On the effect of electron correlation in 3-RDM approximations

M. Rodríguez-Mayorga, E. Ramos-Cordoba, F. Feixas and E. Matito

Debrecen September 2, 2015

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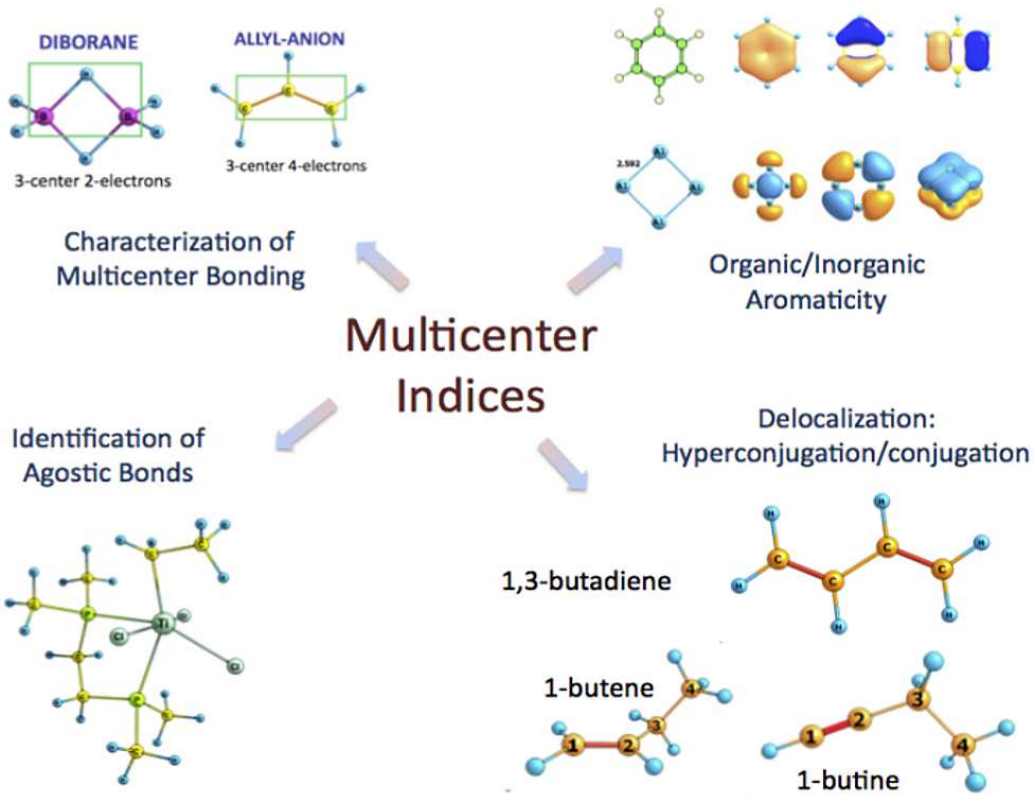
IKERBASQUE

MCI I

$$\delta(A,B,C,...,Z) = \frac{(-2)^{n-1}}{(n-1)!} < (\widehat{N_A} - \overline{N_A})(\widehat{N_B} - \overline{N_B})(\widehat{N_C} - \overline{N_C})...(\widehat{N_Z} - \overline{N_Z}) >$$

$$\text{where } < \widehat{N_A} >= \overline{N_A}$$



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$$- 2 < \widehat{N_B}\widehat{N_C} > \overline{N_A} + 4\overline{N_A N_B N_C}$$

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For two centers we needed the $^{2}\mathbf{D}$, for three centers we need $^{3}\mathbf{D}$,...,for n centers we need the $^{n}\mathbf{D}$

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WE CAN TEST $^{\mathbf{3}}\mathbf{D}$ APPROXIMATIONS!
COMPARING $\delta(A,B,C)^{EXACT}$ WITH THE $\delta(A,B,C)^{APPX}$[1]

[1] We test a piece of the diag. part of the $^{\mathbf{3}}\mathbf{D}$ since we substrac terms of the $^{\mathbf{2}}\mathbf{D}$ and $^{\mathbf{1}}\mathbf{D}$

^{3}D approximations I

- HF:

$$ {}^3D^{lmn}_{ijk} = \begin{vmatrix} D_i{}^l & D_i{}^m & D_i{}^n \\ D_j{}^l & D_j{}^m & D_j{}^n \\ D_k{}^l & D_k{}^m & D_k{}^n \end{vmatrix} $$

in diagonal representation of the ^{1}**D** and defining $S_{ij}(A) = \int_A \psi_i(1)\psi_j(1)d1$:

$$ \widetilde{\delta}(A,B,C) = 2\sum_{i,j,k} n_i n_j n_k S_{ij}(A) S_{jk}(B) S_{ki}(C) $$

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- Valdemoro (using Grassman algebra):

$$ {}^3\mathbf{D}^{VAL} = 3!\left[\frac{3}{2}{}^2\mathbf{D} - 2{}^1\mathbf{D}^2\right] \wedge {}^1\mathbf{D} = 9{}^2\mathbf{D} \wedge {}^1\mathbf{D} - 12{}^1\mathbf{D}^3 $$

^{3}D approximations II

- Nakatsuji:

$$[^3D^{NAK}]^{pqs}_{ijk} = [^3D^{VAL}]^{pqs}_{ijk} + \sum_l \sigma_l \widehat{A}(^2\Delta^{pl}_{ij}\ ^2\Delta^{qs}_{lk})$$

  where $^2\mathbf{\Delta} = {}^2\mathbf{D} - {}^1\mathbf{D}^2$ (called the 2-cumulant), $\widehat{A}$ performs the antisymmetric summation of all superindices and all subindices (without mixing superindices and subindices) excluding l and $\sigma_l = 1$ for occupied and -1 otherwise.

- Mazziotti:

$$[^3D^{MAZ}]^{pqs}_{ijk} = [^3D^{VAL}]^{pqs}_{ijk} - \frac{1}{\chi^{pqs}_{ijk} - 3} \sum_l \widehat{A}(^2\Delta^{pl}_{ij}\ ^2\Delta^{qs}_{lk})$$

  where $\chi^{pqs}_{ijk} = {}^1D^i_i + {}^1D^j_j + {}^1D^k_k + {}^1D^p_p + {}^1D^q_q + {}^1D^s_s$

^{3}D approximations III

Taking the natural orbitals representation:

- HF-like ^{3}**D**:

$$\widetilde{\delta}(A,B,C) = 2\sum_{i,j,k} n_i n_j n_k S_{ij}(A) S_{jk}(B) S_{ki}(C)$$

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Feixas, Rodriguez-Mayorga et al. *CTC*, 1053:173 (2015)

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^{3}D approximations IV

WHAT IS THE EFFECT OF CORRELATION IN THIS APPROXIMATIONS?

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Take a simple three-electron system whose correlation can be tuned and analyze it!

Harmonium Atom (HA)

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- Electrons confined on a parabolic potential ($-Z/r$ is replaced by $\frac{1}{2}\omega^2\mathbf{r}^2$) where ω is the confinement strength:

$$H = \sum_i \left(-\frac{1}{2}\nabla^2_{\mathbf{r}_i} + \frac{1}{2}\omega^2\mathbf{r}_i^2 \right) + \sum_{i>j} \frac{1}{r_{ij}}$$

- Model used for testing, calibrating, benchmarking and developing new DFT functionals.

HA (ω's role)

Small-ω region

1) Parabola is open $\rightarrow$ Electrons are far from each other due to $\frac{1}{r_{ij}}$
2) Correlation Rules! **Even more than in atoms!** ($\frac{2}{3}E \approx V_{ee}$)
   Specially long-range correlation.

Large-ω region

1) Electrons are almost like "independent particles"
2) He-like systems correlation lies in the region of $\omega \geq 0.5$ (2eHA).

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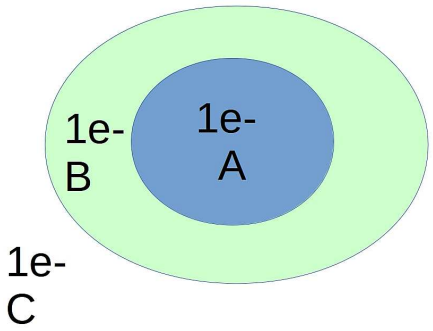
IF WE WORK WITH 3eHA $\rightarrow$ WE CAN COMPUTE $^3\mathbf{D}$

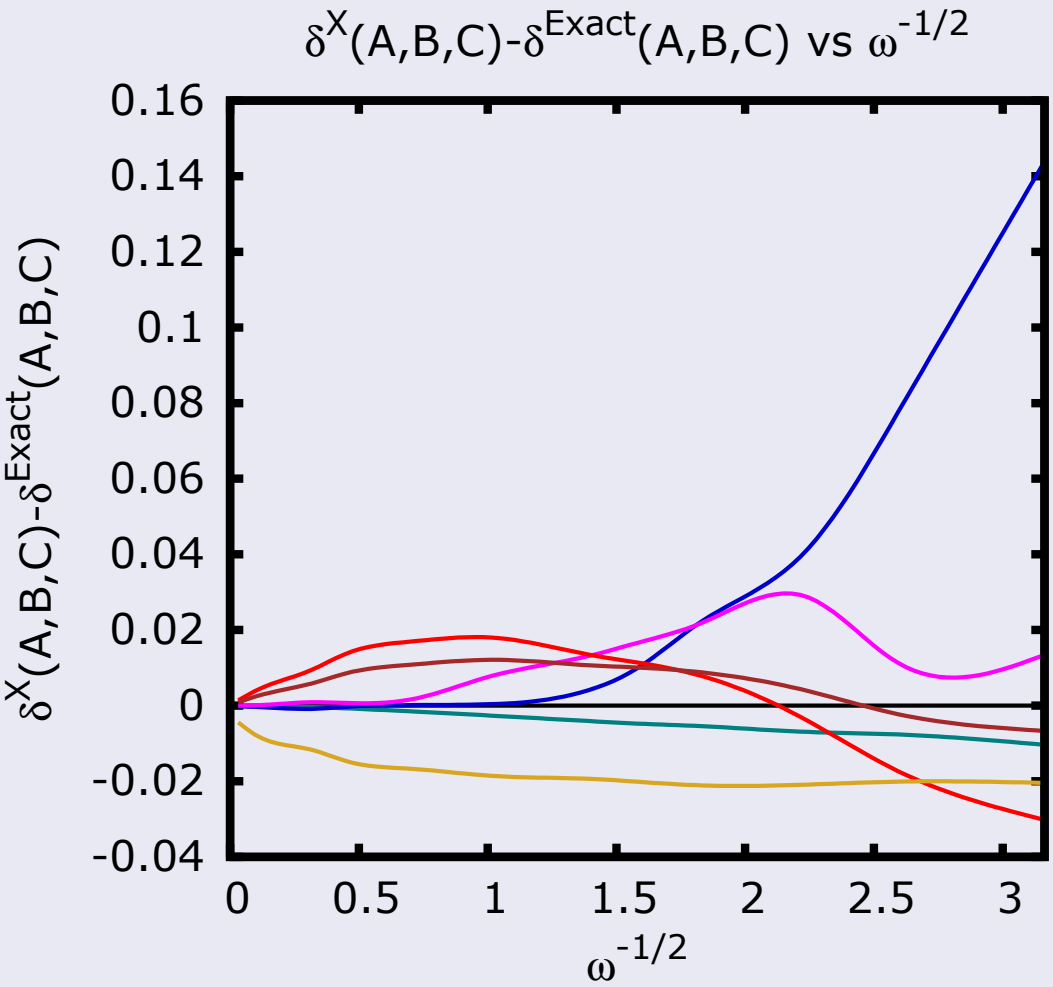
Technical details

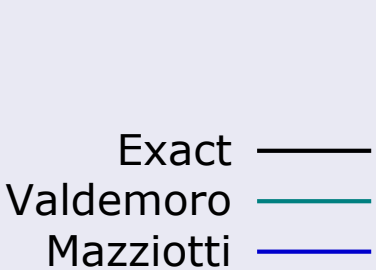
- Calculate FCI 3eHA. [a]
- Get the $^3\mathbf{D}$, $^2\mathbf{D}$ and $^1\mathbf{D}$ (because the three are needed for the MCI)[b] for $S = 1/2$ and $S = 3/2 \rightarrow$ Permits to test pure Fermi vs Fermi+Coulomb correlation.
- Generate regions for the 3eHA.[c]
- Evaluate the MCI to get $\delta(A, B, C)$ and $\widetilde{\delta}(A, B, C)$[d]

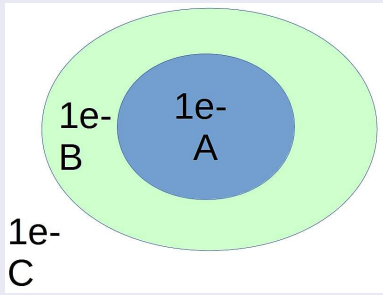


[a] Cioslowski and Matito *JCTC*, 7:915 (2011)
[b] DMN code of Dr. Matito
[c] APOST-3D and RHO.OPS.2.1
[d] ESI-3D of Dr. Matito http://ematito.webs.com

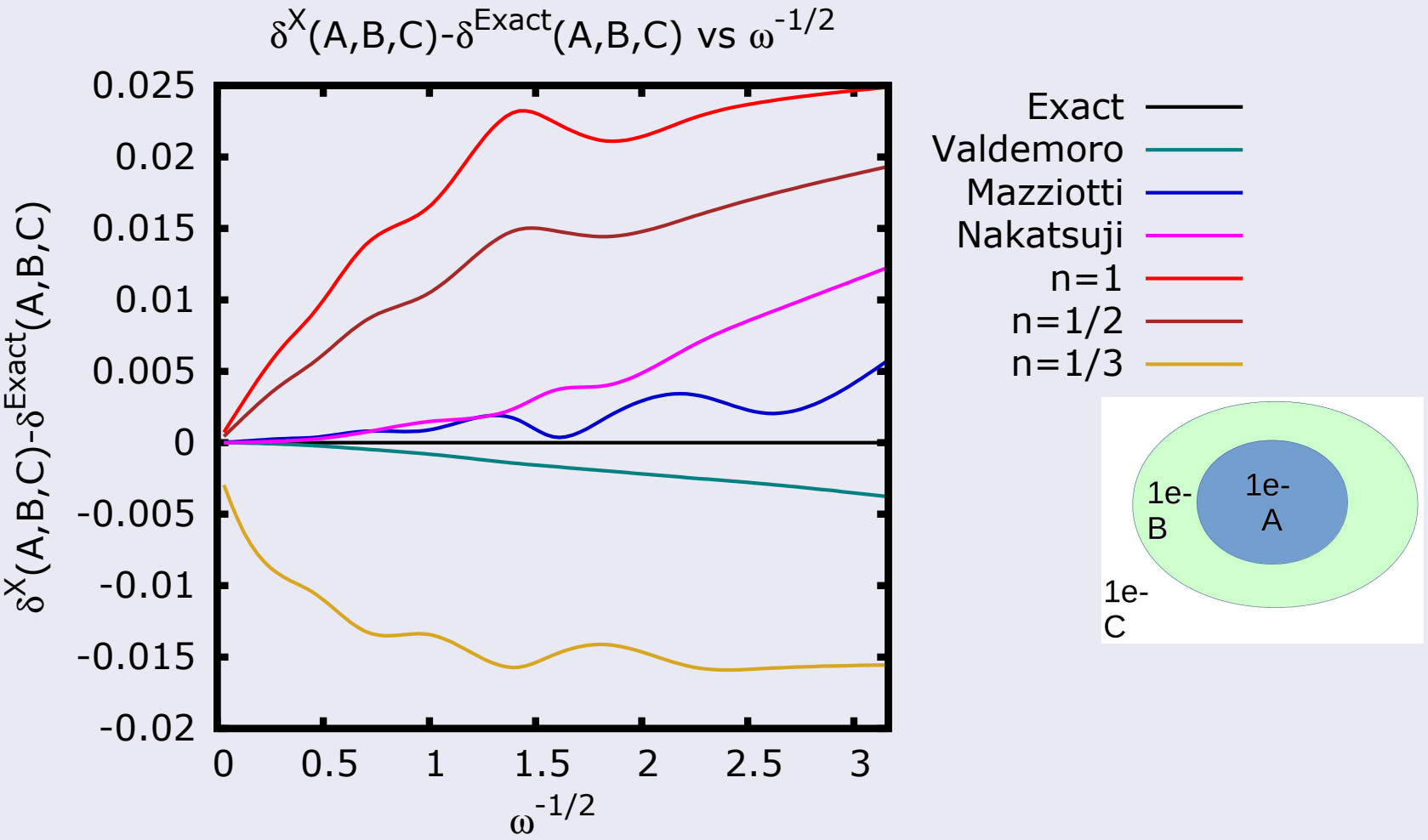
Doublet (Fermi+Coulomb correlation):







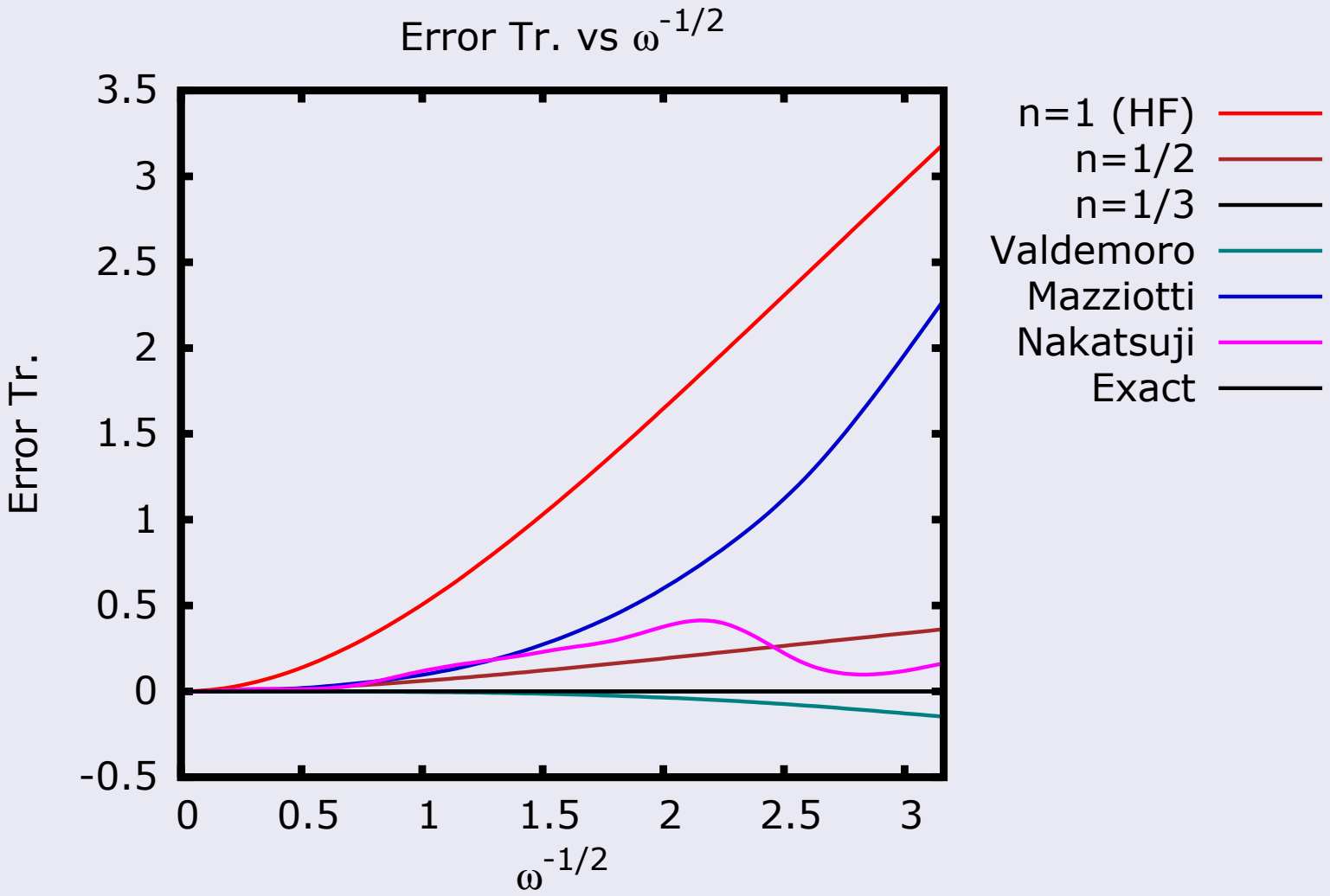
Quartet (Fermi correlation):



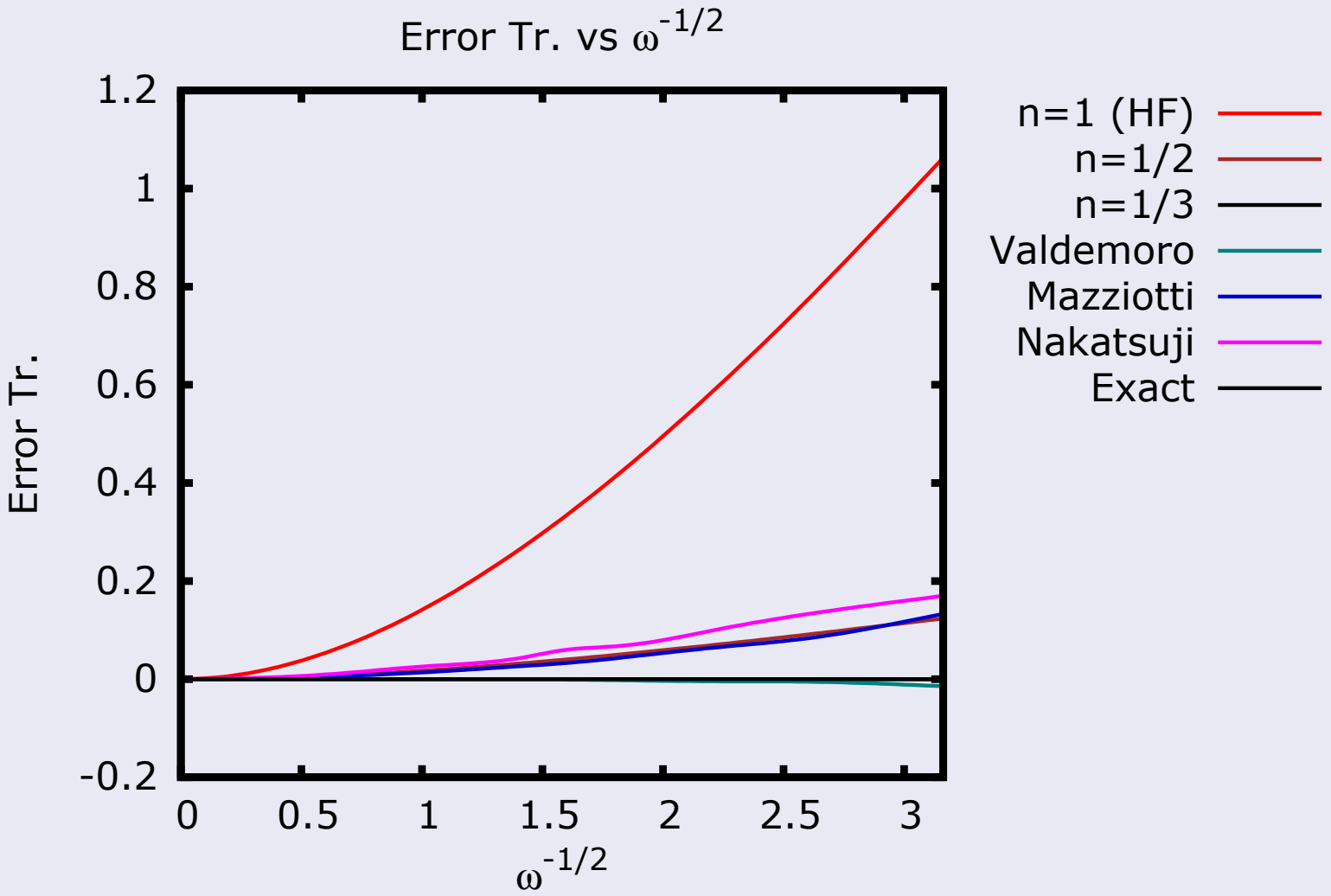
Trace:

Trace of a three-electron $^3\mathbf{D} = \binom{N}{3} 3! = 3! (\equiv 6)$

Doublet:


Error Tr. vs ω^-1/2
Error Tr.
ω^-1/2
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
0
0.5
1
1.5
2
2.5
3
n=1 (HF)
n=1/2
n=1/3
Valdemoro
Mazziotti
Nakatsuji
Exact

Quartet:


Error Tr. vs ω^-1/2
Error Tr.
ω^-1/2
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
0.5
1
1.5
2
2.5
3
n=1 (HF)
n=1/2
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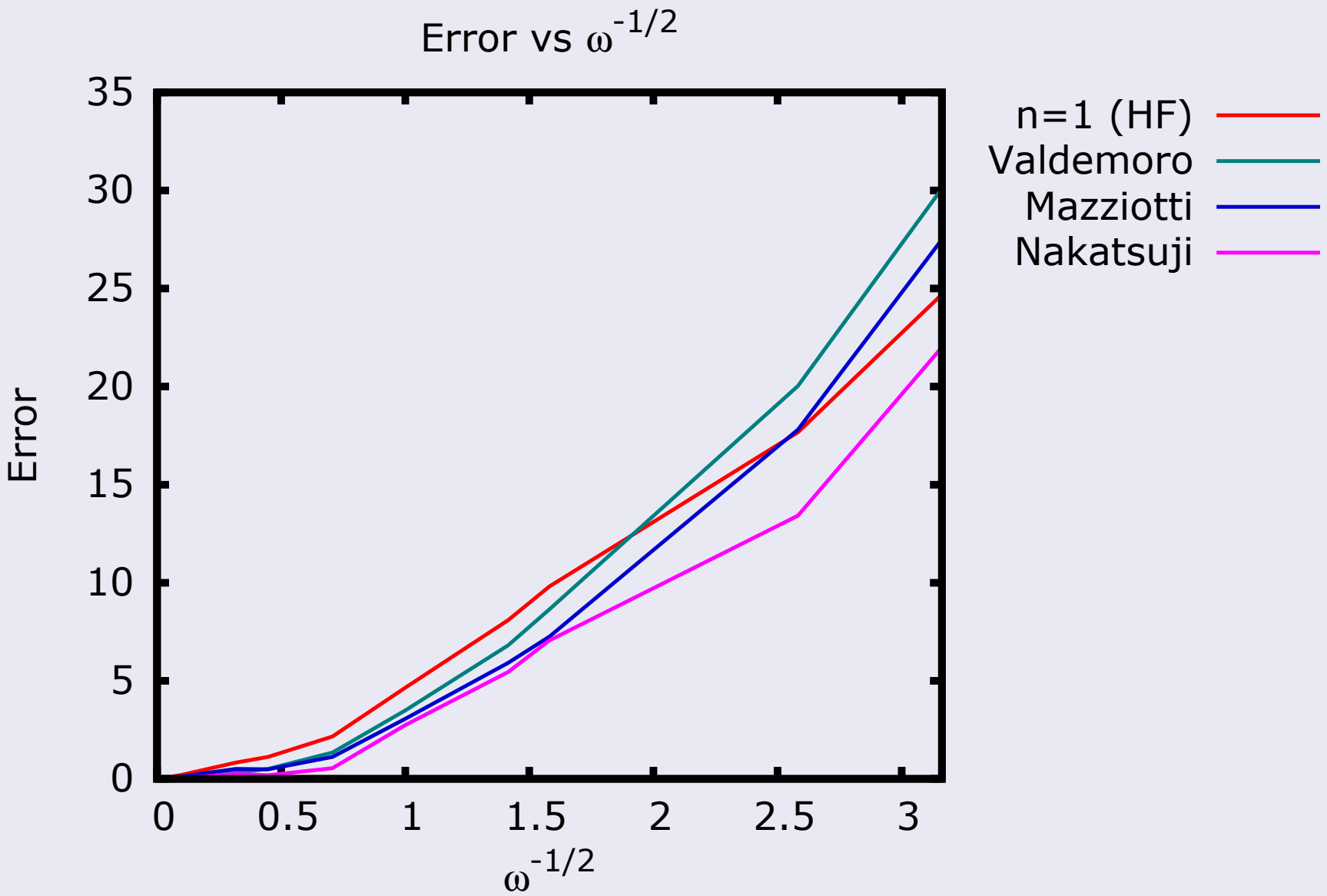
Term-wise error:

$$\sum_{(i<j<k)\leq(l<m<n)} |{}^{3}D_{ijk}^{lmn\ \ Exact} \_ {}^{3}D_{ijk}^{lmn\ \ Approx}|$$

Doublet:


Error vs ω^-1/2
Error
ω^-1/2
0
5
10
15
20
25
30
35
0
0.5
1
1.5
2
2.5
3
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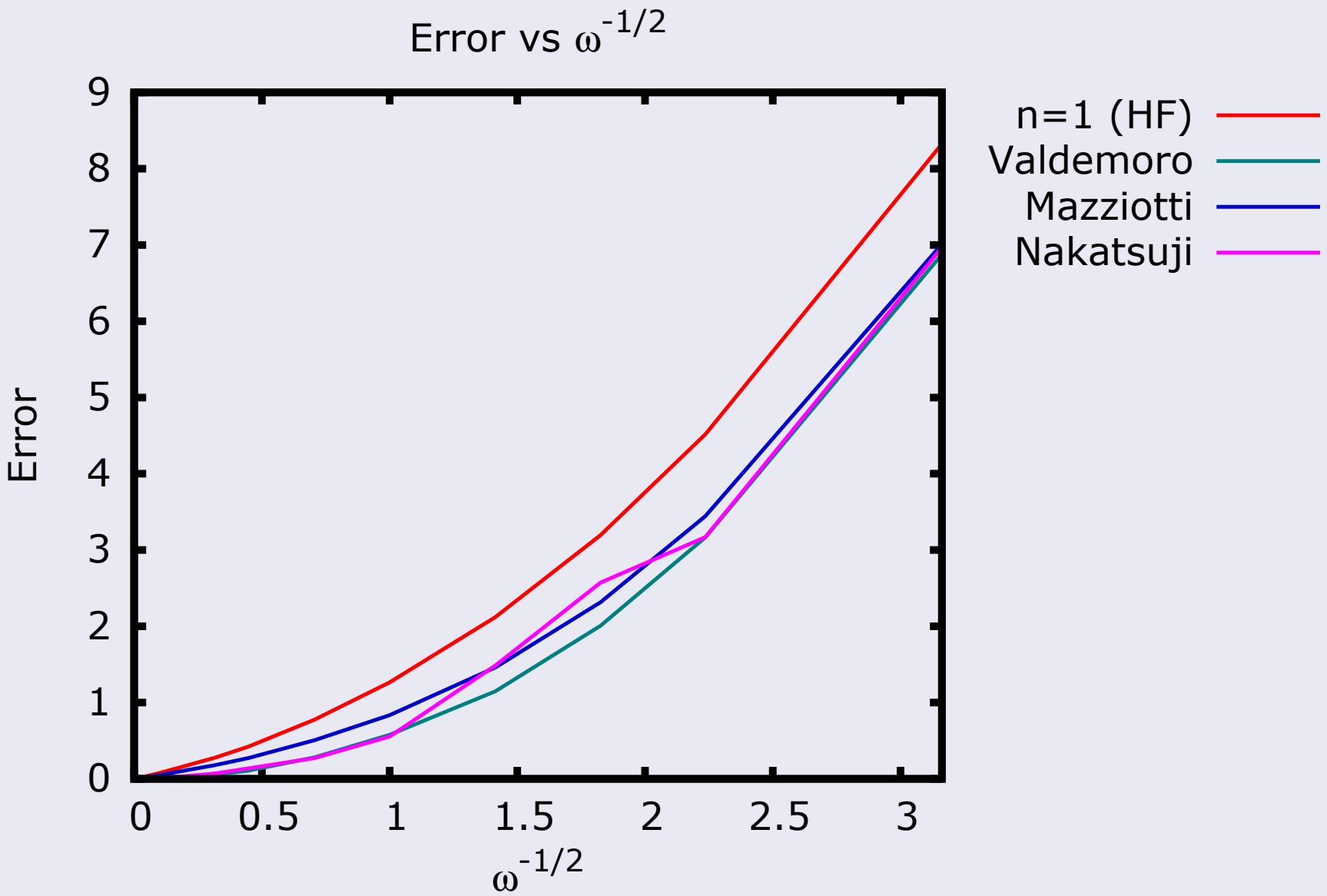
Quartet:


Error vs ω^-1/2
Error
ω^-1/2
0
1
2
3
4
5
6
7
8
9
0
0.5
1
1.5
2
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3
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Conclusions

- Valdemoro approx. is the best approximation for MCI and $n = 1/3$ approx. is strongly competitive when correlation is more important.

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- Nakatsuji approx. phase factor (σ_l) must correct to certain point the Coulomb correlation.

Acknowledgements

GOBIERNO DE ESPAÑA
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GOBIERNO DE ESPANA
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DIPC

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ikerbasque
Basque Foundation for Science

THANKS FOR YOUR KIND ATTENTION!

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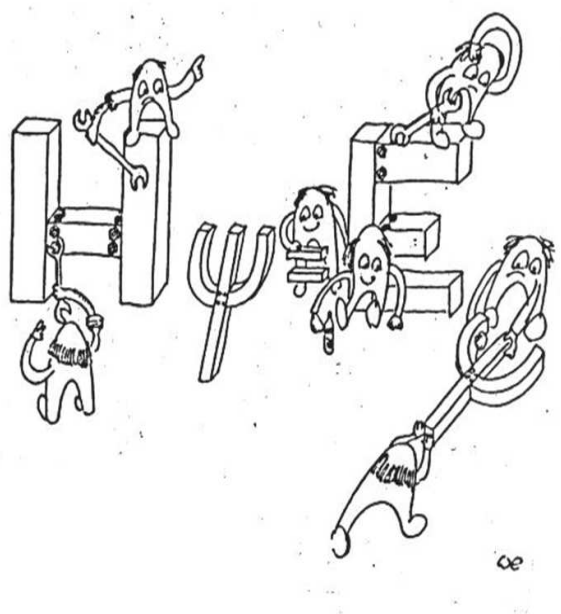

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