Developments in Electronic Structure Theory.

Bastien Mussard

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/

A short presentation

A short presentation (1)

What I do : Quantum Mechanics

- **Wavefunction theories** (WFT)
- **Density Functional theory** (DFT)
- **Range Separation methods** (RS)

Main research interest

- Weak interactions / London dispersion forces / VdW interactions

- **Random Phase Approximation** (RPA)
  - formalism (new approximations, spin-unrestricted generalization, ...)
  - local orbitals (designed new localized orbitals, selection of excitation)
  - gradients of the energy (forces, dipoles, optimization of geometry, ...)
  - ...

Numerous collaborations

- **High Harmonics Generation spectra** (Electron dynamics)
- **Quantum Monte Carlo methods** (QMC)

A short presentation (2)

Notable Developments

- Developments in MOLPRO
  Commercial code
  Versatile (HF,DFT,CI,CC,MCSCF,
  MRCI,MRPT,MRCC,
  FCIQMC,DMRG,
  Gradients and Properties)
  $\sim$ 4 000 000 lines of code
  In charge of the RPA code
  www.molpro.net
- Developments in CHAMP
  Free code
  VMC, DMC
  Optimization of wavefunctions, ...
  Fast calculation of determinants
  CHAMP@Cornell
- Developped personal codes,
  from scratch
  Calculations on grid, parallel codes

Technical side of the work

- **Management of codes** (SVN/GIT/BugZilla)
- Cleaning-up
  Optimizing pre-existing codes (**use of memory**, ...)
- **HPC**
- **Interfaces** between codes

Context of my main research interest

- **Electronic structure** calculations.
- post-DFT calculations in the context of **Range Separation**.
- In the WFT part, for the treatment of London dispersion forces, we use the **Random Phase Approximation**.

Range Separation : Motivation [Savin, Rec.dev. (1996)]

Get the **accurate answer** for the **right reason** at a **reasonable cost**.

WFT (the wavefunction $\Psi(\mathbf{x}^N)$ is the key quantity ; determinants)

- ✖ rather **costly** (size of Hilbert space)
- ✔ improvement of the description is systematic (add more determinants)

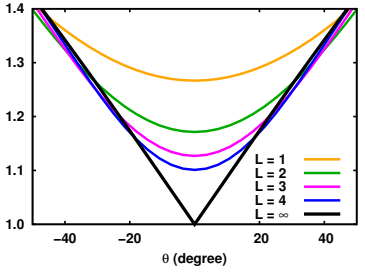
DFT (the density $n(\mathbf{r})$ is the key quantity)

- ✔ cheap methods ; applicable to big systems ; impressive successes
- ✖ need to **approximate** $E_{xc}[n]$; not systematical

Range Separation (a rigourous combination of both approaches)

WFT suffers at short range from the e-e coalescence.

DFAs are **(semi)local approximation**, best at short-range.



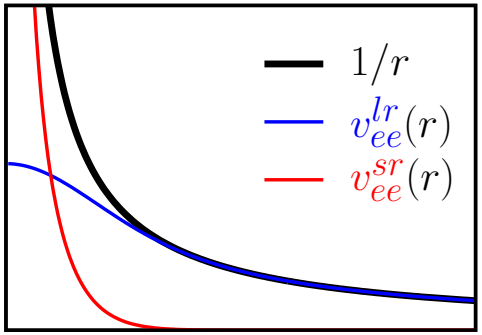
The idea : split the e-e interaction into long- and short-range, treat the **long-range with WFT**, the **short-range with DFT**.

Range Separation : Realisation [Savin, Rec.dev. (1996)]

Split of the Coulomb interaction ; **rigourous mix** of WFT and DFT methods.

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

$\hat{V}_{ee}^{lr}$ long-range e-e interaction
$E_{Hxc}^{sr}[n]$ short-range density functional



- In a variational way :

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

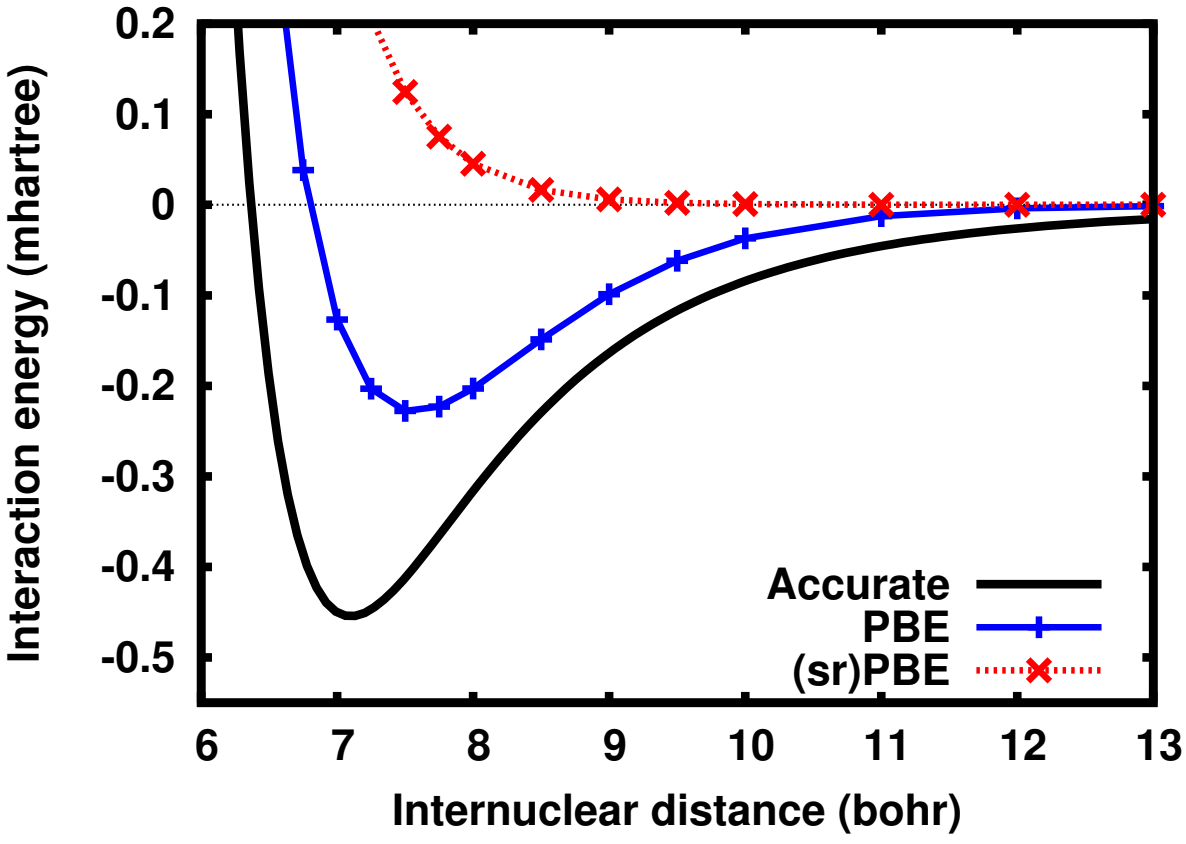
e.g. MCSCF+DFT, CI+DFT,...-> for the **static (strong) correlation**.
[Fromager,Toulouse,Jensen JCP 2007]
[Sharkas,Savin,Jensen,Toulouse JCP 2012]

- With a perturbative treatment, from a mono-determinental reference (**RSH**) :

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

e.g. with RPA -> for **long range dynamical correlation (vdW dispersion)**.
[Ángyán,Gerber,Savin,Toulouse PRA 2005]
[Toulouse,Gerber,Jansen,Savin,Ángyán PRL 2009]

Ar_2, aug-cc-pV5Z basis, $\mu = 0.5$ bohr^{-1}



- RSH reference **contains no dispersion**.

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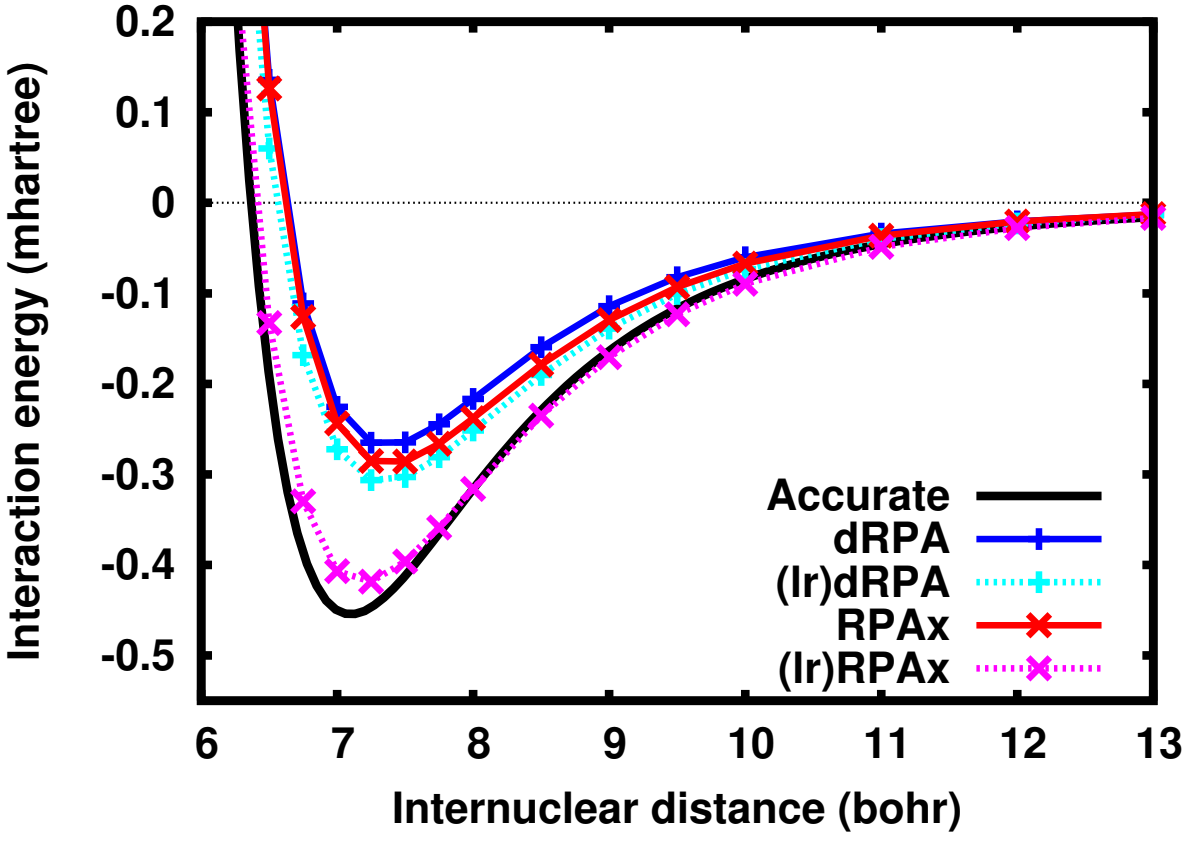

- RSH reference **contains no dispersion**.
- In RPA, it is important to add **exchange effects** for dispersion interactions.

Random Phase Approximation : Origins [Bohm,Pines PR (1951)]

The original intention is to decouple by a canonical transformation the particle and field variables in the description of the Uniform Electron Gaz (UEG).

The physics : mix of **long-range organized behavior** (collective plasma oscillations) and of **short-range screened explicit interactions**.

This emerges naturally by the canonical transformation, and involves a cut-off distance, over which long-range behavior correctly describes the system, and under which it no longer captures the main physics : the short-range interaction is then predominant.

Hence, in RPA, the energy is the sum of **oscillator energies** and of a **short-range correction**. **This seems ideal in a range separation context.**

What is "random" in RPA ?

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

Random Phase Approximation : formalisms and versions

AC-FDT equation

[Ángyán,Liu,Toulouse,Jansen JCTC (2011)]
[BM,Rocca,Jansen,Ángyán JCTC (submitted)]

$$E_c^{\mathrm{RPA}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\,\mathrm{Tr}\Big(\mathbb{V}_{\mathrm{ee}}\Big[\Pi_\alpha^{\mathrm{RPA}}(i\omega) - \Pi_0(i\omega)\Big]\Big) \;\Big|\; (\Pi_\alpha^{\mathrm{RPA}})^{-1} = \Pi_0^{-1} - \mathbb{f}_{\mathrm{Hx},\alpha}$$

Versions (include/exclude **exchange**)

- **direct** or **exchange** RPA
- **single-bar** or **double-bar**

This yields different, non-equivalent **versions of RPA**

Formulations (analytical/numerical **integrals**)

- **density-matrix** formulation $E_c^{\mathrm{RPA}} = \frac{1}{2}\int d\alpha\, \mathrm{tr}\,(\mathbf{P}_{c,\alpha}\,\mathbf{V})$
- **dielectric-matrix** formulation $E_c^{\mathrm{RPA}} = \frac{1}{2}\int \frac{d\omega}{2\pi}\,\mathrm{tr}\,(\log(\boldsymbol{\epsilon}(i\omega)) - \boldsymbol{\epsilon}(i\omega) + \mathbf{1})$
- **plasmon** formula $E_c^{\mathrm{RPA}} = \frac{1}{2}\sum \omega^{\mathrm{RPA}} - \omega^{\mathrm{TDA}}$
- **Ricatti equations** and **rCCD** $E_c^{\mathrm{RPA}} = \frac{1}{2}\mathrm{tr}(\mathbf{BT})$

+Approximations (in each formulations, for each versions...) **SOSEX**, **SO2**

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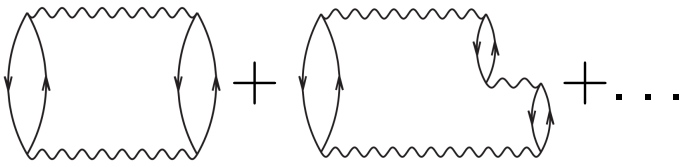
Random Phase Approximation : Feynman diagrams

dRPA-I

$$E_c^{\text{dRPA-I}} = \frac{1}{2}\text{tr}\langle ab|ij\rangle^{\text{lr}}(T^{\text{lr}}_{\text{drCCD}})_{ia,jb}$$



RPAx-II

$$E_c^{\text{RPAx-II}} = \frac{1}{4}\text{tr}\langle ab||ij\rangle^{\text{lr}}(T^{\text{lr}}_{\text{rCCDx}})_{ia,jb}$$

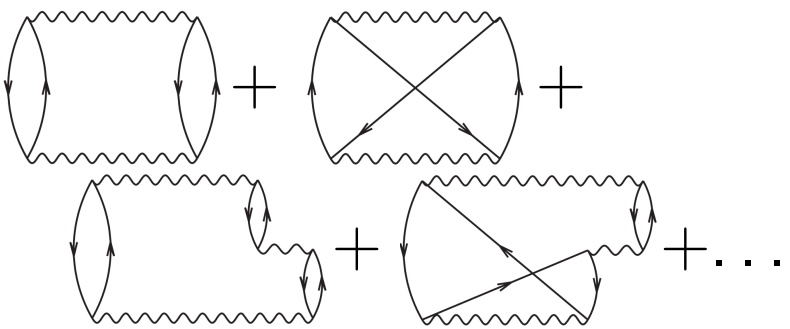
[McLachlan,Ball RMP 1964]

[a lot of diagrams]

SOSEX

$$E_c^{\text{SOSEX}} = \frac{1}{2}\text{tr}\langle ab||ij\rangle^{\text{lr}}(T^{\text{lr}}_{\text{drCCD}})_{ia,jb}$$

[Grüneis,*et. al.* JCP 2009]



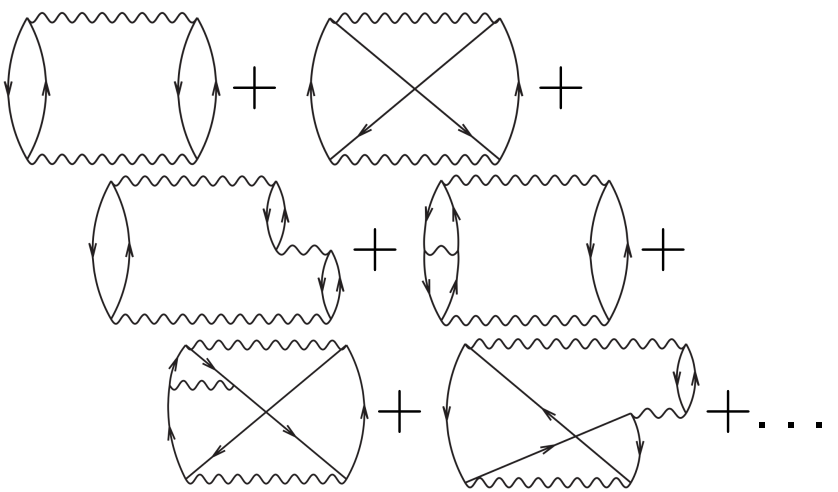
Not that good for weak interactions.

RPAx-SO2

$$E_c^{\text{RPAx-SO2}} = \frac{1}{2}\text{tr}\langle ab|ij\rangle^{\text{lr}}(T^{\text{lr}}_{\text{rCCDx}})_{ia,jb}$$

[Szabo,Ostlund JCP 1977]

[Toulouse *et. al.* JCP 2011]



It is our method of choice.

New developments

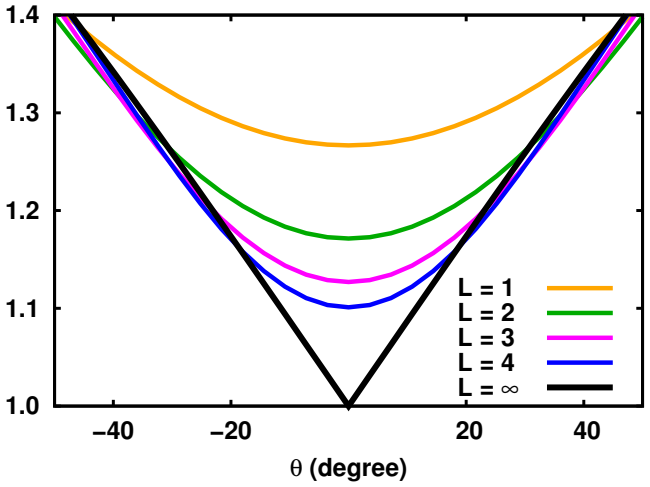
- **Basis Set Convergence** study
  and **Three-point extrapolation scheme**.
  [Franck,BM,Luppi,Toulouse JCP (2015)]
- **Spin-Unrestricted generalization**
  and **Calculations on DBH24/08 and AE49**.
  [BM,Reinhardt,Ángyán,Toulouse JCP (2015)]
- Development and Implementation of
  the **Gradients of RSH+RPA methods**.
  [BM,Szalay,Ángyán JCTC (2014)]
- Development of **Localized Virtual Orbitals**
  and **Application for RPA calculations**.
  [BM,Ángyán TCA (2015)]

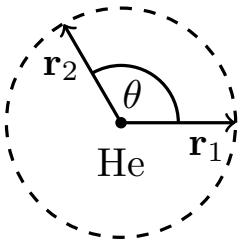
Partial wave expansion of the WF

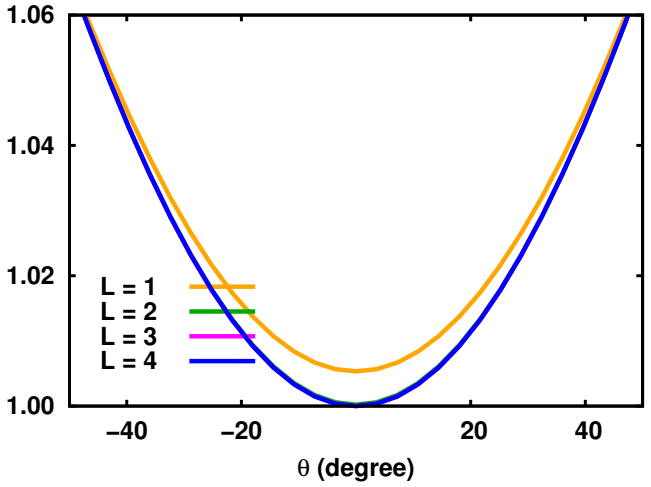
[Gori-Giorgi,Savin PRA (2006)]

$$\frac{\Psi(r_{12})}{\Psi(0)} = 1 + \frac{r_{12}}{2} + \ldots = \sum c_\ell P_\ell(\cos\theta) \quad \text{with } c_\ell \sim \ell^{-2}$$

$$\frac{\Psi^\mu(r_{12})}{\Psi^\mu(0)} = 1 + \frac{\mu r_{12}^2}{3\sqrt{\pi}} + \ldots = \sum c_\ell P_\ell(\cos\theta) \quad \text{with } c_\ell \sim e^{-\alpha\ell}$$

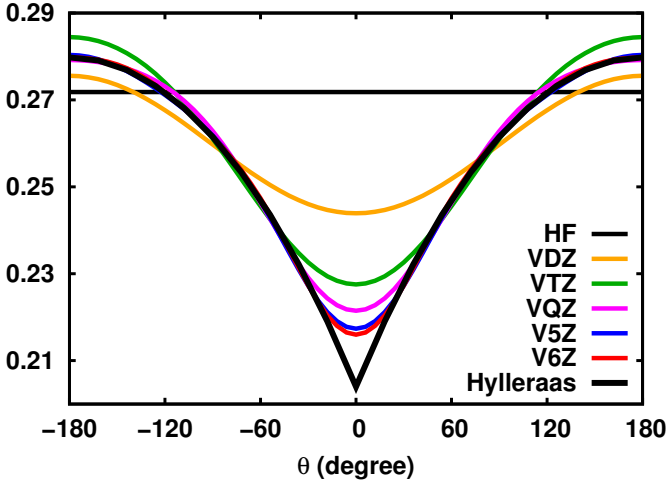


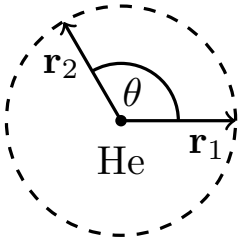


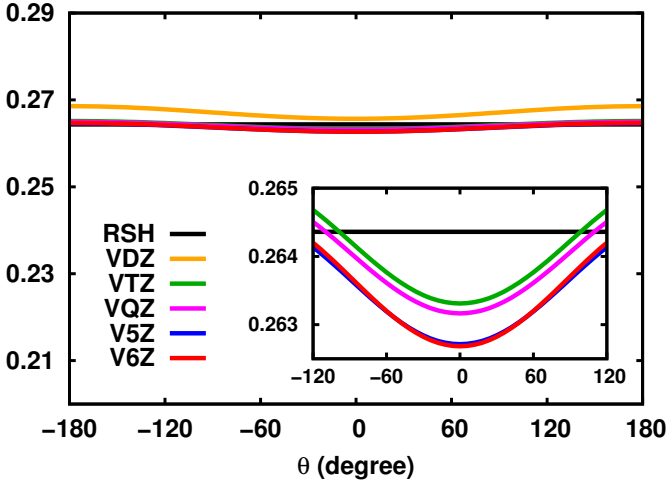


Principal number expansion (wrt one-particule basis)

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \sum c_i \; \phi_i(\mathbf{r}_1) \; \phi_i(\mathbf{r}_2)$$







Spin-Unrestricted RPA

[BM,Reinhardt,Ángyán,Toulouse JCP (2015)]

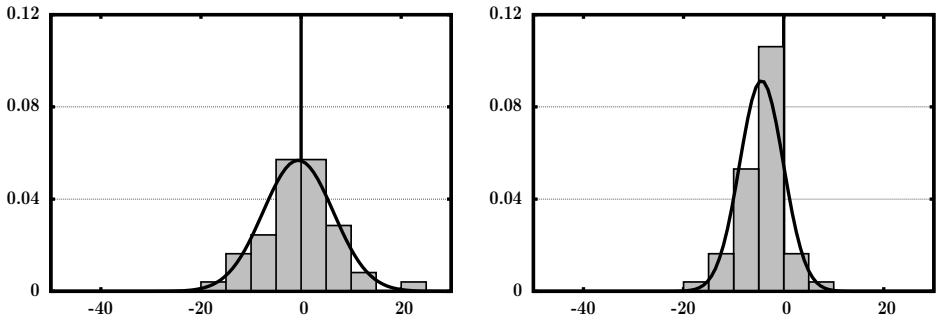
Implemented most of the variants with a nospinflip/spinflip block structure.

Normal distributions of errors (kcal/mol) of calculations on **AE49**.

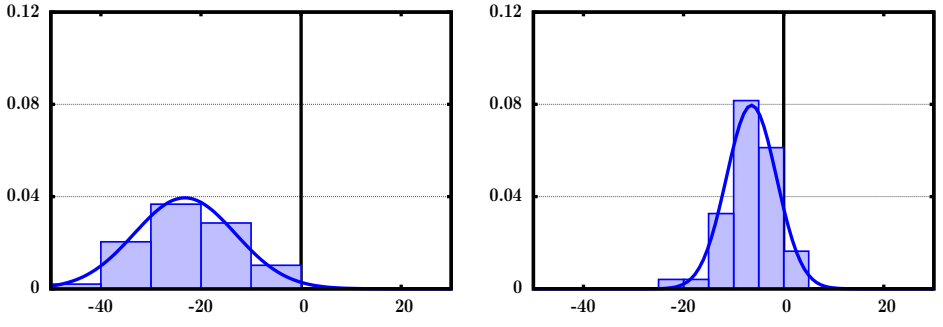
- Mean errors of post-RSH calculation are better.
- Post-RSH calculations dist. of errors have sharper distributions .

Similar results were obtained on the **DBH24/08** dataset.

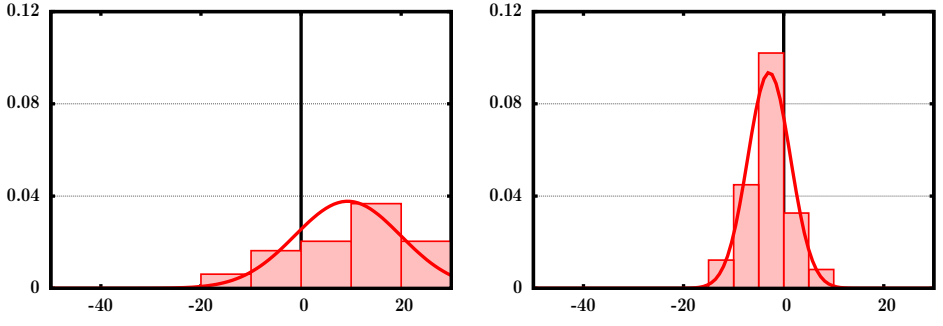
We argue that **RPAx-SO2** is a good method for a wide range of applications.



HF+MP2 RSH+MP2



HF+dRPA-I RSH+dRPA-I



HF+RPAx-SO2 RSH+RPAx-SO2

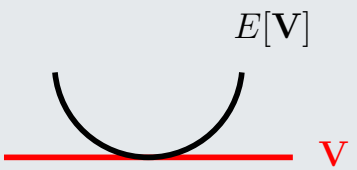
>cc-pVQZ (post-RSH : srPBE, $\mu = 0.5$)

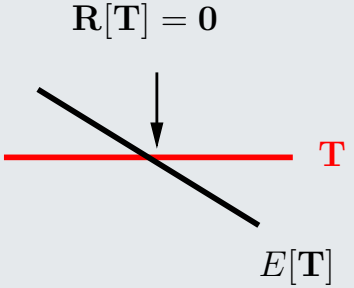
Analytical Gradients : Lagrangian formalism [BM,Szalay,Ángyán JCTC (2014)]

Given an energy $E[\kappa, \mathbf{V}(\kappa), \mathbf{T}(\kappa)]$

you have rules for $\mathbf{V}$: $\partial E/\partial \mathbf{V} = 0$

you have rules for $\mathbf{T}$: $\mathbf{R}[\mathbf{T}] = 0$





$$\frac{\mathrm{d}E}{\mathrm{d}\kappa} = \frac{\partial E}{\partial \kappa} + \cancel{\frac{\partial E}{\partial \mathbf{V}}\frac{\partial \mathbf{V}}{\partial \kappa}} + \boxed{\frac{\partial E}{\partial \mathbf{T}}\frac{\partial \mathbf{T}}{\partial \kappa}}$$

$$\left(\text{in } \frac{\partial E}{\partial \kappa} \text{ there is } \mathbf{h}^{(\kappa)},\ (\mu\nu|\sigma\rho)^{(\kappa)} \text{ and } \mathbf{S}^{(\kappa)}\right)$$

For non-variational methods

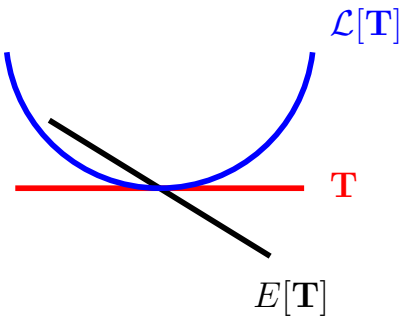
The solution is to work with an **alternative object** that **is** variational :

$$\mathcal{L}[\kappa, \mathbf{V}, \mathbf{T}, \boldsymbol{\lambda}] = E[\kappa, \mathbf{V}, \mathbf{T}] + \mathrm{tr}(\boldsymbol{\lambda}\mathbf{R}[\mathbf{T}])$$

$$\frac{\partial \mathcal{L}}{\partial \mathbf{V}} = \frac{\partial E}{\partial \mathbf{V}} = 0 \quad ✔$$

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{\lambda}} = \mathbf{R}[\mathbf{T}] = 0 \quad ✔$$

$$\boxed{\frac{\partial \mathcal{L}}{\partial \mathbf{T}} = \frac{\partial E}{\partial \mathbf{T}} + \mathrm{tr}\left(\boldsymbol{\lambda}\frac{\partial \mathbf{R}}{\partial \mathbf{T}}\right) = 0}$$



The **RSH+RPA** energy is : $E = \min_{\Phi}\left\{\langle\Phi|\hat{T} + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{ee}}^{\mathrm{lr}}|\Phi\rangle + E_{\mathrm{Hxc}}^{\mathrm{sr}}[n_\Phi]\right\} + E_{\mathrm{c}}^{\mathrm{lr,RPA}}$

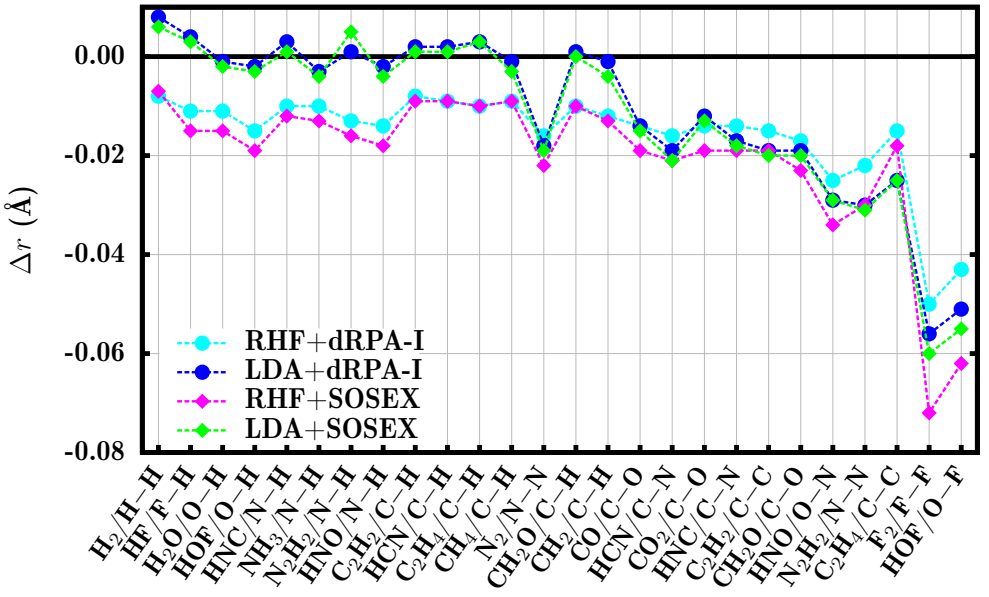
The **equations were derived** (sr and lr terms) and **implemented** in `MOLPRO`.

Analytical Gradients of RSH+RPA

[BM,Szalay,Ángyán JCTC (2014)]

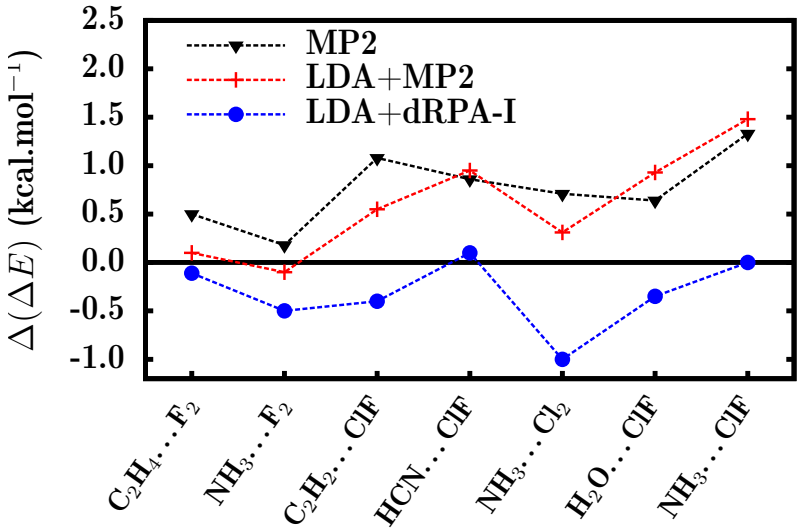
Bond Lengths of simple molecules

> aug-cc-pVQZ



Interaction Energies

> aug-cc-pVTZ



Mean Absolute Errors

Bond Lengths of simple molecules

RHF+dRPA-I	0.016	RHF+SOSEX	0.021
LDA+dRPA-I	**0.013**	LDA+SOSEX	0.014

Interaction Energies

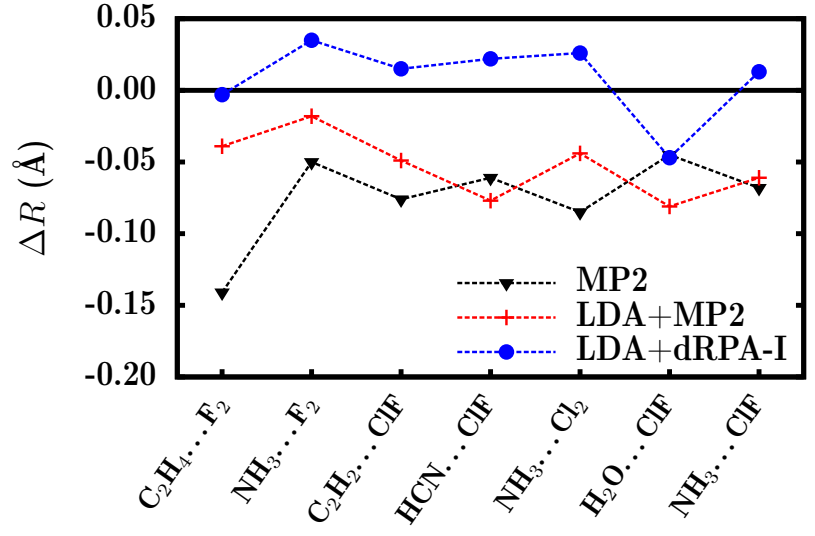
MP2	0.76
LDA+MP2	0.63
LDA+dRPA-I	**0.35**

Intermonomer distances

MP2	0.075
LDA+MP2	0.053
LDA+dRPA-I	**0.023**

Intermonomer distances

> aug-cc-pVTZ



Projected Oscillator Orbitals

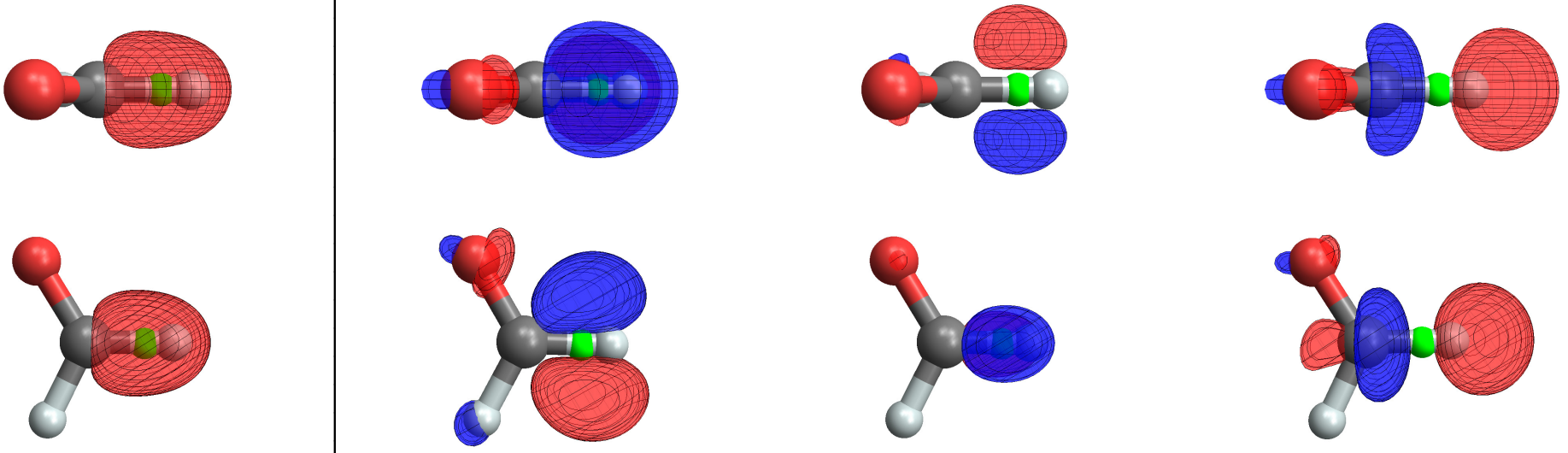
[BM,Ángyán TCA (2015)]

The objective is to construct a set of **localized virtual orbitals** by multiplying the set of occupied Localized Molecular Orbitals (LMOs) with **solid spherical harmonic functions**. The orthogonality to the occupied space is ensured by **projection**.

Dipolar oscillator orbital [Foster, Boys RMP (1960)]

$$|i_\alpha\rangle = \underbrace{(\hat{1} - \hat{P})}_{\text{projector}} \underbrace{(\hat{r}_\alpha - D^i_\alpha)}_{\text{harmonic}} \underbrace{|i\rangle}_{\text{LMO}} \qquad \text{where } D^i_\alpha = \langle i|\hat{r}_\alpha|i\rangle$$

C-H bond in $CH_2{=}O$:



Projected Oscillator Orbitals : Key features [BM,Ángyán TCA (2015)]

Dipolar oscillator orbital

$$|i_\alpha\rangle = (\hat{1} - \hat{P})(\hat{r}_\alpha - D^i_\alpha)\,|i\rangle \qquad \text{where } D^i_\alpha = \langle i|\hat{r}_\alpha|i\rangle$$

This formulation is best employed with **Boys' LMOs**, see :

$$|i_\alpha\rangle = \hat{r}_\alpha\,|i\rangle - \sum |m\rangle\,\langle m|\hat{r}_\alpha|i\rangle$$

The POOs are **non-orthogonal**, with overlap :

$$S^{ij}_{\alpha\beta} = \langle i|\hat{r}_\alpha\hat{r}_\beta|j\rangle - \sum \langle i|\hat{r}_\alpha|m\rangle\langle m|\hat{r}_\beta|j\rangle$$

The **fock matrix element** are found to be :

$$f^{ii}_{\alpha\beta} = \tfrac{1}{2}\delta_{\alpha\beta} + \tfrac{1}{2}\sum(f_{im}\langle m|\hat{r}_\alpha\hat{r}_\beta|i\rangle + \langle i|\hat{r}_\alpha\hat{r}_\beta|m\rangle f_{mi}) - \sum \langle i|\hat{r}_\alpha|m\rangle f_{mn}\langle n|\hat{r}_\beta|i\rangle$$

The two-elec integrals are written with a **multipole expansion** of the lr interaction :

$$\langle i_\alpha j|kl_\beta\rangle = \sum\langle i_\alpha|\hat{r}_\gamma|k\rangle L^{ij}_{\gamma\delta}\langle j|\hat{r}_\delta|l_\beta\rangle + \ldots$$

A **nice result** greatly simplifies the equations :

$$\langle i_\alpha|\hat{r}_\beta|j\rangle = \langle i|\hat{r}_\alpha\hat{r}_\beta|j\rangle - \sum \langle i|\hat{r}_\alpha|m\rangle\langle m|\hat{r}_\beta|j\rangle = S^{ij}_{\alpha\beta}$$

Projected Oscillator Orbitals : RPA and C_6 [BM,Ángyán TCA (2015)]

The working equations are the local RPA Ricatti equations (*i.e.* local rCCD) with the **local excitation approximation** and spherical average approximation.

RPA correlation energy

$$E_c^{\mathrm{RPA,lr}} = \sum_{ij}^{occ} \frac{4}{9} s^i s^j \ \mathrm{tr}\left(\mathbf{L}^{ij}\mathbf{T}^{ij}\right)$$

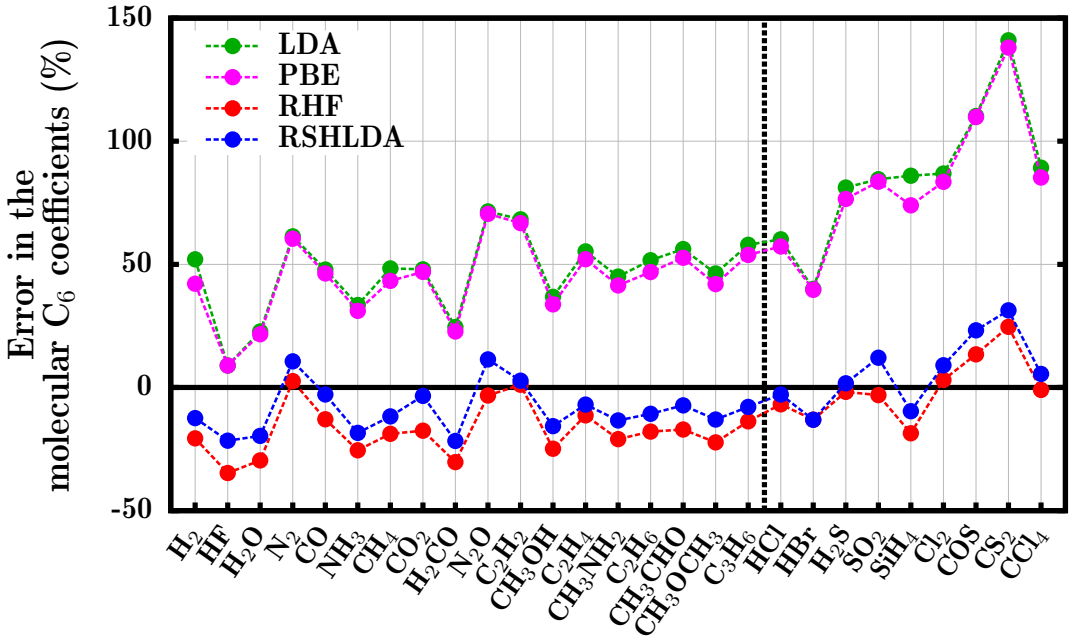
where $s^i = \sum \mathbf{S}^{ii}_{\alpha\alpha}$

C_6 coefficients

$$E_c^{(2),\mathrm{lr}} = \sum_{ij}^{occ} \frac{4}{9} \frac{s^i s^j}{\Delta^i + \Delta^j} \ \mathrm{tr}\left(\mathbf{L}^{ij}\mathbf{L}^{ij}\right)$$

$$= \sum_{ij}^{occ} \frac{8}{3} \frac{s^i s^j}{\Delta^i + \Delta^j} \frac{F^{\mu}_{\mathrm{damp}}(D^{ij})}{D^{ij6}}$$

where $\Delta^i = f_{ii} - f^i/s^i$



$>$ aug-cc-pVTZ (RSH : $\mu = 0.5$)

MA%E		
	LDA	59.8
	PBE	56.7
	RHF	15.2
	RSHLDA	11.8

Other Works

Efficient calculations of determinants in QMC using
the **Sherman-Morrison-Woodbury formula**.

Fractional occupation number calculations
and **Instabilities in the RPA problem**.
[BM,Toulouse (in prep)]

Electron dynamics for High Harmonics Generation spectra
[Coccia,BM,Labeye,Caillat,Taieb,Toulouse,Luppi (submitted)]

In real space : relationship between
the **response functions**, **exchange holes** and **localized orbitals**.
[BM,Ángyán CTC (2015)]

Collaborators : **János Ángyán**, **Roland Assaraf**, **Odile Franck**, **Georg Jansen**, **Eleonora Luppi**, **Peter Reinhardt**, **Dario Rocca**, **Julien Toulouse**, **Cyrus Umrigar**.

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