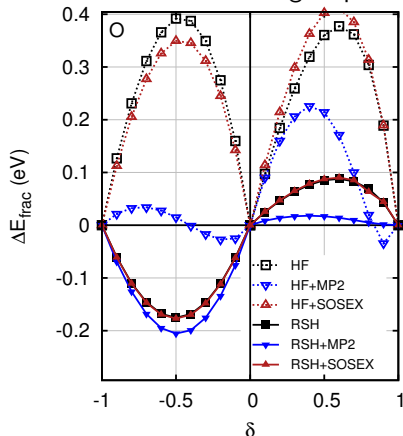
SOSEX systematically has much better results when used with **RSH**.

> aug-cc-pCVTZ, RSH :srPBE, $\mu = 0.5$ 

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

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

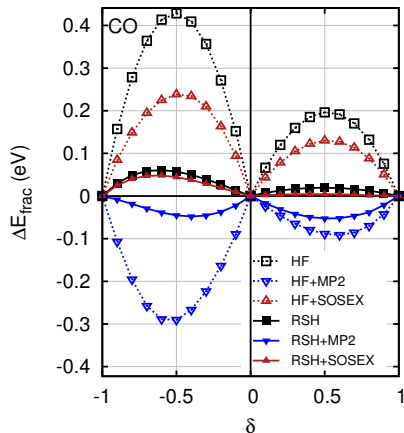
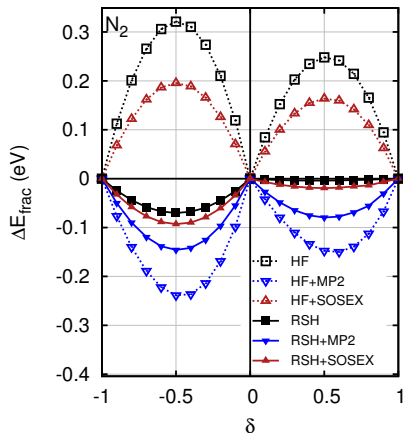
SOSEX systematically has much better results when used with **RSH**.

> aug-cc-pCVTZ, RSH :srPBE, $\mu = 0.5$ 

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

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

SOSEX systematically has much better results when used with **RSH**.

> cc-pVTZ, RSH :srPBE, $\mu = 0.5$ 

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

drPA-I is too bad (not shown); **MP2** is good, and often improved by **RSH**.

SOSEX systematically has much better results when used with **RSH**.

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 Self-Interaction Error.

Use of range-separation improves MP2 and SOSEX errors.

The methods presented here cannot be free from **both the Self-Interaction and the Static Correlation errors**.

- Other inclusion of exchange (other variants of Random Phase Approximation) seem promising for the treatment of both (**SO2**).
- In this context, very interesting questions on the **stability of the RPA equations** arise.