

Range-Separated Random Phase Approximation: Recent Advances

B. Mussard^{a,b}, O. Franck^{a,b}, E. Luppi^b, P. Reinhardt^b, J. Toulouse^b

^a Institut du Calcul et de la Simulation, Université Pierre et Marie Curie, CNRS, 75005 Paris, France

^b Laboratoire de Chimie Theorique, Université Pierre et Marie Curie, CNRS, 75005 Paris, France

bastien.mussard@upmc.fr

RSH+RPA formulation

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

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

Single determinant approximation:

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

Adding long-range correlation:

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

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

(**dRPA-I** includes in no way exchange effects ;

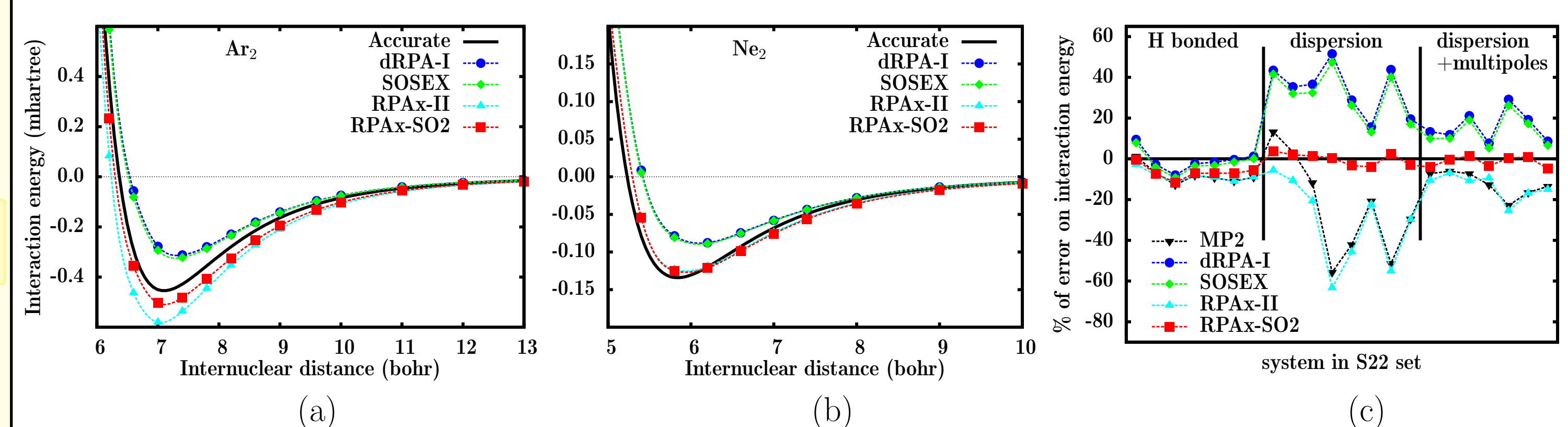
SO2 is a variant of RPA that fully includes exchange effects.)

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

srLDA, srPBE,...

lrMP2, lrRPA,...

Performance on energies



(a,b) > Interaction energy of Ar₂ and Ne₂ dimers^[3]

($\mu = 0.5 \text{ bohr}^{-1}$, srPBE functional, aug-cc-pV6Z).

(c) > Study on the S22 set of weakly-interacting molecular systems^[3]

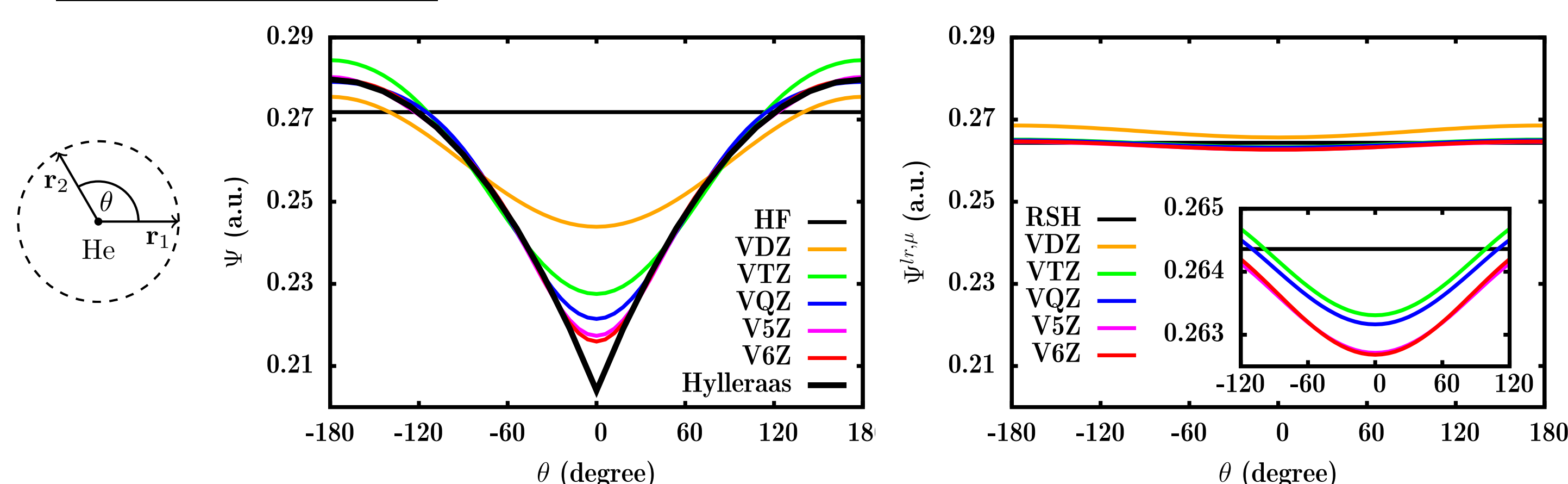
($\mu = 0.5 \text{ bohr}^{-1}$, srPBE functional, aug-cc-pVDZ).

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

Basis set convergence

both **partial wave** and **principal number** expansions lead to an **exponential convergence** of the wavefunction^[4]

> FCI wave function of the He atom calculated with Dunning basis sets



> the **absence of cusp** in the lr-wavefunction accelerates the convergence

> the convergence seems **less systematic**

(Dunning optimized for Coulomb interaction)

Three-point extrapolation

We propose a three-point extrapolation scheme for total RSH+correlation energies^[4]

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

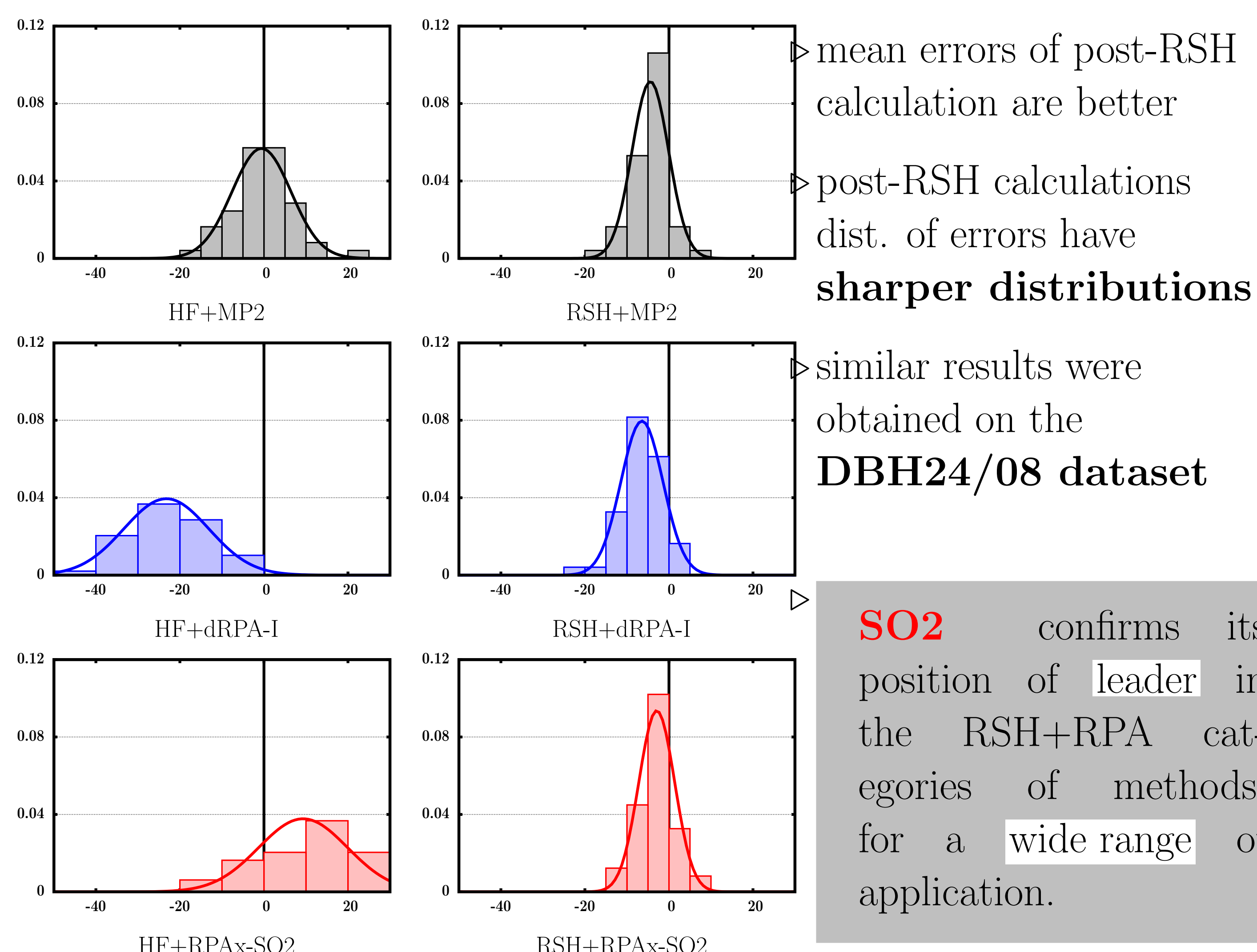
trying to fit:
 $E_X = E_{\infty} + B \exp(-\beta X)$

> errors (mHartree) wrt. cc-pV6Z ($\mu = 0.5 \text{ bohr}^{-1}$, srPBE)

	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

Spin-Unrestricted RPA

> Normal distributions of errors (kcal/mol) of calculations on **AE49**^[5]
($\mu = 0.5 \text{ bohr}^{-1}$, srPBE functional, cc-pVQZ, spin unrestricted)



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**

SO2 confirms its position of leader in the RSH+RPA categories of methods, for a wide range of application.

CONCLUSION AND OUTLOOK

> Careful analysis shows **exponential convergence** of range-separated wavefunctions and energies

> Most RPA formulations and variants have been **generalized to open-shell** expressions (available in MOLPRO^[6]).

> Open-shell (RSH+)RPA calculations have successfully been applied to the **AE49** and **DBH24/08 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.

> Current developments involve **fractional occupation number calculations**

References

1. J. Toulouse, I. Gerber, G. Jansen, A. Savin, J.G. Ángyán, PRL, 2009
2. J.G. Ángyán, R. Liu, J. Toulouse, G. Jansen, JCTC, 2011
3. J. Toulouse, W. Zhu, A. Savin, G. Jansen, J.G. Ángyán, JCP, 2011
4. O. Franck, BM, E. Luppi, J. Toulouse, JCP, 2015
5. BM, P. Reinhardt, J.G. Ángyán, J. Toulouse, JCP, 2015
6. MOLPRO H.-J. Werner, P.J. Knowles, G. Knizia, F.R. Manby, M.