Open-Shell Random Phase Approximation : Application to Atomisation Energies and Energy Barrier Heights

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RSH+RPA formulation

$\frac{\mathrm{erf}(\mu r_{ij})}{r_{ij}}$

Range separation[1] with the range-separation parameter μ :

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

Single determinant approximation :

srLDA,srPBE,...

$$E_0 = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{\text{lr}} | \Phi \rangle + E_{Hxc}^{\text{sr}}[n_\Phi] \right\}$$

Adding long-range correlation :

lrMP2,lrRPA,...

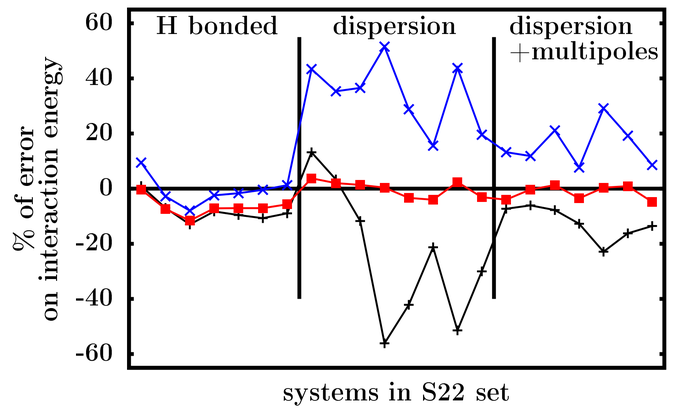
$$E_{\text{exact}} = E_0 + E_c^{\text{lr}}$$

There is a wide variety of RPA formulations and variants[2], focus is here brought to : dRPA-I[2] and Szabo-Ostlund 2 (SO2)[3].

(dRPA-I includes in no way exchange effects ; SO2 is a variant of RPA that fully includes exchange effects.)

Performance on energies

Study on the S22 set of weakly-interacting molecular systems[3] ($\mu = 0.5$ bohr^{-1}, srPBE functional, aug-cc-pVDZ).

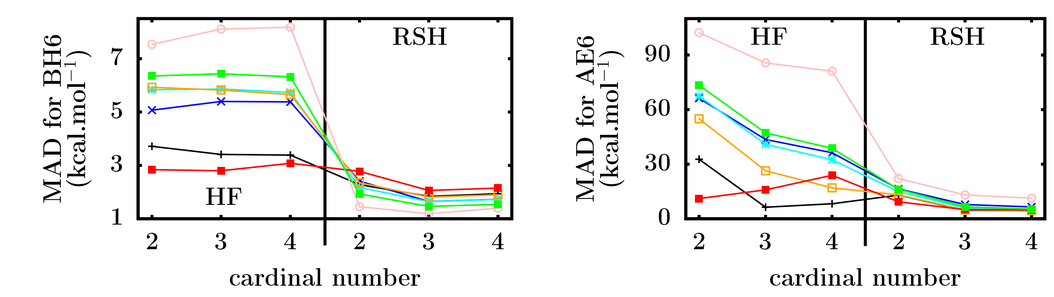


It is seen that SO2 is better for the description of van der Vaals interactions[3].

All data shown are **MAD in kcal.mol^{-1}** of atomization energies of the **AE6 dataset** and of barrier heights of reactions of the **BH6 dataset**.

Dependence on the basis set

($\mu = 0.5$ bohr^{-1}, srPBE functional, spin unrestricted[4])

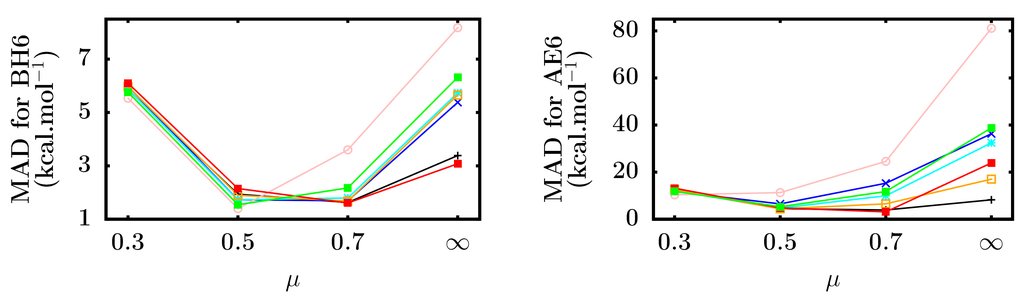


▷ As expected, the use of **range separation facilitates the convergence** with respect to the basis set.

▷ All range-separated methods give about the same accuracy.

Dependence on μ

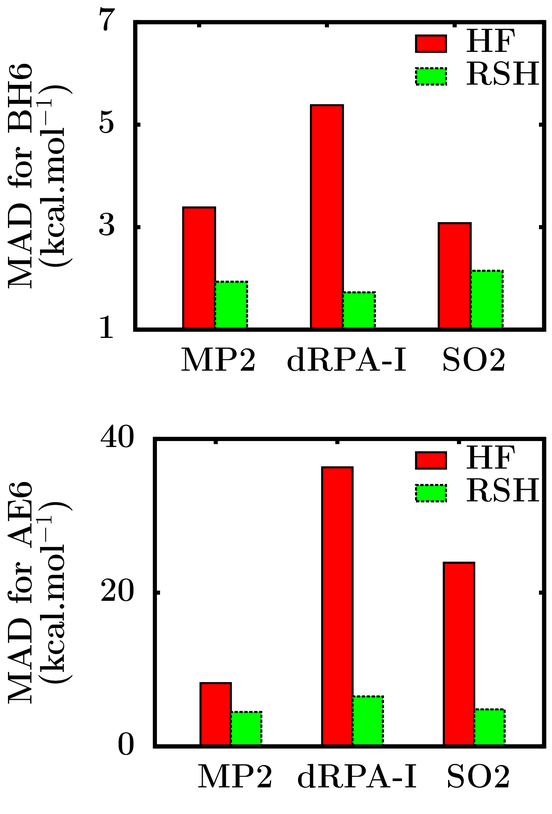
(cc-pVQZ, srPBE functional, spin unrestricted[4])



▷ The canonical value of $\boldsymbol{\mu}$**= 0.5 bohr^{-1}** is here again a sound choice.

RSH+SO2 is a good method

($\mu = 0.5$ bohr^{-1}, cc-pVQZ, srPBE functional, spin unrestricted[4])



▷ Range-separation generally improves the results.

▷ **Szabo-Ostlund 2** confirms it's position of leader in the RSH+RPA categories of methods.

Conclusion and Outlook

▷ Most RPA formulations and variants have been **generalized to open-shell** expressions.

▷ Working implementation as been done in **MOLPRO**[5].

▷ Open-shell (RSH+)RPA calculations have successfully been applied to the **AE6 and BH6 dataset**.

▷ Results confirm that **RSH+SO2 is a good method** to calculate : - interaction energies
- atomization energies
- barrier heights

▷ Future developments could include a way to estimate **spin-contamination** in these RPA calculations and a **spin-adapted open-shell RPA** formulation.

References

1. Toulouse, Gerber, Jansen, Savin, Ángyán, PRL, 2009
2. Ángyán, Liu, Toulouse, Jansen, JCTC, 2011
3. Toulouse, Zhu, Savin, Jansen, Ángyán, JCP, 2011
4. Mussard, Toulouse, Luppi, Reinhardt, *to be published*
5. MOLPRO 2012.1, Werner, Knowles, Knizia, Manby, Schütz