

# Correlated electron calculations with Hartree-Fock scaling\*

Roberto Car  
Princeton University



*ES2013, William & Mary, June 12 2013*

\* Collaboration with R. Gebauer (ICTP) and M.H. Cohen (Rutgers & Princeton)

RC and MHC acknowledge support from DOE-BES

# SUMMARY

- Introduction
- OP-NOFT: conceptual basis
- Results on simple molecular systems
- Conclusions

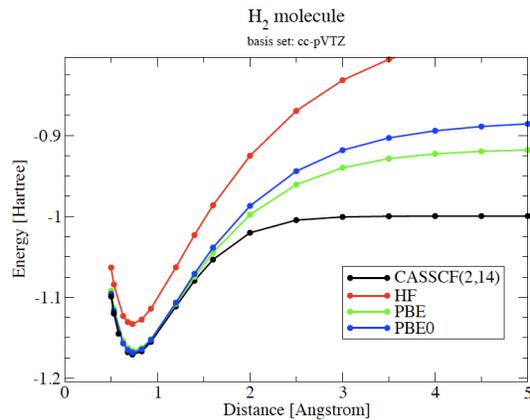
# Introduction

- Reducing the complexity of the many-body electron problem significantly below that of the wavefunction has been a major goal since the early days of QM
- The most successful realization of this program has been obtained with DFT (Kohn, Hohenberg and Sham):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \leftrightarrow \psi_i(\mathbf{r}) \quad (i = 1, \dots, N)$$

- However, difficulties limit the accuracy of DFT: xc-functional approximation (self-interaction error, strong correlations)

Conceptually DFT difficulties can be attributed to the Mean Field form of the theory



From Mulliken (1928) to Heitler-London (1927)  
(1 determinant to 2 determinant)

KS orbitals: 
$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i \text{ occ}} \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}')$$

Misses entanglement due to correlations:

Natural orbitals (NO): 
$$\rho(\mathbf{r}, \mathbf{r}') = \sum_i n_i \varphi_i(\mathbf{r}) \varphi_i^*(\mathbf{r}')$$

Different ways to overcome the difficulties have been explored:

- 1-DM functional theories: NO and occupation numbers (NOFT) face a similar difficulty of DFT with xc-functional of the 1-DM
- 2-DM functional theories: the functional is known explicitly but one has to deal with the N-representability problem (in principle QMA hard)

# Occupation probabilities-natural orbital functional theory (OP-NOFT) (with R. Gebauer (ICTP) and M.H. Cohen (Rutgers & Princeton))

- Retain conceptual simplicity of single-particle theory by using NO (NSO) (to be determined self-consistently) and their *joint occupation probabilities* (OP) to represent 1-DM ( $\rho$ ) and 2-DM ( $\pi$ )
- Exploit explicit form of the  $N$ -particle wavefunction to get physical insight and devise valuable approximations for  $\pi$  (forward vs inverse approach)

# NSO and seniority

$$\Psi(x_1, x_2, \dots, x_N) = \sum_{\mathbf{n}} C_{\mathbf{n}} \Phi_{\mathbf{n}}(x_1, x_2, \dots, x_N) \quad (\mathbf{n} \equiv n_1 n_2 \dots n_{N/2})$$

$$\Phi_{\mathbf{n}} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \{ \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) \dots \varphi_{n_N}(x_N) \} \quad (\mathbf{n} \equiv n_1 n_2 \dots n_N)$$

- *Pair difference theorem (PDT)*: determinants differ by pairs of NSO
- Limit consideration to *even N global singlet (S=0)*
- The *seniority number A* (G. Racah (1943)) is the number of singly occupied states in a Slater Determinant

$\Omega = 0$ ( $n_{ph} = 0$ )	$\Omega = 0$ ( $n_{ph} = 2$ )	$\Omega = 0$ ( $n_{ph} = 4$ )	$\Omega = 0$ ( $n_{ph} = 6$ )	$\Omega = 2$ ( $n_{ph} = 2$ )	$\Omega = 2$ ( $n_{ph} = 3$ )	$\Omega = 4$ ( $n_{ph} = 2$ )	$\Omega = 4$ ( $n_{ph} = 4$ )
—	↑↓	↑↓	↑↓	↑	↑↓	—	↑↓
—	—	—	↑↓	—	↑	↑↓	↑↓
↑↓	↑↓	—	—	—	↑↓	↑↓	↑
↑↓	—	—	—	↑↓	—	↑	↑↓
↑↓	↑↓	↑↓	—	↑↓	↑↓	↑↓	—

If in the ground state all NSO are occupied (however small their occupation) in the  $A=0$  sector, *only seniorities  $A=4n$  are allowed by PDT*, i.e.  $A=0, 4, \dots$  ( $A=0$ : pairs only,  $A=4$ : 2 broken pairs, ...)

Consequences:

- Convergence in seniority is faster with NSO
- For 2 electrons  $A=0$  is exact

# 1-DM

$$\rho(x', x) = N \int dx_2 \cdots dx_N \Psi(x', x_2, \cdots, x_N) \Psi^*(x, x_2, \cdots, x_N)$$

$$\rho(\mathbf{r}', \mathbf{r}) = 2 \sum_k p_1(k) \phi_k(\mathbf{r}') \phi_k(\mathbf{r})$$

$$p_1(k) \equiv \sum_{\mathbf{n}} C_{\mathbf{n}}^2 \nu_{k, \mathbf{n}}$$

$$0 \leq p_1(k) \leq 1 \text{ and } \sum_k p_1(k) = N$$

## 2-DM

$$\pi(x'_1, x'_2; x_1, x_2) = N(N-1) \int dx_3 \cdots dx_N \Psi(x'_1, x'_2, \cdots, x_N) \Psi^*(x_1, x_2, \cdots, x_N),$$

$$\begin{aligned} \pi(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) &= \pi^d(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) + \pi^{od}(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) \\ \pi^d(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) &= 2 \sum_{ij} p_{11}(ij) [2\phi_i(\mathbf{r}'_1)\phi_j(\mathbf{r}'_2)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2) \\ &\quad - \phi_i(\mathbf{r}'_1)\phi_j(\mathbf{r}'_2)\phi_j(\mathbf{r}_1)\phi_i(\mathbf{r}_2)] \\ \pi^{od}(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) &= \sum_{i \neq j} \sum_{\mathbf{k}} s(i\mathbf{k})s(j\mathbf{k})p_{11\dots 1}^{1/2}(i\mathbf{k})p_{11\dots 1}^{1/2}(j\mathbf{k}) \\ &\quad \phi_i(\mathbf{r}'_1)\phi_i(\mathbf{r}'_2)\phi_j(\mathbf{r}_1)\phi_j(\mathbf{r}_2). \end{aligned} \quad (5)$$

$$\begin{aligned} p_{11}(ij) &\equiv \sum_{\mathbf{n}} C_{\mathbf{n}}^2 \nu_{i,\mathbf{n}} \nu_{j,\mathbf{n}} \\ &\sup(p_1(i) + p_1(j) - 1, 0) \leq p_{11}(ij) \leq p_1(<) \\ &\sup(p_1(i) + p_1(j) + p_1(k) - 1, 0) \leq p_{11}(ij) + p_{11}(ik) + p_{11}(jk) \\ &2 \sum_{j(\neq i)} p_{11}(ij) = (N-2)p_1(i). \end{aligned} \quad (6)$$

$$p_{11\dots 1}(i\mathbf{k}) \equiv C_{i\mathbf{k}}^2$$

Complexity is in  $\pi^{od}$

## Complexity is reduced in 2 steps

$$\pi^{od}(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j} \sum_{\mathbf{k}} s(i\mathbf{k})s(j\mathbf{k})p_{11\dots 1}^{1/2}(i\mathbf{k})p_{11\dots 1}^{1/2}(j\mathbf{k}) \phi_i(\mathbf{r}'_1)\phi_i(\mathbf{r}'_2)\phi_j(\mathbf{r}_1)\phi_j(\mathbf{r}_2). \quad (5)$$

$$s(i\mathbf{k}) = s(i) \quad s(j\mathbf{k}) = s(j)$$

Sign Rule:  $s(i) = s(j) = -1$  if  $i, j \leq N/2$ ;  $s(i) = 1, s(j) = -1$  if  $i \leq N/2, j > N/2$

or vice versa;  $s(i) = s(j) = -1$  if  $i, j > N/2$

Scalar product:  $\sum_{\mathbf{k}(\neq ij)} p_{11\dots 1}^{1/2}(i\mathbf{k})p_{11\dots 1}^{1/2}(j\mathbf{k}) = p_{10}^{1/2}(ij)p_{01}^{1/2}(ij)\xi(ij)$  with  $0 \leq \xi(ij) \leq 1$

$$p_{10}(ij) \equiv \sum_{\mathbf{n}} C_n^2 v_{n,i}(1 - v_{n,j}) = \sum_{\mathbf{k}(\neq ij)} p_{11\dots 1}(i\mathbf{k}) \quad \text{A 2-state OP!}$$

So far everything is exact (for  $A=0$ ), or at least variational; all the complexity is in  $\xi(ij)$

$$\xi(ij) = \frac{\sum_{\mathbf{k}(\neq ij)} p_{11\dots 1}^{1/2}(i\mathbf{k})p_{11\dots 1}^{1/2}(j\mathbf{k})}{\left(\sum_{\mathbf{k}(\neq ij)} p_{11\dots 1}(i\mathbf{k})\right)^{1/2} \left(\sum_{\mathbf{k}(\neq ij)} p_{11\dots 1}(j\mathbf{k})\right)^{1/2}} \implies \xi(ij) \simeq \frac{\sum_{\mathbf{k}(\neq ij)} p_{11}^{1/2}(i\mathbf{k})p_{11}^{1/2}(j\mathbf{k})}{\left(\sum_{\mathbf{k}(\neq ij)} p_{11}(i\mathbf{k})\right)^{1/2} \left(\sum_{\mathbf{k}(\neq ij)} p_{11}(j\mathbf{k})\right)^{1/2}}$$

## Approximate 2-DM satisfies:

$$\int d\mathbf{r}_2 \pi(\mathbf{r}', \mathbf{r}_2; \mathbf{r}, \mathbf{r}_2) = (N - 1)\rho(\mathbf{r}, \mathbf{r}') \text{ and}$$
$$\int d\mathbf{r}_1 d\mathbf{r}_2 \pi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)w(r_{12}) \geq 0,$$

## (A=0) OP-NOFT functional

$$E = 2 \sum_i h_{ii} p_1(i) + \sum_{ij} p_{11}(ij) [2J_{ij} - K_{ij}] + \sum_{i \neq j} p_{10}^{1/2}(ij) p_{01}^{1/2}(ij) s(i) s(j) \xi(ij) K_{ij}$$

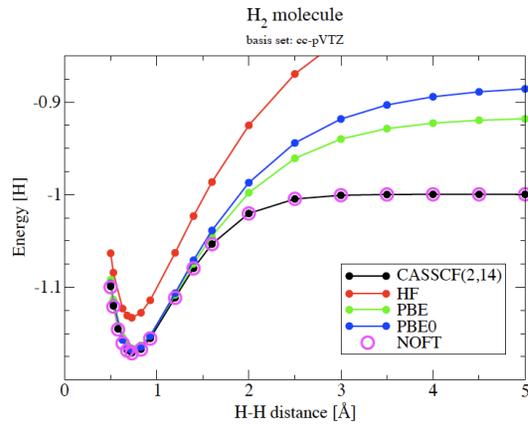
$$J_{ij} \equiv \langle \varphi_i \varphi_j | v | \varphi_i \varphi_j \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2)}{r_{12}}$$

$$K_{ij} \equiv \langle \varphi_i \varphi_j | v | \varphi_j \varphi_i \rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) \varphi_j(\mathbf{r}_1) \varphi_i(\mathbf{r}_2)}{r_{12}}$$

Computational cost scales with size like HF energy minimization (but with a larger prefactor due to the larger number of NO that need to be included)

The infimum of  $E$  subject to constraints and sum rules gives the ground state energy. It can be found via damped CP dynamics (Car and Parrinello 1985):

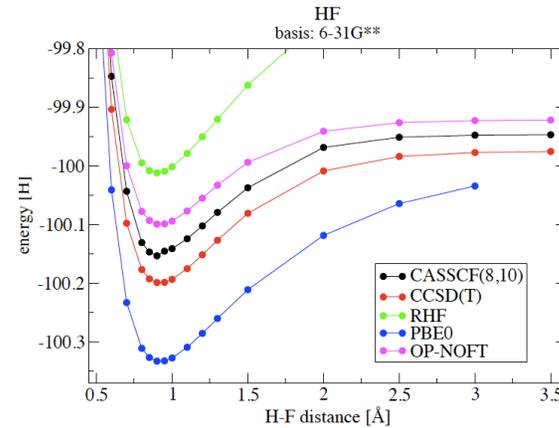
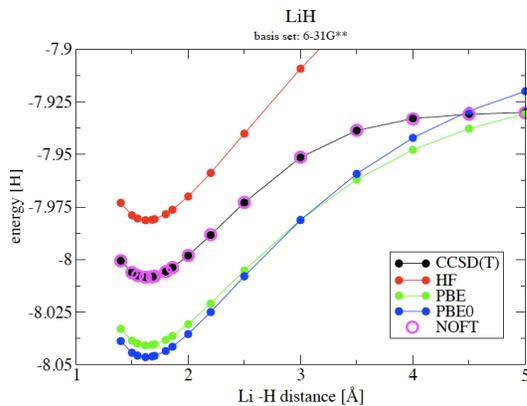
# How well does it work?



2 electrons

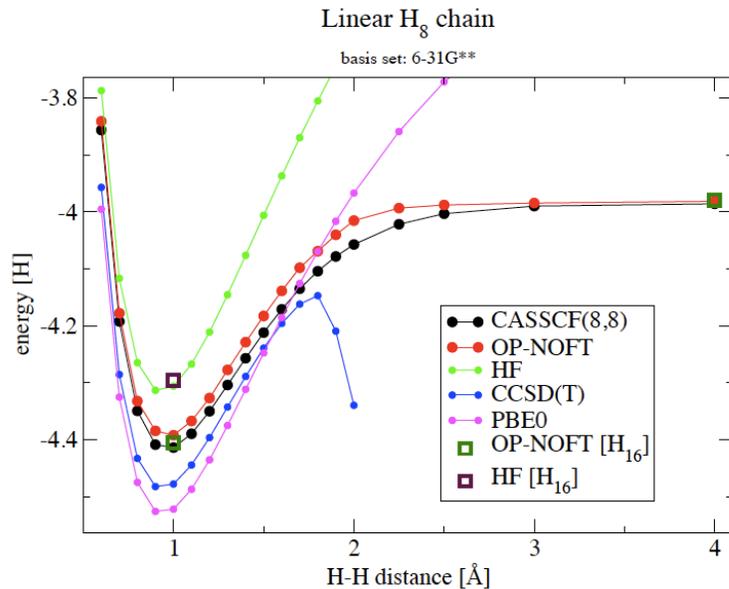
For 2 electrons  $A=0$  is exact and our formula reduces to the exact Lowdin-Shull (1958) form (which depends only on 1-OP)

For 4 electrons  $\xi$  is exact but  $A=0$  is not



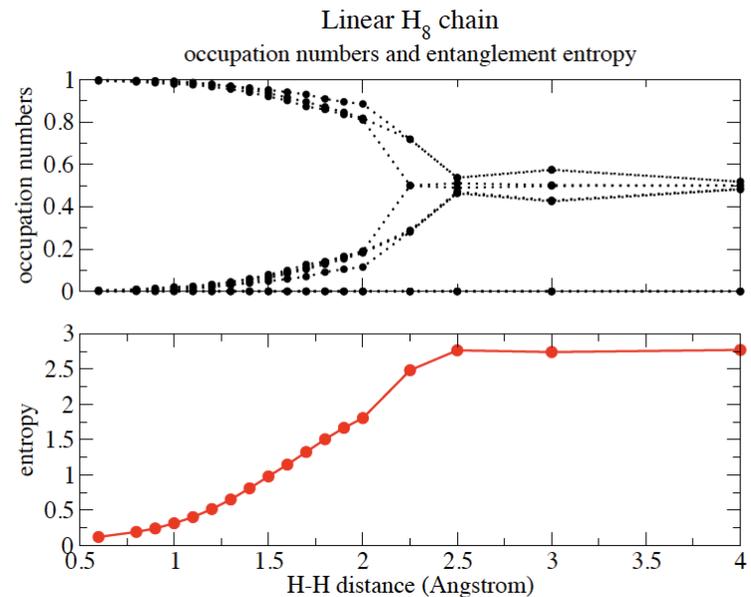
10 electrons: the first serious test of the approximations

# A more challenging case: H<sub>8</sub>

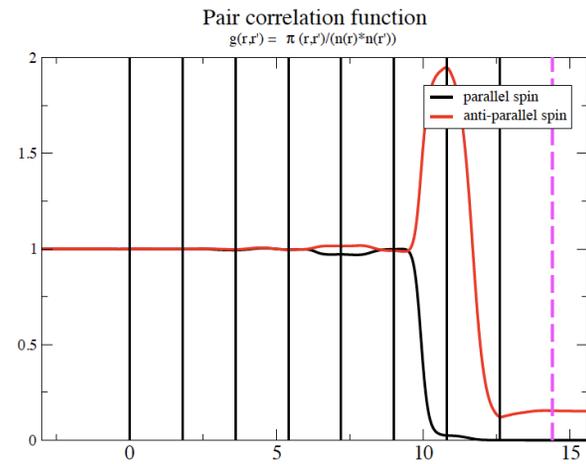
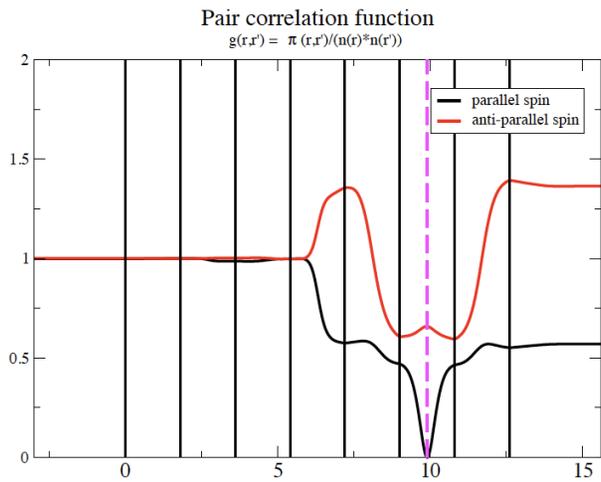
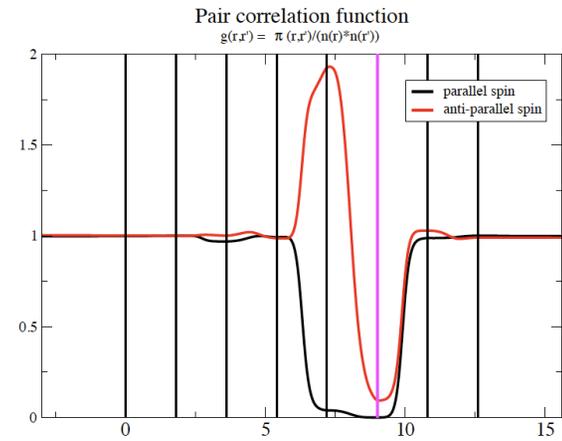
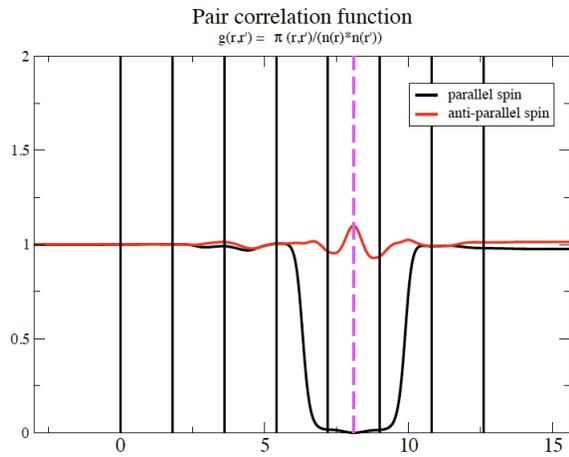


Symmetric dissociation curve

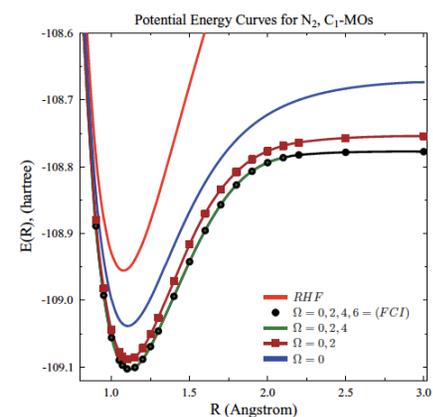
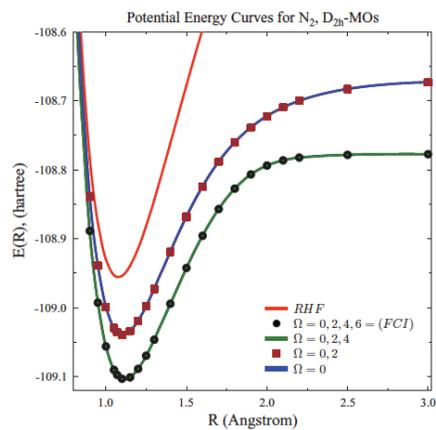
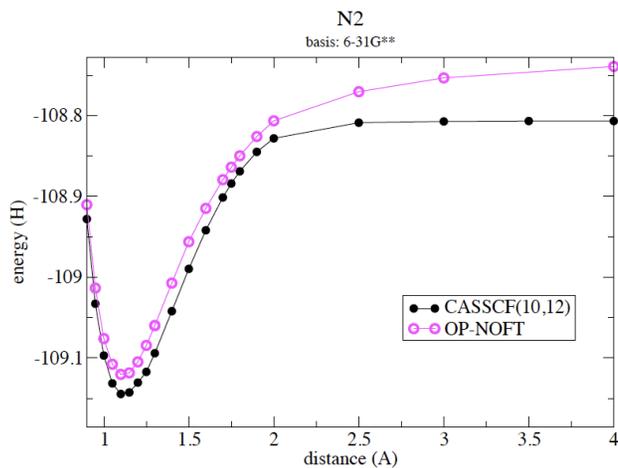
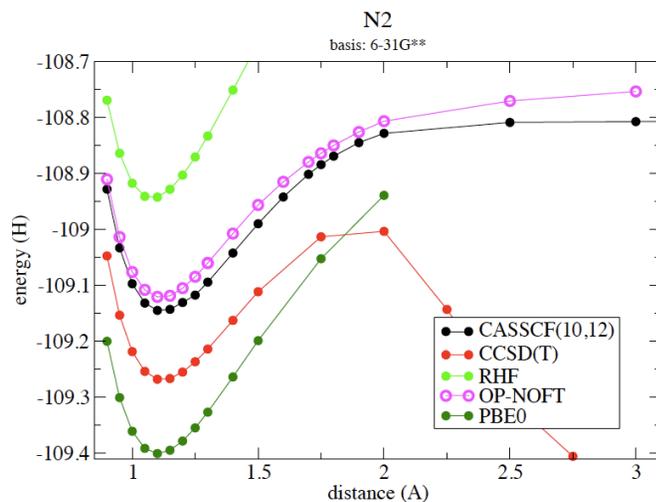
The importance of correlation can be gauged from the occupation numbers and the Von Neuman entanglement entropy



# e-e pair correlations



# N<sub>2</sub>: an even more challenging case



From G. Scuseria and co. *JCP* (2011)

# Concluding remarks

- Beyond  $A=0$ :  $A=4$  contribution could be added perturbatively or fully self-consistently. This would retain polynomial scaling but with higher power than HF.
- Energy functional minimization: forces on nuclei, structural optimization, *ab-initio* MD
- Applications to condensed matter, e.g homogeneous electron liquid: would correlation be described appropriately? Wigner transition? What about Mott insulators?
- Models with an effective attractive (instead of repulsive) interaction: The sign analysis would need reconsideration. Would the approximation that we make on the 2-DM still keep the possibility of a macroscopic eigenvalue (pairing): how would that appear in the structure of the 2-DM?