

Supplementary Information

Comprehensive Benchmarking for Density Matrix Functional Approximations

M. Rodríguez-Mayorga,^{†,‡} Eloy Ramos-Cordoba,^{†,¶} M. Via-Nadal,[†] M. Piris,^{†,§}
and Eduard Matito^{*,†,§}

[†]*Kimika Fakultatea, Euskal Herriko Unibertsitatea, UPV/EHU, and Donostia
International Physics Center (DIPC). P.K. 1072, 20080 Donostia, Euskadi, Spain*

[‡]*Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química,
University of Girona, 17071 Girona, Catalonia, Spain*

[¶]*Currently at Kenneth S. Pitzer Center for Theoretical Chemistry, University of
California, Berkeley*

[§]*IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain.*

E-mail: ematito@gmail.com

1 $\alpha(\omega)$ optimization for the POWER¹⁻³ Functional

The best $\alpha(\omega)$ parameters were obtained by taking the two-electron integrals in the basis of natural orbitals and first scanning the interval $0 \leq \alpha \leq 1$. Then selecting the best alpha iteratively reducing the size of the interval until the error was $\leq 10^{-5}$. The exact V_{ee} , the best α and the errors are collected in Table 1.

Table 1: $\alpha(\omega)$ values which minimize the difference $V_{ee}^{POWER} - V_{ee}$

ω	V_{ee} (a.u.)	α
0.03	0.07564	0.540430
0.033	0.08052	0.539340
0.036	0.08524	0.538200
0.0365373	0.08607	0.538020
0.04	0.09132	0.537110
0.05	0.10563	0.536140
0.06	0.11891	0.536110
0.08	0.14319	0.535190
0.10	0.16523	0.534120
0.15	0.21376	0.531544
0.20	0.25600	0.529410
0.30	0.32880	0.526060
0.40	0.39157	0.523610
0.50	0.44762	0.521657
1.00	0.67184	0.516090
2.00	0.99493	0.511085
5.00	1.64342	0.506484
10.0	2.37889	0.502882
100.0	7.82805	0.493154
1000.0	25.0768	0.474605

2 Exact DI

The exact value of the DI between regions A and B is plotted in Figure 1. The decay of the DI with $\omega^{-1/2}$ is due to two effects: the less compact electronic density which is produced by the weakening of the harmonic confinement and the enhanced role of the electron-electron repulsion.

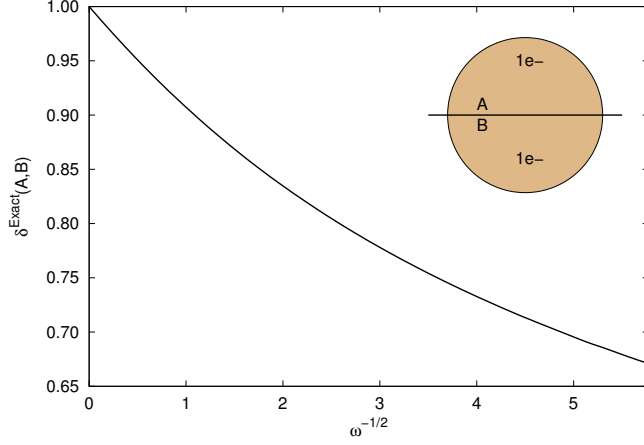


Figure 1: Exact delocalization index between regions A and B against $\omega^{-1/2}$.

3 Short-range radial intracule density for $\omega = 0.03$

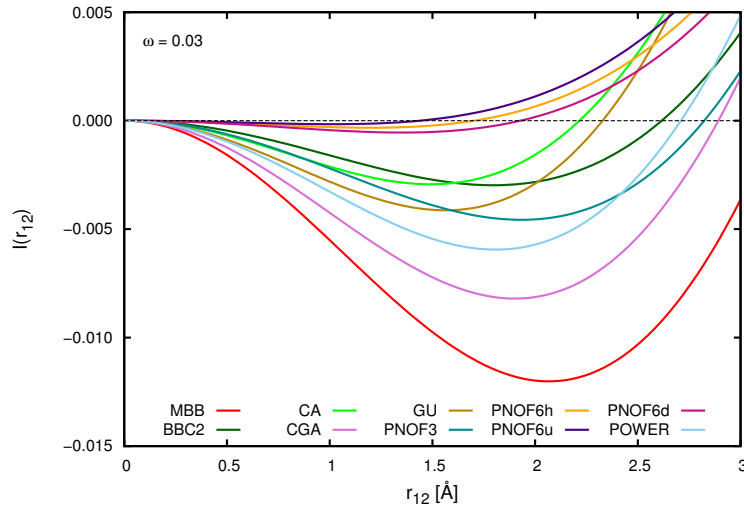


Figure 2: Radial intracule density (Eq. 16 in the text) against r_{12} for $\omega = 0.03$. ML, MLSIC, PNOF2, PNOF4 and SD have been not included because they do not present negative radial intracule density values.

Where MBB, BBC2, CA, CGA, GU, PNOF3, PNOF6 and the POWER functionals produce negative radial intracule densities for small r_{12} values.

References

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