Developments in Electronic Structure Theory.

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"Developments in Electronic Structure Theory"

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

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

✔ cheap methods ; applicable to big systems

✘ unable to systematically improve the results

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

✘ rather costly

✔ improvement of the description is systematic

QMC (stochastic method)

✔ good method in terms of accuracy and scaling

✘ costly ; ideal for parallelisation

Accuracy & Cost

Range Separation

WFT as input for QMC

DFT+WFT

- 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**.

WFT suffers at short range from the description of the e-e coalescence.
DFAs are essentially **(semi)local approximation** and are best at short-range.

The idea is to split the e-e interaction into **long**- and **short**- range parts:

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

versus
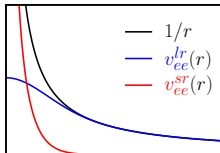
... and as a result to rigourously **mix WFT and DFT** methods :

▶ in a variational way:

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

*e.g.* MCSCF+DFT, CI+DFT,... -> for the **static correlation**.

▶ with a perturbative treatment, from a mono-determinental reference (RSH):

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

e.g. with RPA -> for **long range dynamical correlation**.

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

Go from $\hat{H} = \hat{H}_{\text{part.}} + \hat{H}_{\text{field}} + \hat{H}_{\text{part./field}}$ to $\hat{H}^{\text{RPA}} = \hat{H}_{\text{part.}} + \hat{H}_{\text{oscillations}} + \hat{H}_{\text{part./part.}}^{\text{sr}}$
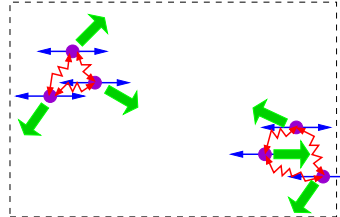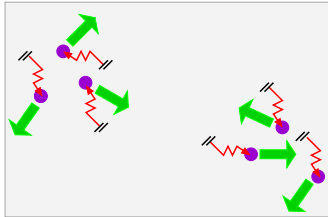
The physics: mix of **long-range organized behavior** (collective plasma oscillations) and of **short-range screened interactions**.

Hence, in RPA, the energy is the sum of $\boxed{\text{oscillator energies}}$ and of a short-range correction. This seems ideal in a range separation context.

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 flavors

ACFDT equation [Langreth,Perdew PRB **15** (1977)]

$$E_c^{\text{ACFDT}} = \frac{1}{2}\int_0^1 d\alpha \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{Tr}\left(\mathbb{W}_{\text{ee}}\left[\mathbb{\Pi}_\alpha^{\text{RPA}}(i\omega) - \mathbb{\Pi}_0(i\omega)\right]\right) \quad \bigg| \quad (\mathbb{\Pi}_\alpha^{\text{RPA}})^{-1} = \mathbb{\Pi}_0^{-1} - \mathbb{f}_{\text{Hx},\alpha}$$

Flavors (include/exclude **exchange**) [Ángyán,Liu,Toulouse,Jansen JCTC **7** (2011)]

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

This yields the flavors of RPA called: dRPA-I, dRPA-II, RPAx-I, RPAx-II

Formulations (analytical or numerical **integrals**)

- density-matrix formulation $\qquad E = \frac{1}{2}\int d\alpha \, \text{tr}\left(\mathbf{P}_\alpha \, \mathbf{W}\right)$

- dielectric-matrix formulation $\qquad E = \frac{1}{2}\int \frac{d\omega}{2\pi} \, \text{tr}\left(\log(\epsilon(i\omega)) + \mathbf{1} - \epsilon(i\omega)\right)$

- plasmon formula $\qquad E = \frac{1}{2}\sum \omega_{\text{RPA}} - \omega_{\text{TDA}}$

- **Ricatti equations** and rCCD $\qquad E = \frac{1}{2}\text{tr}(\mathbf{BT})$

+Approximations (in each formulations, for each flavors...) **SOSEX**, **RPAx-SO2**

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Full-range DFT + RPA

DFT calculation followed by an **RPA calculation with KS orbitals and energies**.

$$E^{\text{DFT}} = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hxc}}[n_{\Phi}] \right\}$$

$$E = \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} | \Phi \rangle + E_{\text{Hx}}^{\text{HF}}[\Phi] + E_{\text{c}}^{\text{RPA}}$$

- DFT (LDA/GGA/...) do not describe correctly the **long-range dispersion forces**, while RPA does .

- Still problems with: **short-range correlation energies** (far too negative)
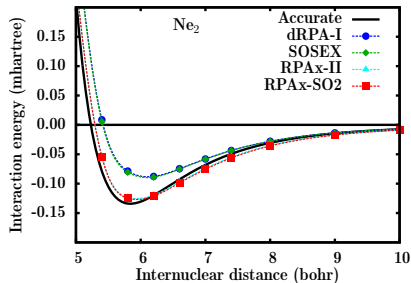 strong dependence on basis size
  simple van der Waals dimers
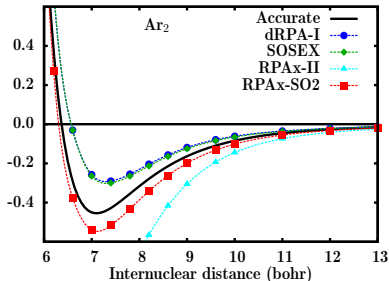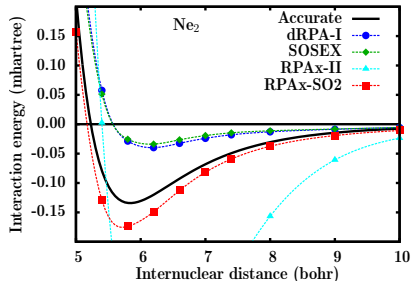
>PBE, aug-cc-pV6Z

[Toulouse,Zhu,Savin,Jansen,Ángyán JCP **135** (2011)]

Range-Separated Hybrid + RPA

Hybrid **DFT** with exact HF exchange and RPA correlation, both at **long-range**.

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

▸ Range separation greatly **improves RPA** (see **srPBE+RPAx-SO2**).

▸ Basis dependence is reduced.
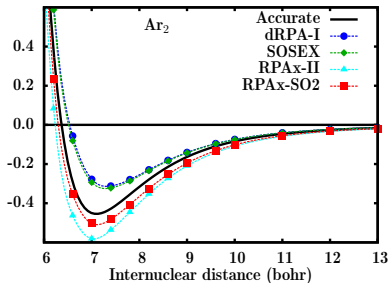
>srPBE, aug-cc-pV6Z, $\mu = 0.5$ [Toulouse,Zhu,Savin,Jansen,Ángyán JCP **135** (2011)]

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- ▶ Range separation greatly **improves RPA** (see **srPBE+RPAx-SO2**).
- ▶ Basis dependence is reduced.
- ▶ for ex.: performance on the S22 dataset is very good for **srPBE+RPAx-SO2**.

>srPBE, aug-cc-pVDZ, $\mu = 0.5$ [Toulouse,Zhu,Savin,Jansen,Ángyán JCP **135** (2011)]
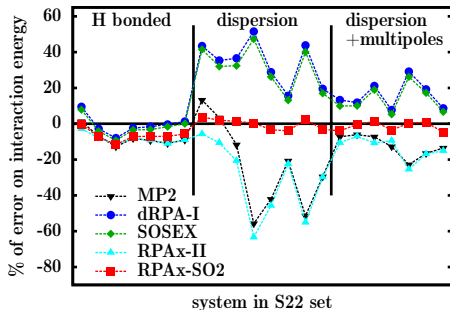
New developments

DFT+WFT

- ▶ **Basis Set Convergence** study
  and **Three-point extrapolation scheme**.

- ▶ **Spin-Unrestricted generalization**
  and **Calculations on DBH24/08 and AE49**.

- ▶ Development and Implementation of
  the **gradients of RSH+RPA methods**.

In general

- ▶ Development of **Localized Virtual Orbitals**
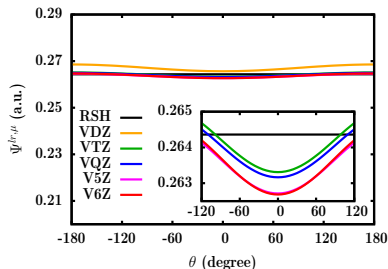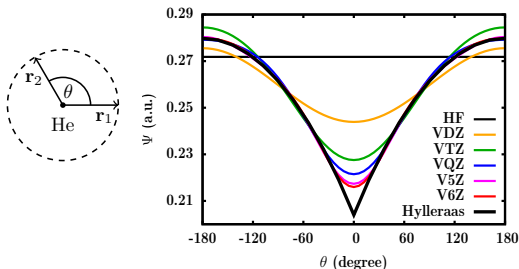 and **Application for RPA calculations**.

WFT+QMC

- ▶ Implementation of the calculation
  of **weights of VB structures in QMC**.

Wavefunction basis convergence   [Gori-Giorgi,Savin PRA **73** (2006)]

Both **partial wave** and **principal number** expansions
lead to **exponential convergence** of the wavefunction.

Extrapolation formula for total energies
We proposed a **three-point extrapolation scheme** for total RSH+correlation energies
(fitting $E_X = E_\infty + B\exp(-\beta X)$).

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

>errors (mHartree) wrt. cc-pV6Z

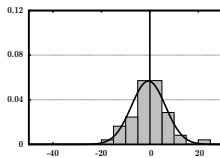|	He	Ne	N_2	H_2O
ΔE_D	8.488	74.523	51.581	55.850
ΔE_T	0.781	20.337	13.406	14.736
ΔE_Q	0.245	5.763	4.090	4.499
ΔE_5	0.078	0.751	0.810	0.726
ΔE_{DTQ}	0.205	0.401	1.083	1.105
ΔE_{TQ5}	0.002	-1.876	-0.972	-1.475

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

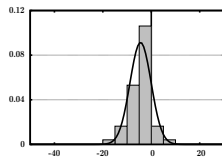Normal distributions of errors (kcal/mol) of calculations on **AE49**.

▶ Mean errors of post-RSH calculation are better.

▶ Post-RSH calculations dist. of errors have sharper distributions .

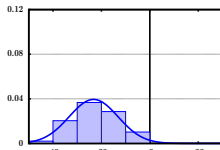Similar results were obtained on the **DBH24/08** dataset.

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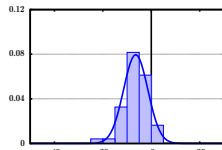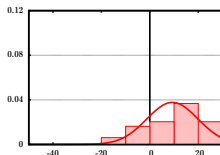

HF+MP2   RSH+MP2

HF+dRPA-I   RSH+dRPA-I
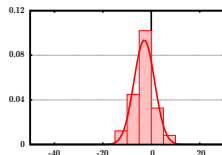
HF+RPAx-SO2   RSH+RPAx-SO2
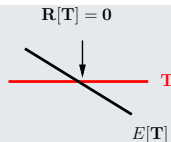
>cc-pVQZ (post-RSH: srPBE, $\mu = 0.5$)

Analytical Gradients: Lagrangian formalism [BM,Szalay,Ángyán JCTC **10** (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 $\mathbf{T}$: $\mathbf{R}[\mathbf{T}] = 0$

$$\frac{d E}{d \kappa} = \frac{\partial E}{\partial \kappa} + \frac{\partial E}{\partial \mathbf{V}} \frac{\partial \mathbf{V}}{\partial \kappa} + \boxed{\frac{\partial E}{\partial \mathbf{T}} \frac{\partial \mathbf{T}}{\partial \kappa}} \qquad \left(\text{in } \frac{\partial E}{\partial \kappa} \text{ there is } \mathbf{h}^{(\kappa)}, (\mu\nu|\sigma\rho)^{(\kappa)} \text{ and } \mathbf{S}^{(\kappa)} \right)$$

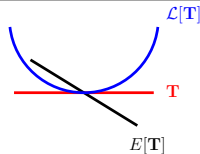**For non-variational methods**

The solution is to work with an **alternative object** that **is variational** :
$$\mathcal{L}[\kappa, \mathbf{V}, \mathbf{T}, \boldsymbol{\lambda}] = E[\kappa, \mathbf{V}, \mathbf{T}] + \text{tr}(\boldsymbol{\lambda} \mathbf{R}[\mathbf{T}])$$

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

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

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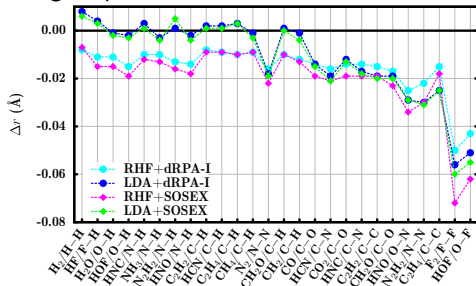

For **RSH+RPA** the energy is: $E = \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}^{\text{lr}} | \Phi \rangle + E_{\text{Hxc}}^{\text{sr}}[n_\Phi] \right\} + E_{\text{c}}^{\text{lr,RPA}}$

The **equations were derived** (sr and lr terms) and **implemented** in MOLPRO.
(based on RSH+MP2 of [Chabbal, Stoll, Werner, Leininger, MP **108** (2010)])

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
LDA+dRPA-I	0.013
RHF+SOSEX	0.021
LDA+SOSEX	0.014
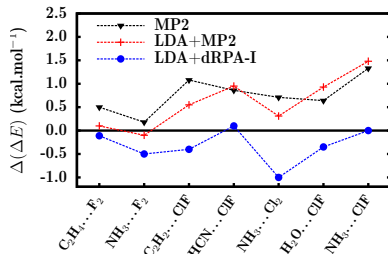
Intermonomer distances
> aug-cc-pVTZ

| Interaction Energies		Intermonomer distances	
MP2	0.76	MP2	0.075
LDA+MP2	0.63	LDA+MP2	0.053
LDA+dRPA-I	0.35	LDA+dRPA-I	0.023
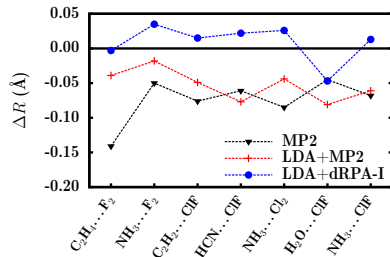
The objective is to construct a set of **localized virtual orbitals** by multiplying the set of occupied Localized Molecular Orbitals (LMOs) with **solid spherical harmonic functions**. The orthogonality to the occupied space is ensured by **projection**.
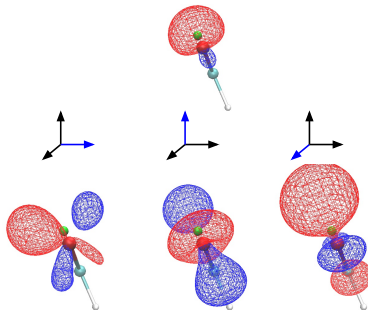
Dipolar oscillator orbital [Foster, Boys RMP **32** (1960)]

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

C-H bond in CH_2O:
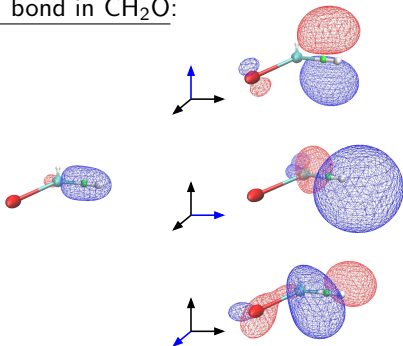
Lone pair in CH_2O:

Dipolar oscillator orbital

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

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:

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

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

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

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

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

A **nice result** simplifies the equations:

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

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

The working equations are the local RPA Ricatti equations (*i.e.* local rCCD) with the **local excitation approximation** ($\mathbf{M}^{ij}_{k_\alpha l_\beta} \to \mathbf{M}^{ij}_{i_\alpha j_\beta} \doteq \mathbf{M}^{ij}_{\alpha\beta}$) and **spherical average approximation** ($\mathbf{M}^{ii}_{\alpha\beta} \to \delta_{\alpha\beta} \frac{1}{3} \sum \mathbf{M}^{ii}_{\alpha\alpha} \doteq \delta_{\alpha\beta} \frac{1}{3} m^i$).

RPA correlation energy

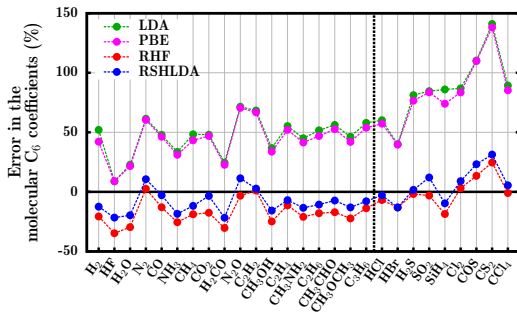$$E_c^{\text{RPA,lr}} = \sum_{ij}^{occ} \frac{4}{9} s^i s^j \operatorname{tr}\left(\mathbf{L}^{ij}\mathbf{T}^{ij}\right)$$

where $\mathbf{R}^{ij} = \cdots = \mathbf{0}$

C_6 coefficients

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

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

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

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

	LDA	59.8
MA%E	PBE	56.7
	RHF	15.2
	RSHLDA	11.8

VB-QMC: Motivation

VB-SCF (VB structures = Lewis structures)

- ✔ Good dissociation energies

- ✔ Interpretative tools (weight of structures, ...)

- ✘ **Non-orthogonal orbitals** -> costly

- ✘ Introduce dynamical correlation by "**breathing**"
  (L-BO-, S-BO-, SD-BOVB) -> costly

VB-QMC in the hope of treating **big systems**

$$\Psi = e^J \left(\; \overset{\frown}{\bigcirc\!-\!\bigcirc} \; + \; \odot \quad \bigcirc \; + \; \bigcirc \quad \odot \; \right)$$

- ▶ Static correlation taken care of by VB.

- ▶ Non-orthogonality of orbitals is not an issue for QMC.

- ▶ Dynamical correlation hopefully taken care of by Jastrow.

- ▶ But: **we wish to conserve the interpretative tools**,
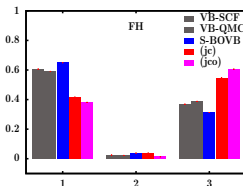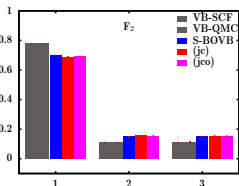 *i.e.* the weights (and the calculation of separated structure).
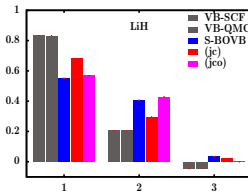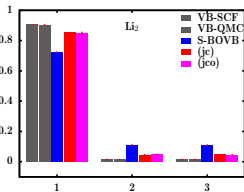
WFT as input for QMC

VB-QMC: weights of VB structures

We wish to transfer the weights of structures to VB-QMC.

Chirgwin-Coulson weights $w_i = \dfrac{\sum_j c_i c_j S_{ij}}{\sum_{ij} c_i c_j S_{ij}}$ and **Löwdin** weights $w_i = \dfrac{(\sum_j c_j (S^{\frac{1}{2}})_{ji})^2}{\sum_i (\sum_j c_j (S^{\frac{1}{2}})_{ji})^2}$

In both cases, S_{ij} needs to be computed, *via* $S_{ij} = \displaystyle\int d\mathbf{R} \; \dfrac{\Psi_i(\mathbf{R})}{\Psi_0(\mathbf{R})} \dfrac{\Psi_j(\mathbf{R})}{\Psi_0(\mathbf{R})} \Psi_0^2(\mathbf{R})$

✔ **VB-QMC = VB-SCF**

Li$_2$: mainly covalent character ionic too important in BOVB (structures are mixing)

F$_2$: Jastrow very similar to BO no mixing of structures

It is unclear if the VB weights are the referent ones (when there is a too preponderant structure, mixing occurs).

Other Works

All (and more) is implemented in the **Quantum Chemistry Package** MOLPRO

Fractional occupation number calculations
and **Instabilities in the RPA problem**.

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

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  Dario Rocca

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