Fractional Occupation Numbers : Early Thoughts

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Remember $\hat{H}|\Psi\rangle = E|\Psi\rangle$

$$n(\mathbf{r}_1) = \int d\mathbf{r}_2 \ldots d\mathbf{r}_N \;\; \Psi(\mathbf{r}^N)\Psi^\dagger(\mathbf{r}^N)$$

- Focus on $\Psi(\mathbf{r}^N)$

  Wavefunction methods (WF)

  Random Phase Approximation

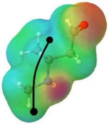
- Focus on the density $n(\mathbf{r}_1)$

  Density Functional Theory

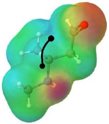
  approximations for $E_{xc}[n]$

- Rigourously mix the two

  Range separation (*e.g.* RSH)



versus



Daily work

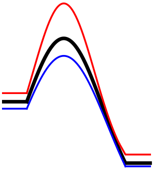
- Methodology developments and systematic analysis
- Implementation (software called `MOLPRO`)

Current centers of interest

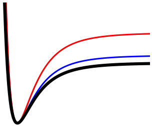
- Systematic exploration of the RPA formalism**s**
- Basis set convergence properties
  of the wavefunction Ψ and of the energy E (Odile)
- Spin-unrestricted version of all (RSH+)RPA variants
  access to atomisation energies and energy barrier heights
- Fractional occupation numbers

Fractional Occupation Numbers : Motivation (some failures of $E_{xc}[n]$)

- Barrier heights energies
- Dissociation of molecules



and



Fractional Occupation Numbers : Motivation (usual explanations)

- Self-Interaction error (SIE)

  one-electron point of view (also : N-SIE)

  spurious interaction of the electron with itself

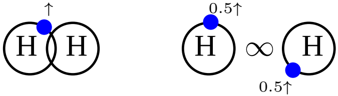
  (De)localisation error

- Static correlation error (SCE)

  multi-determinantal picture

Fractional Occupation Numbers : Origins

- Study of systems with a non-integer charge



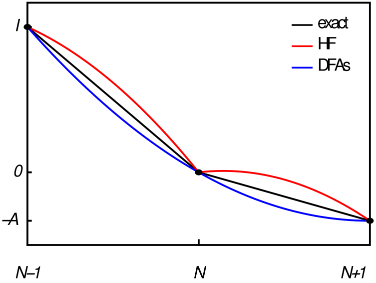
- $E^{N+\delta} = \min_{\hat{\Gamma}\to N+\delta} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \hat{V}_{\mathrm{ext}} + \hat{V}_{\mathrm{ee}}\right)\right]$

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

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

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

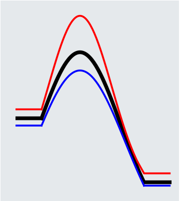
E is piecewise linear wrt N and
has a derivative discontinuity at integer N



- $E^{N+\delta} = \min_{\hat{\Gamma}\to N+\delta} \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \hat{V}_{\mathrm{ext}}\right) + E_{Hxc}[n_{\hat{\Gamma}}]\right]$

$$\hat{\Gamma}_s^{N+\delta} = (1-\delta)\hat{\Gamma}_s^{N,\delta} + (\delta)\hat{\Gamma}_n^{N+1,\delta}$$

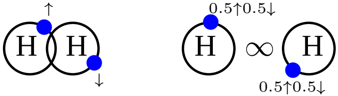
$$n^{N+\delta}(\mathbf{r}) = \sum f_i\,|\phi_i^{N+\delta}(\mathbf{r})|^2$$



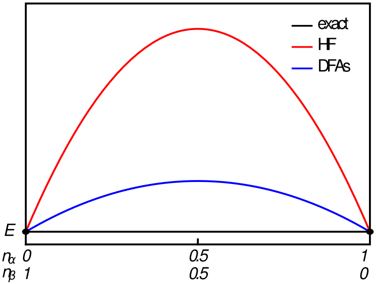
Mori-Sánchez, Cohen, Yang JCP **125** 2006

Fractional Occupation Numbers : Origins

- Study of systems with a non-integer spin

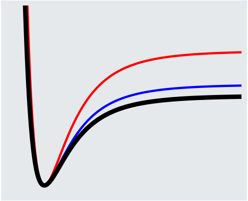


- Systems with fractional occupation of degenerate spin states should have the same energy as the integer-spin states



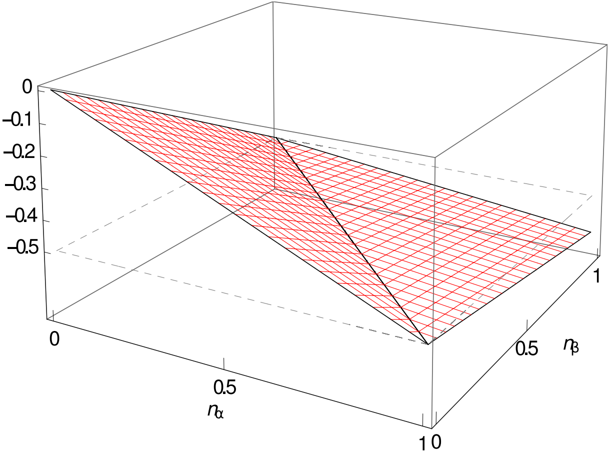
- Constancy condition

$$E\left[\sum c_i n_i\right] = E[n] = E(N)$$



Cohen, Mori-Sánchez, Yang JCP **129** 2008

Fractional Occupation Numbers : Unified vision $H[n_\alpha, n_\beta]$



Flat-plane condition

Mori-Sánchez, Cohen, Yang PRL **102** 2009

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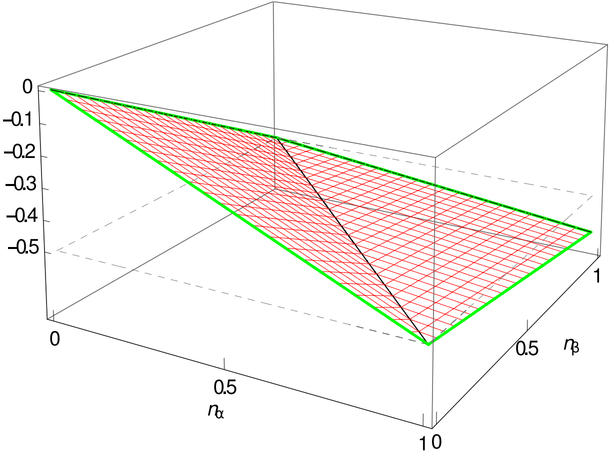

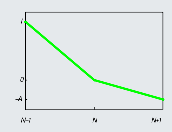

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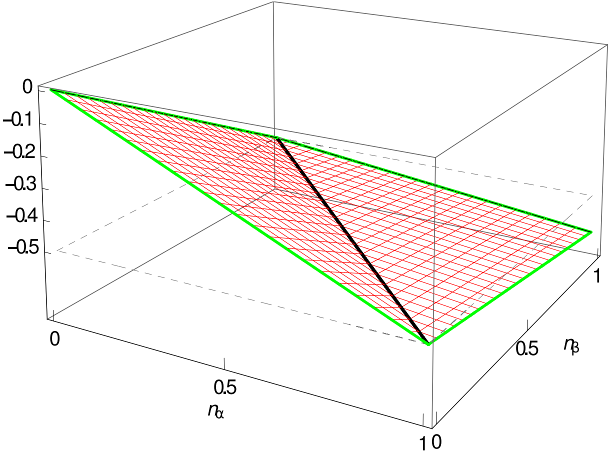

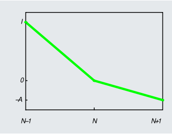

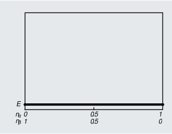

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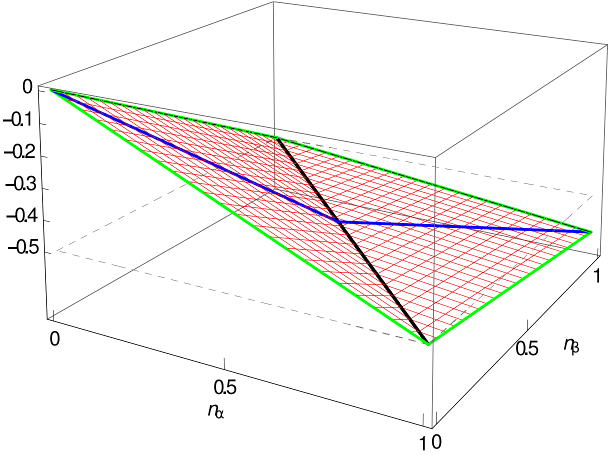

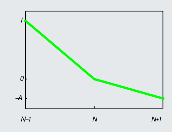

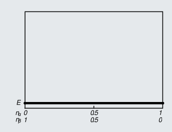

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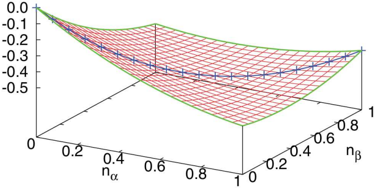
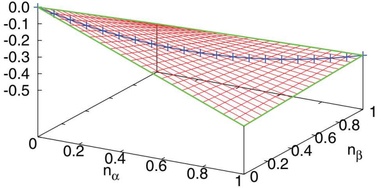


dRPA-I

- remarkably good with the constancy condition (good atomisation energies ?)
- extremely convex behavior delocalization error (bad barrier heights ?)

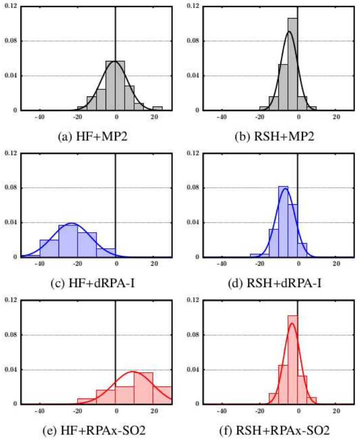


RPAx-II

- no massive delocalization error (good barrier heights ?)
- no longer satisfy constancy condition (bad atomisation energies ?)

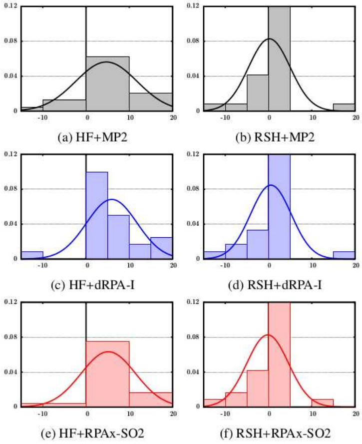
Mori-Sánchez, Cohen, Yang PRA **85** 2012

AE49



- 49 atomisation energies

DBH24/08



- 24 barrier heights energies (forward and reverse)

generally quite good results, especially with RSH !

Mussard,Reinhardt,Ángyan,Toulouse *draft*

SCF (simple change in the density matrix) $n^{N+\delta}(\mathbf{r}) = \sum f_i \, |\phi_i^{N+\delta}(\mathbf{r})|^2$

RPA (simple change in the Green's function)

- BUT : it imposes that the partially occupied orbitals be treated as partially uncoccupied orbitals too

$n_{\text{occ.}} = n_{\text{full}} + n_{\text{partial}}$ $n_{\text{virt.}} \to n_{\text{partial}} + n_{\text{unocc.}}$

- this change of dimensions is a problem because :

SCF Hessian	RPA matrix	RPA matrix	"Hessian"
$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}$	$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix}$	$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix}$	$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix}$

$(f+p).u = fu+pu$

$(f+p).(p+u) = fp+fu+pp+pu$

size of the optimisation space

Yang, Mori-Sánchez, Cohen JCP **139** 2013

SCF (simple change in the density matrix) $\quad n^{N+\delta}(\mathbf{r}) = \sum f_i \, |\phi_i^{N+\delta}(\mathbf{r})|^2$

optimisation *via* unitary transformation :

$$exp(\hat{\kappa}) \begin{pmatrix} I_{ff} & 0 & 0 \\ 0 & F_{pp} & 0 \\ 0 & 0 & 0 \end{pmatrix} exp(-\hat{\kappa}) \qquad \text{with :} \quad \hat{\kappa} = \begin{array}{c} \begin{array}{ccc} \overbrace{\text{full}} & \overbrace{\text{partial}} & \overbrace{\text{unocc.}} \end{array} \\ \begin{pmatrix} 0 & 0 & -\kappa_{fu}^{\dagger} \\ 0 & 0 & -\kappa_{pu}^{\dagger} \\ \kappa_{fu} & \kappa_{pu} & 0 \end{pmatrix} \end{array}$$

What should be done :

$$exp(\hat{\kappa}) \begin{pmatrix} I_{ff} & 0 & 0 \\ 0 & \mathcal{F}_{pp} + \kappa_{pp} & 0 \\ 0 & 0 & 0 \end{pmatrix} exp(-\hat{\kappa}) \qquad \text{with :} \quad \hat{\kappa} = \begin{array}{c} \begin{array}{ccc} \overbrace{\text{full}} & \overbrace{\text{partial}} & \overbrace{\text{unocc.}} \end{array} \\ \begin{pmatrix} 0 & -\kappa_{fp}^{\dagger} & -\kappa_{fu}^{\dagger} \\ \kappa_{fp} & 0 & -\kappa_{pu}^{\dagger} \\ \kappa_{fu} & \kappa_{pu} & 0 \end{pmatrix} \end{array}$$

- rotation between full and partial should be permitted, *via* κ_{pu}
- F_{pp} is a diagonal matrix filled with fixed fractional occupation numbers
  $\mathcal{F}_{pp} + \kappa_{pp}$ is a general, optimised, matrix
  i.e fractional occupation numbers should be variational

Cancès, Kudin, Scuseria, Turinici JCP **118** 2003