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Basis sets and technical details of the calculations of correlation pair densities

Supporting Information

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In all calculations of correlation pair densities the frequency integration required in the evaluation of correlation energies and potentials was performed numerically with a Gauss-Legendre quadrature with 20 points. Tests with higher numbers of quadrature points showed that 20 points are sufficient. The OEP equations were solved without using a Tichonov regularization.

A. Helium atom

For the helium atom the AO basis set (atomic orbital basis set to represent the Kohn-Sham orbitals) and the RI basis set (resolution of the identity basis set to represent dynamic response functions) were Gaussian basis sets containing s-functions with exponents forming a geometric series with progression factors of 1.5[1]. For the higher angular momenta the aug-cc-pV6Z[2] basis set was used as AO basis set and the aug-cc-pV5Z-MP2FIT[3,4] basis set as RI basis set. The OEP basis (optimized effective potential basis set to represent the Kohn-Sham exchange-correlation potential) was an aug-cc-pVTZ-MP2FIT[3,4] basis set. If the reference electron is not located at the nucleus a chargeless dummy atom carrying AO, RI, and OEP basis sets was placed at the position of the reference electron. The AO basis on the dummy atom is equal to that on the He atom, whereas the RI basis contains only the s-functions listed below. The OEP basis on the dummy atom contains only one s-function given below.

List of s-functions of the basis sets for the case the reference electron is located at the nucleus:

```
AO Basis:
0.01988
0.02982
0.04473
0.067095
0.100642
0.150964
0.226446
0.339668
```

0.509503

0.764254

1.14638

1.71957

2.57936

3.86904

5.80355

8.70533

13.058

19.587

29.3805

44.0707

66.1061

99.1592

148.739

223.108

334.662

501.993

752.99

1129.48

1694.23

2541.34

3812.01

5718.02

8577.02

12865.5

19298.3

28947.4

43421.2

65131.7

97697.6

146546

219820

329729

494594

RI Basis:

0.0804293

0.120644

0.180966

0.271449

0.407173

0.61076

0.91614

1.37421

2.06131

3.09197

4.63796

6.95694

10.4354

15.6531

23.4797

35.2195

52.8292

79.2439

118.866

178.299

267.448

401.172

601.758

902.637

1353.96

2030.94

3046.41

4569.61

6854.42

10281.6

15422.4

23133.6

34700.4

52050.6

78075.9

117114

List of s-functions of the basis sets for the case the reference electron is not located at the nucleus (dummy atom at the position of the reference electron):

AO Basis on the He atom and on the dummy atom:

0.01988

0.02982

0.04473

0.067095

0.100642

0.150964

0.226446

0.339668

0.509503

0.764254

1.14638

1.71957

2.57936

3.86904

5.80355

8.70533

13.058

19.587

29.3805

44.0707

66.1061

99.1592

148.739

223.108

334.662

501.993

752.99

1129.48

1694.23

2541.34

3812.01

5718.02

8577.02

RI Basis on the He atom and on the dummy atom (The function in square brackets were only used on the helium atom but not on the dummy atom.):

[0.0804293]

[0.120644]

[0.180966]

0.271449

0.407173

0.61076

0.91614

1.37421

2.06132

3.09197

4.63796

6.95694

10.4354

15.6531

```
23.4797
35.2195
52.8293
79.2439
118.866
178.299
267.448
401.172
601.758
902.637
[1353.96]
[2030.93]
[3046.4]


OEP Basis on the dummy atom (only one function)
1.185426
```

B. Hydrogen molecule

For the hydrogen molecule the AO and OEP basis sets (both for H atoms and the dummy atom) were slightly modified versions of basis sets originally designed to calculate reference correlation potentials from electron densitites from configuration interaction calculations[5]. For the s-functions of the RI basis Gaussian basis functions with exponents forming a geometrical series with progression factor 1.5 were used[1]. For the higher angular momenta the aug-cc-pV5Z-MP2FIT[3,4] basis set was used on the H atoms. On the dummy atom no basis functions with higher angular momentum were used.

These basis sets were used for all distances and positions of the reference atom.

List of basis functions:

```
AO Basis on the H atoms:
s,0.0084
s,0.0126
```

s,0.0189

s,0.02835

s,0.042525

s,0.0637875

s,0.0956812

s,0.143522

s,0.215283

s,0.322924

s,0.484386

s,0.726579

s,1.08987

s,1.6348

s,2.45221

s,3.67831

s,5.51746

s,8.27619

s,12.4143

s,18.6214

s,27.9322

s,41.8982

s,62.8474

s,94.271

s,141.407

s,212.11

s,318.165

s,477.247

s,715.871

s,1073.81

s,1610.71

s,2416.06

s,3624.1

p,5.97458

p,2.05217

p,1.24866

p,0.805545

p,0.347892

p,0.196067

d,3.85816

d,1.71063

d,0.979237

d,0.625366

d,0.233601

f,3.10151

f,1.19811

f,0.572873

f,0.236155

g,2.9878

g,1.23192

g,0.79632

h,3.24739

h,1.03498

AO Basis on the dummy atom:

s,2.80963

s,4.21445

s,6.32168

s,9.48251

s,14.2238

s,21.3357

s,32.0035

s,48.0052

s,72.0078

s,108.012

s,1.873089

s,0.526184

p,2.372549

p,1.180408

d,1.809637

d,1.143973

s-functions of the RI Basis on the H atoms:

0.0492938

0.0739407

0.110911

0.166367

0.24955

0.374325

0.561487

0.84223

1.26335

1.89502

2.84253

4.26379

6.39569

9.59353

14.3903

21.5854

32.3782

48.5672

72.8509

109.276

163.914

245.871

s-functions of the RI Basis on the dummy atom
(The two functions in square brackets were used only
in the calculations at equilibrium distance.):
0.84223
1.26335
1.89502
2.84253
4.26379
6.39569
9.59353
14.3903
21.5854
32.3782
[48.5672]
[72.8509]

OEP Basis on the H atoms:
s,5.11589
s,1.142965
s,0.291662
s,0.11272
p,0.986401
p,0.28586
d,1.172083

OEP Basis on the dummy atom:
s,1.142965
s,0.2916662
s,0.112720

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