Supporting Information:

Extraction of a first order reduced density matrix from a Quantum Monte Carlo electronic density: A new tool for studying nondynamic correlation

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Contents

1 Geometries of the molecules [a.u.]

beh2(ts)

Be	0.000	0.000	-2.825
H	0.000	1.297	0.000
H	0.000	-1.297	0.000

o3

O	0.000	0.000	0.437
O	0.000	-1.0951	-0.2185
O	0.000	1.0951	-0.2185

cyclobutadiene(D2H)

C	0.000000	-1.493225	-1.262007
C	0.000000	1.493225	-1.262007
C	0.000000	-1.493225	1.262007
C	0.000000	1.493225	1.262007
H	0.000000	-2.935813	-2.715341
H	0.000000	2.935813	-2.715341
H	0.000000	-2.935813	2.715341
H	0.000000	2.935813	2.715341

cyclobutadiene(D4H)

C	-0.000006	-1.361449	-1.361449
C	0.000006	1.361449	-1.361449
C	0.000006	-1.361449	1.361449
C	-0.000006	1.361449	1.361449
H	-0.000008	-2.788967	-2.788867
H	0.00001	2.788967	-2.788867
H	0.00001	-2.788967	2.788867
H	-0.000008	2.788967	2.788867

m-benzyne

```
C   0.000000    0.000000    -2.617839
C   0.000000    2.235539    -1.222452
C   0.000000    -2.235539   -1.222452
H   0.000000    4.054873    -2.114456
H   0.000000    -4.054873   -2.114456
C   0.000000    2.054945    1.374787
C   0.000000    -2.054945   1.374787
C   0.000000    0.000000    2.96302
H   0.000000    0.000000    4.978591
H   0.000000    0.000000    -4.648777
```

o-benzyne

```
C   0.000000    1.181411    -2.362196
C   0.000000    2.734768    -0.226435
C   0.000000    -1.181411   -2.362196
H   0.000000    4.757633    -0.242076
C   0.000000    1.340383    1.99887
C   0.000000    -2.734768   -0.226435
H   0.000000    2.311749    3.780642
H   0.000000    -4.757633   -0.242076
C   0.000000    -1.340383   1.99887
H   0.000000    -2.311749   3.780642
```

p-benzyne

```
C   0.000000    -2.285164   1.319339
C   0.000000    2.285164    -1.319339
C   0.000000    -2.285164   -1.319339
C   0.000000    2.285164    1.319339
C   0.000000    0.000000    -2.638679
C   0.000000    0.000000    2.638679
H   0.000000    -4.063026   2.345789
H   0.000000    4.063026    -2.345789
H   0.000000    -4.063026   -2.345789
H   0.000000    4.063026    2.345789
```

psb4

C	7.619405	1.239675	0.000000
C	5.077643	0.978666	0.000000
C	3.912732	-1.475747	0.000000
C	1.371368	-2.052847	0.000000
C	-0.611869	-0.25783	0.000000
C	-3.154676	-0.884354	0.000000
C	-5.00956	1.004941	0.000000
H	8.510562	3.100451	0.000000
H	8.868972	-0.406958	0.000000
H	3.893446	2.671305	0.000000
H	5.221319	-3.079879	0.000000
H	0.842459	-4.049964	0.000000
H	-0.122821	1.752857	0.000000
H	-3.730279	-2.870276	0.000000
H	-4.440582	2.994071	0.000000
H	-8.725158	2.047786	0.000000
H	-8.196836	-1.185276	0.000000
N	-7.471973	0.595043	0.000000

2 Wavefunction of the QMC calculations

In our calculations, we have chosen the trial wavefunction in a Slater-Jastrow form: a combination of Slater determinants multiplied by the Jastrow factor[S1] which takes into account the Coulomb interactions at short distances. Due to the fact that our Hamiltonian does not contain the spin, we can write

$$\psi_T(\vec{r}_1, ..., \vec{r}_N) = J \sum_k^{N_{det}} d_k D_k^{\uparrow}(\vec{r}_1, ..., \vec{r}_{N_{up}}) D_k^{\downarrow}(\vec{r}_{N_{up}+1}, ..., \vec{r}_N)$$

where the Jastrow factor J has the form in the eq. S.1.

$$J = J_A J_B J_C \tag{S.1}$$

It is made by three components: J_A takes into account the effects of the interaction of the nuclei and the electrons (e-n), J_B stands for the electronics two-body interaction (e-e), meanwhile J_C is for the three-body interaction between two electrons and a nucleus. Each factor is parameterized, the full expression of these factors is the following.

$$ln(J_A) = \sum_k^{atoms} \sum_i^N \left[\frac{A_0^{(k)} R_{ki}}{1 + A_1^{(k)} R_{ki}} + A_2^{(k)} R_{ki}^2 + A_3^{(k)} R_{ki}^3 + ... \right]$$

$$ln(J_B) = \sum_{i<j}^N \left[\frac{B_0 R_{ij}}{1 + B_1 R_{ij}} + B_2 R_{ij}^2 + B_3 R_{ij}^3 + ... \right]$$

$$ln(J_C) = \sum_k^{atoms} \sum_{i<j}^N \sum_{t,s} C_{ij}^{(k)} (R_{ki} + R_{kj})^t R_{ij}^s$$

in which $R_{ij} = [1 - \exp(-\lambda r_{ij})]/\lambda$. The parameter B_0 will be $1/2$ for two electrons with opposite spins, and $1/4$ for electrons with the same spin to satisfy e-e cusp condition. The local energy is calculated at every sampled configuration. The use of this kind of wavefunction guarantees the high accuracy of the method, with a very good description of both dynamic

and nondynamic correlation.

The initial setup of the calculation has been provided by the software GAMESS.[S2] We used a pseudopotential[S3] and the corresponding VTZ basis set, to exclude the core electrons. We determined an initial set of orbitals through an HF calculation and these orbitals have been reoptimized through an appropriate CAS optimization considering the different molecules under investigation. The number of determinants in CASSCF computations is too high for a standard QMC calculation, so we have taken a threshold in order to reduce the number of determinants. The combination of the Slater determinants is then multiplied by the Jastrow factor as in Eq.S.1 above to the fifth order. The optimization of the wavefunction was made through the software CHAMP,[S4] and following the method of Umrigar et collaborators.[S5]

3   The QMC electronic densities

The resulted electronic density for each molecule has been plotted in Fig S1

(a) BeH2(TS) ISO=0.0003

(b) O3 ISO=0.004

(c) cyclob(D2h) ISO=0.002

(d) cyclob(D4h) ISO=0.002

(e) m-benzyne ISO=0.005

(f) o-benzyne ISO=0.002

(g) p-benzyne ISO=0.0045

(h) psb4(0) ISO=0.001
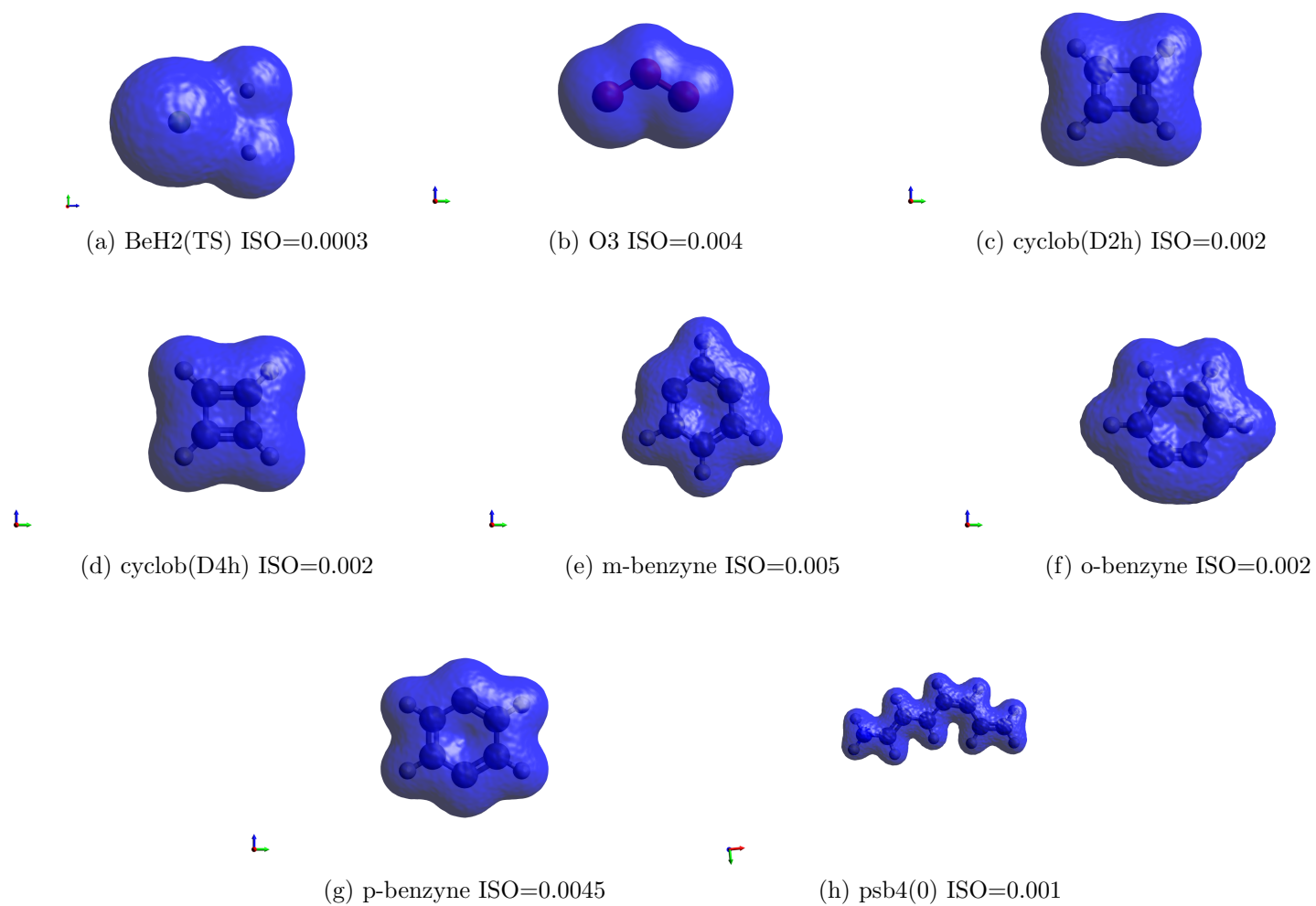
Figure S1: Electronic densities interpolated from QMC samplings.

4 Global indicators of correlation for CASSCF and the QMC-Fit

Table S1: Collection of the global indicators of the fit and comparison between CASSCF computations.

Molecule	I_{ND}		I_D	
	CAS	QMC	CAS	QMC
Be + H2 (TS)	0.65	0.50	0.25	0.12
O3	0.32	0.38	0.20	0.26
cyclobutadiene (D2H)	0.22	0.17	0.24	0.27
cyclobutadiene (D4H)	0.59	0.52	0.12	0.18
o-benzyne	0.38	0.27	0.47	0.52
m-benzyne	0.49	0.38	0.44	0.66
p-benzyne	0.74	0.43	0.36	0.13
PSB4	0.29	0.16	0.45	0.72

5 Local indicators of correlation for the QMC-fit

(a) BeH2(TS)
$I_{ND}(\vec{r})$ ISO=0.003

(b) O3
$I_{ND}(\vec{r})$ ISO=0.004

(c) cyclob(D2h)
$I_{ND}(\vec{r})$ ISO=0.002

(d) cyclob(D4h)
$I_{ND}(\vec{r})$ ISO=0.002

(e) m-benzyne
$I_{ND}(\vec{r})$ ISO=0.005

(f) o-benzyne
$I_{ND}(\vec{r})$ ISO=0.002

(g) p-benzyne
I_{ND} ISO=0.0045

(h) psb4(0)
I_{ND} ISO=0.001
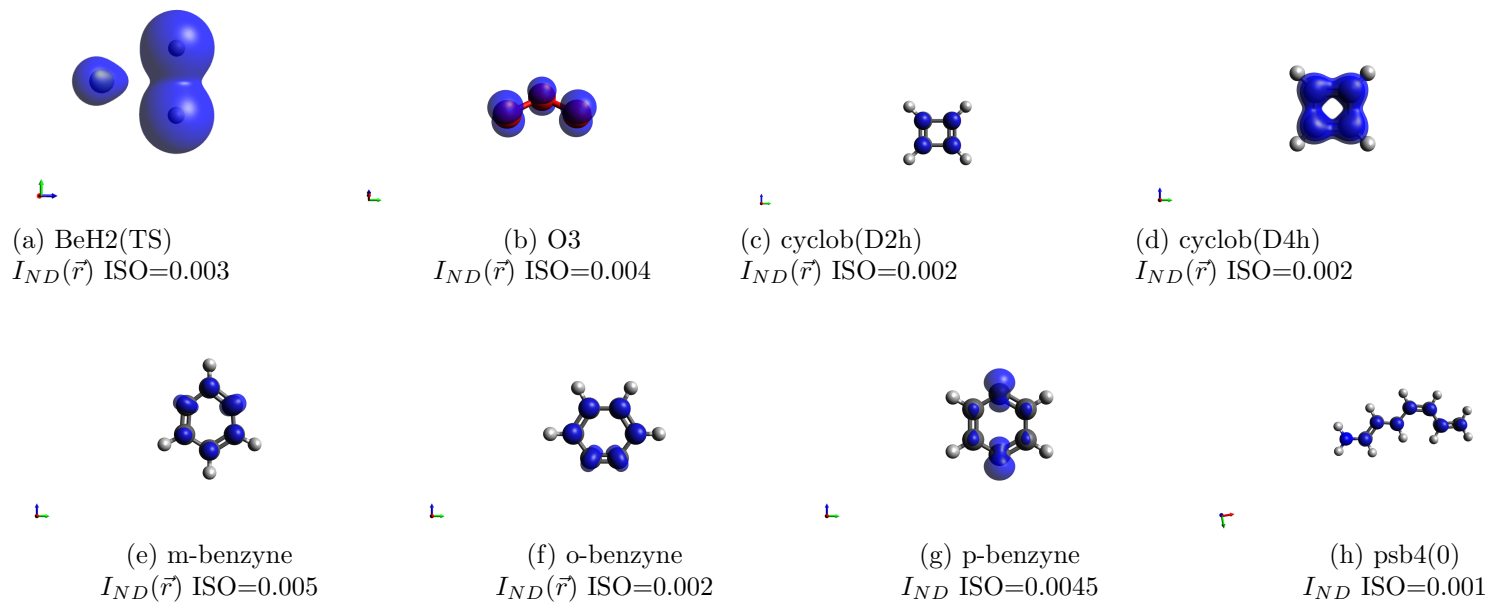
Figure S2: Local indicators of nondynamic correlation ($I_{ND}(\vec{r})$)computed with natural orbitals and occupancies of QMC-fit.

(a) BeH2(TS)
$I_D(\vec{r})$ ISO=0.003

(b) O3
$I_D(\vec{r})$ ISO=0.004

(c) cyclob(D2h)
$I_D(\vec{r})$ ISO=0.002

(d) cyclob(D4h)
$I_D(\vec{r})$ ISO=0.002

(e) m-benzyne
$I_D(\vec{r})$ ISO=0.005

(f) o-benzyne
$I_D(\vec{r})$ ISO=0.002

(g) p-benzyne
I_D ISO=0.0045

(h) psb4(0)
$I_D(\vec{r})$ ISO=0.001
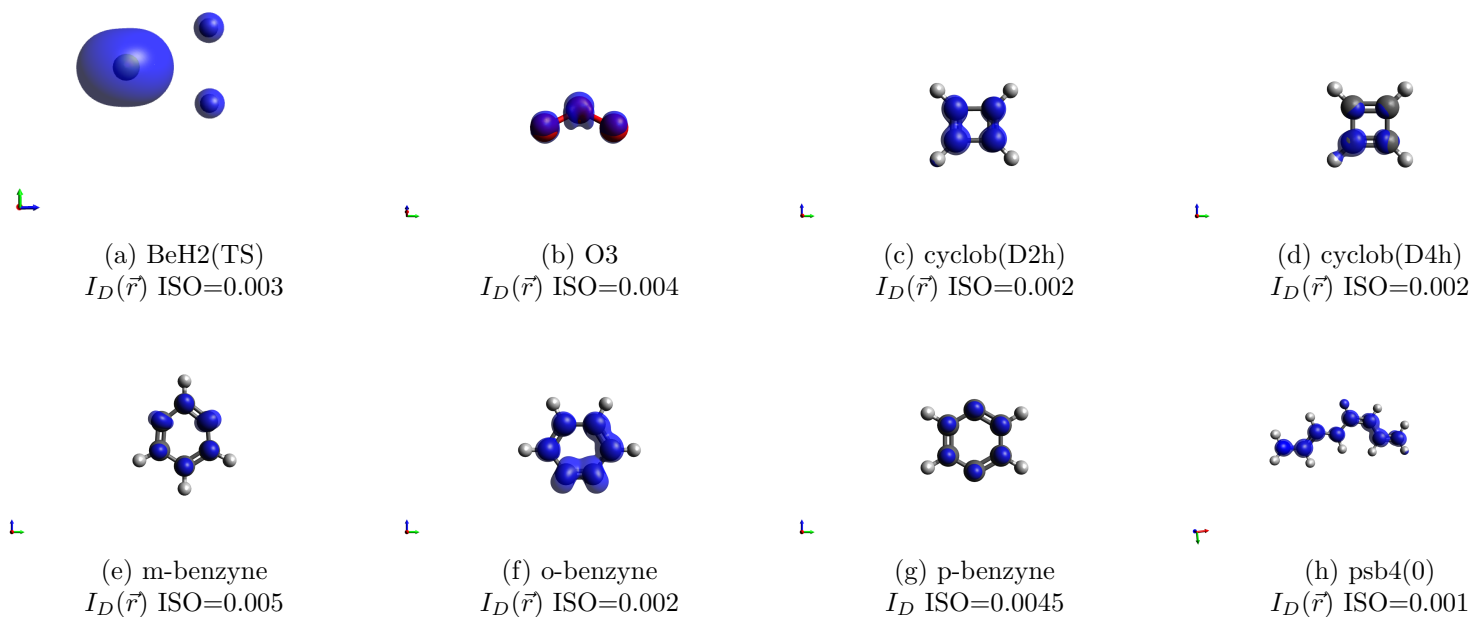
Figure S3: Local indicators of dynamic correlation $(I_D(\vec{r}))$computed with natural orbitals and occupancies of QMC-fit

6 Unrestricted KS computations

Table S2: Collection of results of correlation energies and indicators of nondynamic correlation for broken symmetry computations.

Molecule	Functional	S^2	ΔE^U [Kcal/mol]	I_{ND}	I_{ND}
Be+H$_2$(TS)	UBLYP	0.99	26.90	0.50	0.06
-	UB3LYP	1.00	25.90	0.50	0.07
-	UBH&H	1.01	22.73	0.50	0.08
-	UM06-2X	0.98	19.90	0.49	0.06
-	UCAM-B3LYP	1.00	25.00	0.50	0.07
-	ULC-BLYP	1.02	24.70	0.51	0.08
-	UHF	1.09	36.00	0.54	0.11
O$_3$	UBLYP	0.00	0.00	-	-
-	UB3LYP	0.00	0.00	-	-
-	UBH&H	0.00	0.00	-	-
-	UM06-2X	0.00	0.00	-	-
-	UCAM-B3LYP	0.00	0.00	-	-
-	ULC-BLYP	0.00	0.00	-	-
-	UHF	0.00	0.00	-	-
cyclobutadiene (D2H)	UBLYP	0.00	0.00	-	-
-	UB3LYP	0.16	0.20	0.08	0.22
-	UBH&H	0.27	0.56	0.13	0.27
-	UM06-2X	0.00	0.00	-	-
-	UCAM-B3LYP	0.24	0.40	0.17	0.25
-	ULC-BLYP	0.35	1.10	0.12	0.29
-	UHF	0.96	15.50	0.48	0.42
cyclobutadiene (D4H)	UBLYP	1.04	24.00	0.52	0.19
-	UB3LYP	1.07	27.70	0.53	0.21
-	UBH&H	1.09	44.38	0.54	0.24
-	UM06-2X	1.06	16.80	0.53	0.24
-	UCAM-B3LYP	1.08	29.70	0.54	0.20
-	ULC-BLYP	1.11	33.00	0.55	0.28
-	UHF	1.25	59.40	0.62	0.22

Molecule	Functional	S^2	ΔE^U [Kcal/mol]	I_{ND}	I_D
o-benzyne	UBLYP	0.00	0.00	-	-
-	UB3LYP	0.01	0.00	0.00	0.07
-	UBH&H	0.23	0.82	0.12	0.24
-	UM06-2X	0.00	0.00	-	-
-	UCAM-B3LYP	0.16	0.40	0.08	0.20
-	ULC-BLYP	0.31	1.50	0.15	0.28
-	UHF	1.38	24.80	0.69	0.64
m-benzyne	UBLYP	0.35	1.30	0.18	0.19
-	UB3LYP	0.61	5.80	0.30	0.19
-	UBH&H	0.74	13.13	0.37	0.19
-	UM06-2X	0.70	3.80	0.35	0.21
-	UCAM-B3LYP	0.73	11.90	0.36	0.17
-	ULC-BLYP	0.81	20.50	0.41	0.17
-	UHF	0.93	45.90	0.47	0.61
p-benzyne	UBLYP	0.92	14.50	0.46	0.17
-	UB3LYP	0.98	27.40	0.49	0.20
-	UBH&H	1.03	44.05	0.52	0.26
-	UM06-2X	1.03	32.90	0.52	0.24
-	UCAM-B3LYP	1.02	40.40	0.51	0.23
-	ULC-BLYP	1.07	57.40	0.54	0.30
-	UHF	1.81	109.70	0.91	0.61
PBS4	UBLYP	0.00	0.00	-	-
-	UB3LYP	0.00	0.00	-	-
-	UBH&H	0.00	0.00	-	-
-	UM06-2X	0.00	0.00	-	-
-	UCAM-B3LYP	0.00	0.00	-	-
-	ULC-BLYP	0.00	0.00	-	-
-	UHF	0.73	4.40	0.36	0.55

7 Fit of the Fermi distribution

Molecule	Functional	$T_{eff}[K \cdot 10^{-4}]$	δT_{eff} [%]	$\mu_{eff}[a.u.]$	$\sqrt{\sigma^2}$
Be+H$_2$(TS)	QMC	2.2(7)	31	-0.17(2)	2.0E-01
	UHF	3.3(4)	13	-0.126(4)	2.2E-02
	UB3LYP	2.38(3)	1	-0.1254(3)	2.8E-03
	UB&HLYP	2.51(7)	3	-0.1306(6)	5.4E-03
	UCAM	2.42(6)	3	-0.1266(6)	5.4E-03
	ULC-BLYP	2.48(1)	5	-0.127(1)	1.0E-02
	UBLYP	2.36(3)	0	-0.1249(1)	3.0E-04
	UM06-2X	2.16(2)	1	-0.1298(2)	2.2E-03
cycloD2H	QMC	2.46(2)	1	-0.059(2)	4.3E-03
	UHF	3.59(6)	2	-0.083(2)	1.1E-02
	UB3LYP	1.841(6)	0	-0.0793(6)	1.0E-03
	UB&HLYP	2.088(8)	0	-0.0863(7)	1.9E-03
	UCAM	2.057(8)	0	-0.0804(7)	1.8E-03
	ULC-BLYP	2.30(1)	1	-0.082(1)	3.0E-03
	UBLYP	-	-	-	-
	UM06-2X	-	-	-	-
cycloD4H	QMC	2.87(2)	1	-0.0712(2)	1.4E-03
	UHF	3.8(1)	4	-0.082(3)	1.6E-02
	UB3LYP	2.83(8)	3	-0.0794(6)	4.5E-03
	UB&HLYP	2.99(7)	2	-0.0854(7)	5.0E-03
	UCAM	2.98(8)	3	-0.0804(7)	5.4E-03
	ULC-BLYP	3.17(9)	3	-0.0813(9)	6.7E-03
	UBLYP	2.61(8)	3	-0.0797(4)	3.3E-03
	UM06-2X	2.71(5)	2	-0.0810(3)	2.5E-03

Table S3: Collection of fit's results of the Fermi distribution of the occupation numbers.

Molecule	Functional	$T_{eff}[K \cdot 10^{-4}]$	δT_{eff} [%]	$\mu_{eff}[a.u.]$	$\sqrt{\sigma^2}$
o-benzyne	QMC	2.91(4)	1	-0.086(3)	7.6E-03
	UHF	3.5(2)	5	-0.116(9)	4.9E-02
	UB3LYP	1.13(4)	3	-0.109(7)	1.2E-03
	UB&HLYP	2.0(1)	5	-0.11(1)	2.0E-02
	UCAM	1.86(9)	5	-0.10(1)	1.4E-02
	ULC-BLYP	2.2(1)	5	-0.10(1)	2.6E-02
	UBLYP	-	-	-	-
	UM06-2X	-	-	-	-
m-benzyne	QMC	2.75(7)	3	-0.114(6)	2.1E-02
	UHF	3.1(2)	8	-0.12(1)	6.0E-02
	UB3LYP	2.5(1)	4	-0.114(5)	2.8E-02
	UB&HLYP	2.7(1)	5	-0.122(7)	3.8E-02
	UCAM	2.7(1)	5	-0.115(7)	3.7E-02
	ULC-BLYP	2.9(2)	6	-0.117(8)	4.5E-02
	UBLYP	2.03(5)	2	-0.115(4)	1.3E-02
	UM06-2X	2.6(1)	4	-0.117(6)	3.4E-02
p-benzyne	QMC	1.96(7)	4	-0.153(2)	2.1E-02
	UHF	3.0(2)	6	-0.150(6)	4.5E-02
	UB3LYP	2.1(1)	7	-0.152(4)	3.7E-02
	UB&HLYP	2.0(1)	7	-0.161(4)	4.0E-02
	UCAM	2.1(1)	7	-0.154(4)	3.9E-02
	ULC-BLYP	2.1(2)	7	-0.156(4)	4.0E-02
	UBLYP	2.0(1)	5	-0.151(3)	3.2E-02
	UM06-2X	2.1(2)	7	-0.155(4)	4.1E-02
O3	QMC	3.9(2)	4	-0.260(7)	2.8E-02
	UHF	-	-	-	-
	UB3LYP	-	-	-	-
	UB&HLYP	-	-	-	-
	UCAM	-	-	-	-
	ULC-BLYP	-	-	-	-
	UBLYP	-	-	-	-
	UM06-2X	-	-	-	-
PSB4	QMC	2.30(6)	3	-0.262(8)	1.0E-02
	UHF	5.32(2)	0	-0.5405(1)	2.1E-03
	UB3LYP	-	-	-	-
	UB&HLYP	-	-	-	-
	UCAM	-	-	-	-
	ULC-BLYP	-	-	-	-
	UBLYP	-	-	-	-
	UM06-2X	-	-	-	-

Figure S4: Fit of the Fermi distribution for BeH2(TS) tested for different functionals and QMC.
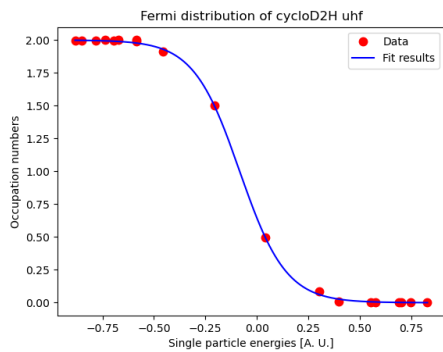
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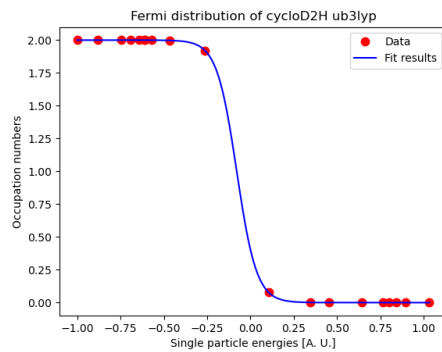
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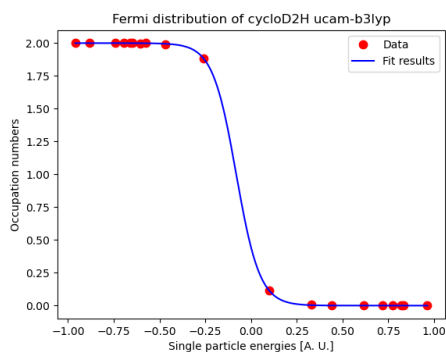
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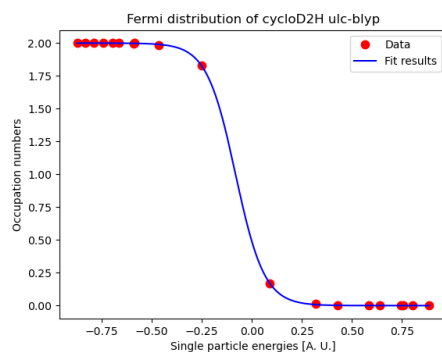
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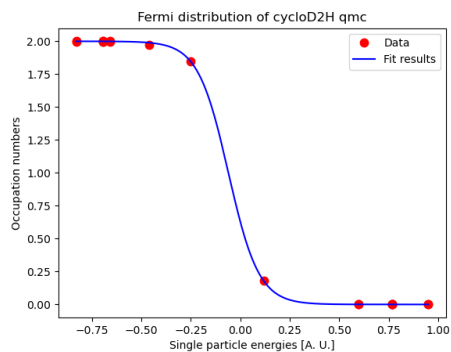
(e)

Figure S5: Fit of the Fermi distribution for the cyclobutadiene (D2h) tested for different functionals and QMC.
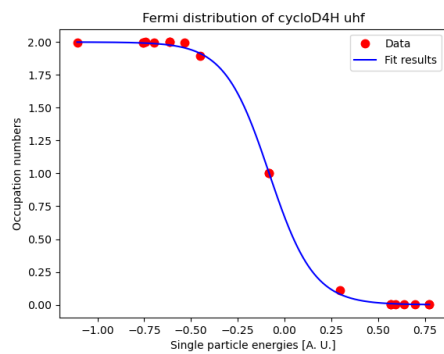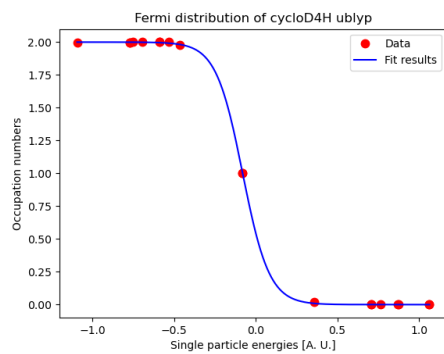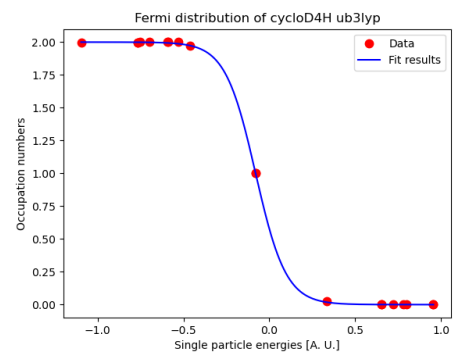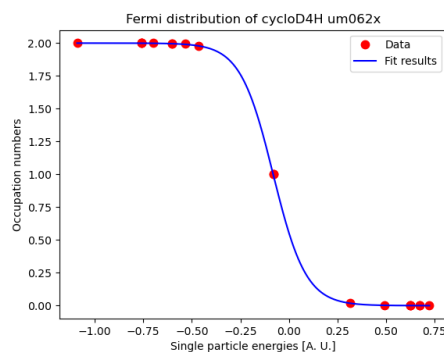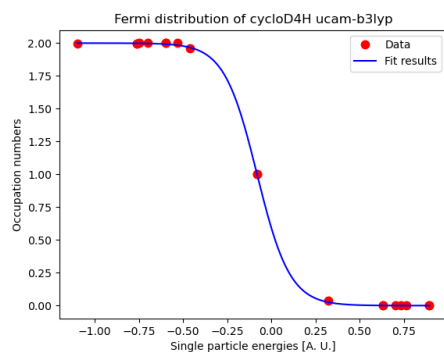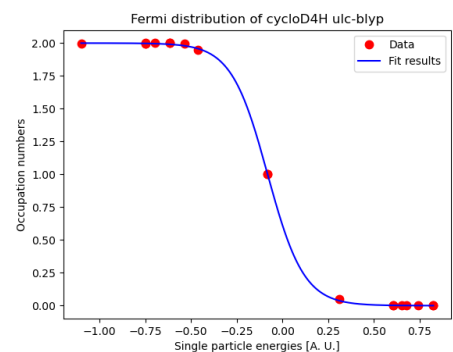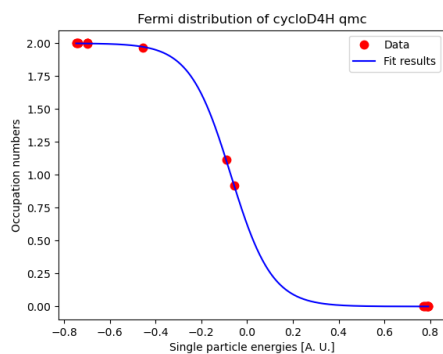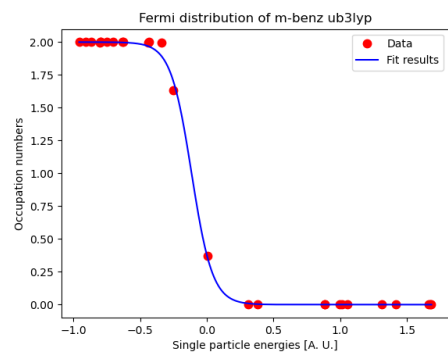
Figure S6: Fit of the Fermi distribution for the cyclobutadiene (D4h) tested for different functionals and QMC.
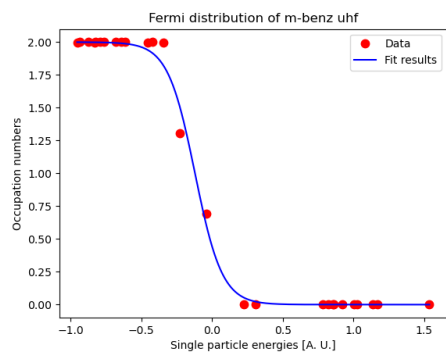
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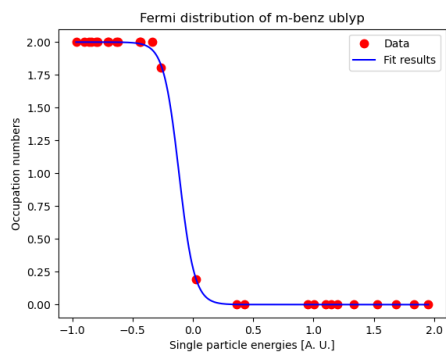
(b)

(c)

(d)

(e)

(f)

(g)
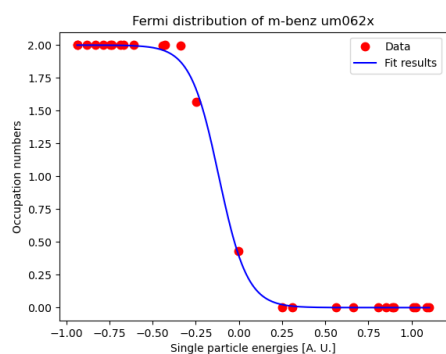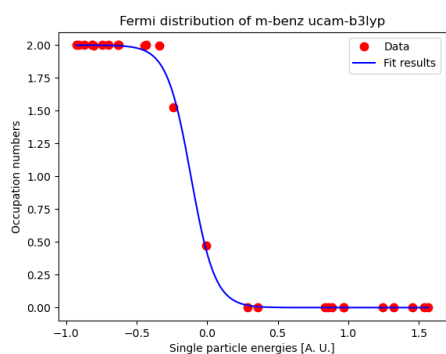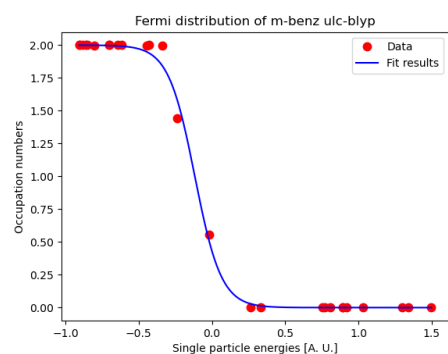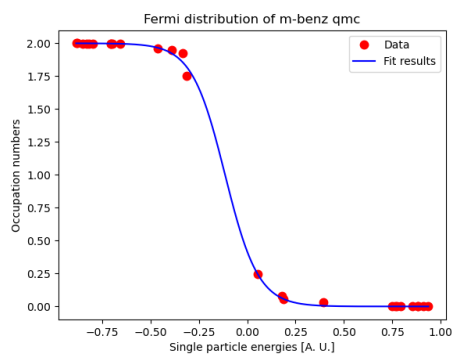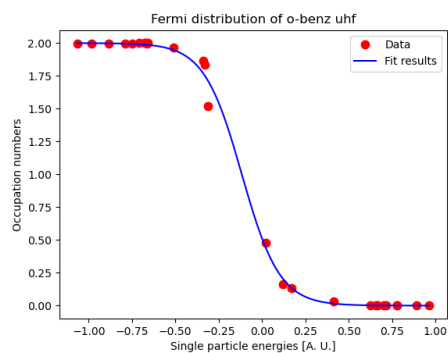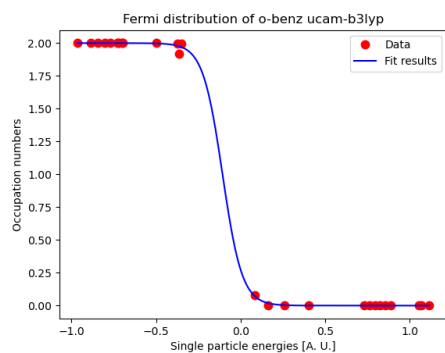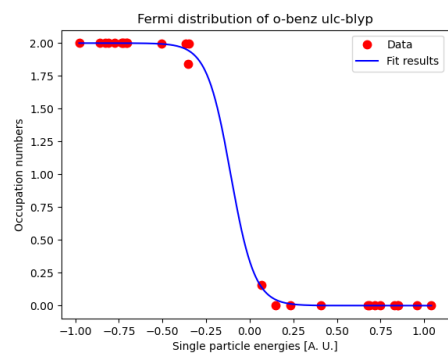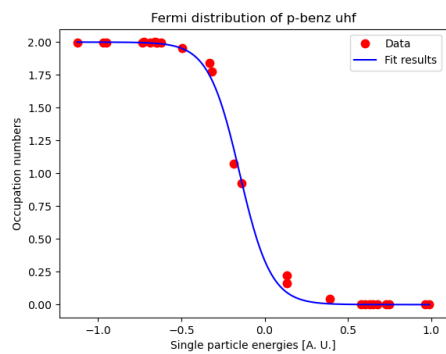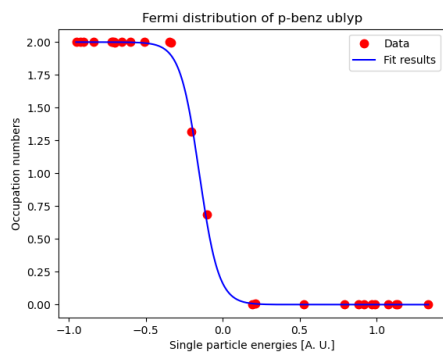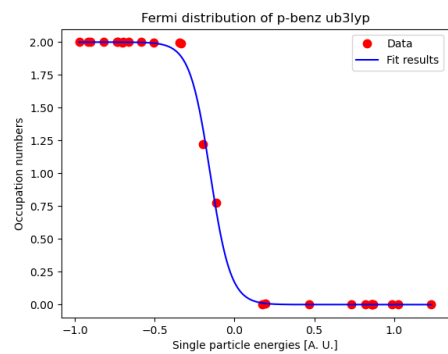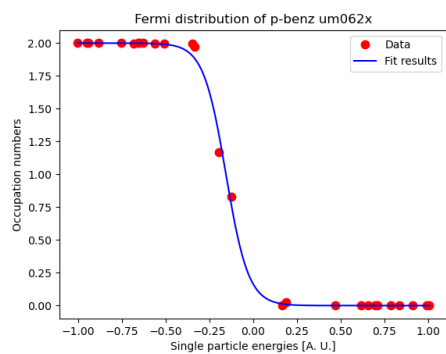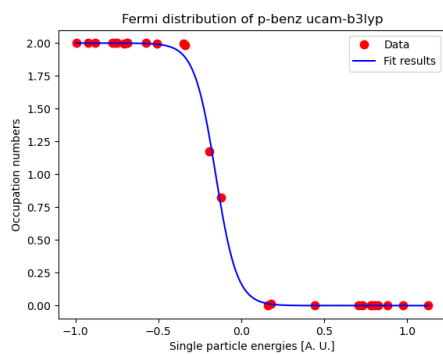
Figure S7: Fit of the Fermi distribution for the meta-benzyne tested for different functionals and QMC.

(a)

(b)

(c)
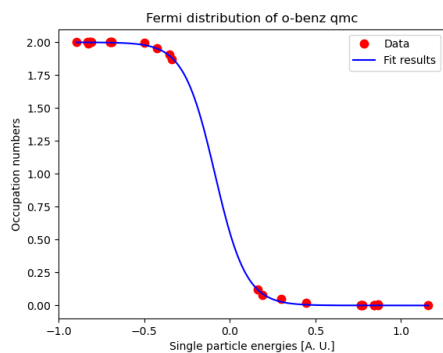
(d)

Figure S8: Fit of the Fermi distribution for the ortho-benzyne tested for different functionals and QMC.
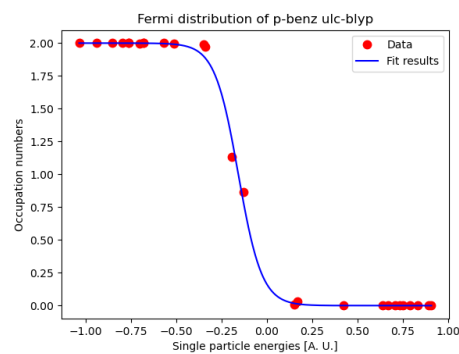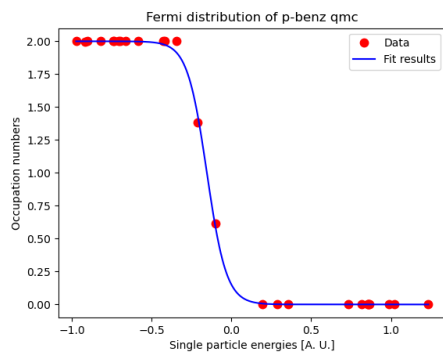
(a)

(b)

(c)

(d)

(e)

(f)

(g)

Figure S9: Fit of the Fermi distribution for the para-benzyne tested for different functionals and QMC.
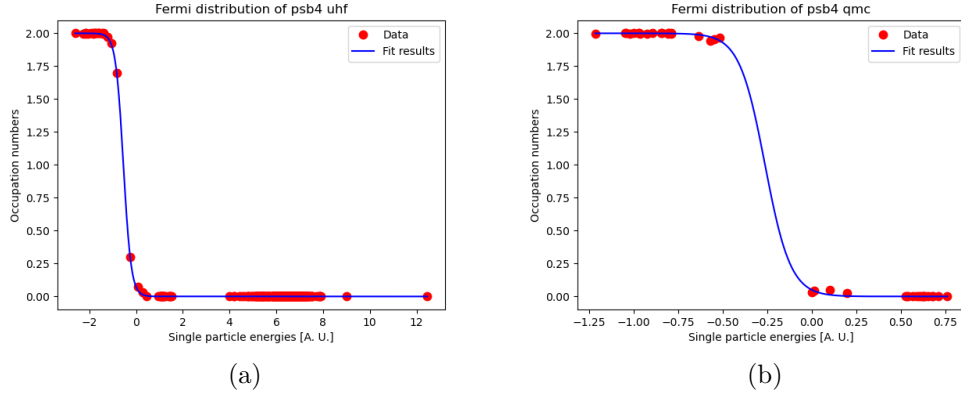
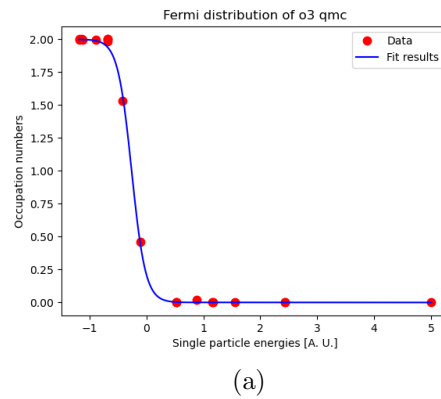Figure S10: Fit of the Fermi distribution for the psb4(0) tested for different functionals and QMC.

Figure S11: Fit of the Fermi distribution for the O3 tested for QMC-fit.

References

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