Supporting Information to: Explicitly correlated PNO-MP2 and PNO-CCSD and its application to the S66 set and large molecular systems

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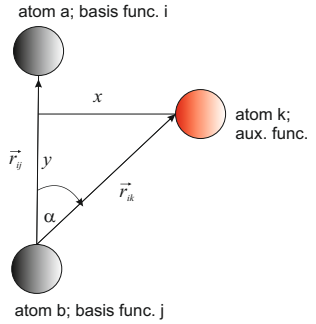
1 supplementary material

1.1 Integral screening for short range operators

For the integral screening we follow the work of Adler et al. [**?**] and implemented their introduced bounds. Additional we derived simpler and cheaper estimates by using only the most diffuse functions[1] and setting the corresponding contraction coefficients C_μ etc. to one. In this way many quantities can be precomputed and with the additional approximation that the distance x of the Gaussians is set to the shortest distance x' between the center of the auxiliary function and the line connecting the atoms at which, the two Gaussians are located (see Figure 1), we get always an upper bound to their estimate. To denote the we used the most diffuse functions we use a prime for the corresponding exponents α and β and basis functions μ, ν. The bounds are given as:



$$\cos\alpha = \frac{\vec{r}_{ij}\cdot\vec{r}_{ik}}{||r_{ij}||\cdot||r_{jk}||}$$

$$x' = \sin\alpha\cdot||r_{jk}|| = \sqrt{1-\cos^2\alpha}||r_{jk}||$$

$$y' = \cos\alpha\cdot||r_{jk}|| = \frac{\vec{r}_{ij}\cdot\vec{r}_{ik}}{||r_{ij}||}$$

Figure 1: Demonstration how the distance x' of the auxiliary function to the basis functions is calculated.

[1] In our derivation we assumed normalized functions, otherwise the normalization hast to be incorporated

$$
\begin{aligned}
f_{12}: \quad & \ln \sum_{\mu\nu} \sum_{Q} C_Q C_\mu C_\nu K_{\mu\nu} \left(S_{\mu\nu} \right| f_{12} \left| Q \right) \\
& \leq -\ln \gamma + 3 \ln \pi \\
& - \frac{3}{2} \ln \left(a_{\mu'\nu'} \beta' \right) - \gamma x' + \gamma^2 / (4\xi') - \frac{a_{\mu'} a_{\nu'}}{a_{\mu'\nu'}} r_{ab}^2
\end{aligned}
$$

$$
\begin{aligned}
f_{12} g_{12}: \quad & \ln \sum_{\mu\nu} \sum_{Q} C_Q C_\mu C_\nu K_{\mu\nu} \left(S_{\mu\nu} \right| f_{12} g_{12} \left| Q \right) \\
& \leq -\ln \gamma x' + 3 \ln \pi \\
& - \frac{3}{2} \ln \left(a_{\mu'\nu'} \beta' \right) - \gamma x' + \gamma^2 / (4\xi') - \frac{a_{\mu'} a_{\nu'}}{a_{\mu'\nu'}} r_{ab}^2
\end{aligned}
$$

$$
\begin{aligned}
f_{12}^2: \quad & \ln \sum_{\mu\nu} \sum_{Q} C_Q C_\mu C_\nu K_{\mu\nu} \left(S_{\mu\nu} \right| {f_{12}}^2 \left| Q \right) \\
& \leq -2 \ln \gamma + 3 \ln \pi \\
& - \frac{3}{2} \ln \left(a_{\mu'\nu'} \beta' \right) - 2\gamma x' + \gamma^2 / \xi' - \frac{a_{\mu'} a_{\nu'}}{a_{\mu'\nu'}} r_{ab}^2
\end{aligned}
$$

$$
\begin{aligned}
f_{12}^2 r_{12}^2: \quad & \ln \sum_{\mu\nu} \sum_{Q} C_Q C_\mu C_\nu K_{\mu\nu} \left(S_{\mu\nu} \right| {f_{12}}^2 \left| Q \right) \\
& \leq \ln \left(1 + \frac{2}{\gamma x} \right) - 3 \ln \pi \\
& + \frac{3}{2} \ln \left(a_{\mu'\nu'} \beta' \right) - \gamma x' + \gamma^2 / \left(4\xi' \right) - \frac{a_{\mu'} a_{\nu'}}{a_{\mu'\nu'}} r_{ab}^2
\end{aligned}
$$

As usual $K_{\mu\nu}$ is the preexponential factor of a Gaussian product center, $\alpha_{\mu\nu}$ is the sum of the exponents α_μ α_ν and ξ is defined as $\xi = \frac{\alpha_{\mu\nu}\beta}{\alpha_{\mu\nu}+\beta}$. Moreover r_{ab} is the distance of two Gaussians centered at Atom A and B and $S_{\mu\nu}$ an overlap.
In our algorithm first the cheap estimate is used. If the matrix element is smaller than the threshold it is discarded, but if it is in tolerance range of +2 on a logarithmic scale it is checked again with the estimate involving the contracted GTOs. For large systems we expect a benefit of this approach. Nevertheless also the more evolved estimate is relatively cheap to compute.

1.2 CCSD/CBS limits for the S66 set

Dimer	$E_{\mathrm{lim}}^{\mathrm{CCSD}}$ (kcal/mol)	$E_{\mathrm{aQZ}}^{\mathrm{HF}} + E_{\mathrm{lim}}^{\mathrm{CCSD}}$ (kcal/mol)	$E_{\mathrm{aTZ}}^{\mathrm{HF,CABS}} + E_{\mathrm{lim}}^{\mathrm{CCSD}}$ (kcal/mol)	$\Delta_{[\mathrm{F12}],(2)_{\overline{\mathrm{F12}}}}$ (kcal/mol)
01 Water-Water	-1.062	-4.728	-4.718	-0.019
02 Water-MeOH	-1.590	-5.306	-5.294	0.010
03 Water-MeNH2	-1.929	-6.542	-6.535	-0.084
04 Water-Peptide	-1.938	-7.723	-7.711	-0.013
05 MeOH-MeOH	-1.850	-5.383	-5.372	-0.097
06 MeOH-MeNH2	-2.735	-6.985	-6.980	-0.045
07 MeOH-Peptide	-2.460	-7.687	-7.677	-0.059
08 MeOH-Water	-1.258	-4.752	-4.743	-0.073
09 MeNH2-MeOH	-1.796	-2.705	-2.699	-0.046
10 MeNH2-MeNH2	-2.726	-3.639	-3.635	-0.013
11 MeNH2-Peptide	-3.243	-4.727	-4.720	-0.047
12 MeNH2-Water	-2.323	-6.846	-6.839	-0.110
13 Peptide-MeOH	-2.546	-5.690	-5.682	-0.031
14 Peptide-MeNH2	-3.311	-6.774	-6.771	-0.082
15 Peptide-Peptide	-3.270	-7.881	-7.872	-0.073
16 Peptide-Water	-1.425	-4.840	-4.834	0.021
17 Uracil-Uracil BP	-3.368	-16.220	-16.200	0.072
18 Water-Pyridine	-2.009	-6.446	-6.441	-0.042
19 MeOH-Pyridine	-2.583	-6.829	-6.824	-0.040
20 AcOH-AcOH	-2.777	-18.372	-18.351	0.075
21 AcNH2-AcNH2	-3.237	-15.547	-15.528	0.019
22 AcOH-Uracil	-2.971	-18.681	-18.660	0.017
23 AcNH2-Uracil	-3.068	-18.378	-18.358	0.053
24 Benzene-Benzene π-π	-5.362	-1.403	-1.401	-0.048
25 Pyridine-Pyridine π-π	-5.712	-2.382	-2.379	-0.013
26 Uracil-Uracil π-π	-7.950	-7.571	-7.563	-0.244
27 Benzene-Pyridine π-π	-5.581	-1.964	-1.962	-0.056
28 Benzene-Uracil π-π	-7.199	-3.759	-3.754	-0.087
29 Pyridine-Uracil π-π	-6.971	-4.901	-4.895	-0.090
30 Benzene-Ethene	-3.448	-0.585	-0.584	0.001
31 Uracil-Ethene	-3.804	-2.408	-2.406	-0.072
32 Uracil-Ethyne	-3.237	-2.861	-2.859	-0.119
33 Pyridine-Ethene	-3.605	-0.978	-0.976	-0.048
34 Pentane-Pentane	-5.947	-2.585	-2.583	0.015
35 Neopentane-Pentane	-4.158	-1.846	-1.843	0.063
36 Neopentane-Neopentane	-2.869	-1.195	-1.194	-0.019
37 Cyclopentane-Neopentane	-3.906	-1.600	-1.598	0.010
38 Cyclopentane-Cyclopentane	-4.614	-2.033	-2.031	0.002
39 Benzene-Cyclopentane	-5.223	-2.361	-2.359	-0.035
40 Benzene-Neopentane	-4.082	-1.952	-1.950	0.028
41 Uracil-Pentane	-6.708	-3.264	-3.262	-0.083
42 Uracil-Cyclopentane	-5.911	-2.746	-2.744	-0.012
43 Uracil-Neopentane	-4.670	-2.604	-2.603	-0.047
44 Ethene-Pentane	-3.175	-1.360	-1.359	0.005
45 Ethyne-Pentane	-2.634	-1.171	-1.170	0.008
46 Peptide-Pentane	-5.798	-3.003	-3.000	-0.039
47 Benzene-Benzene TS	-3.476	-2.029	-2.028	-0.009
48 Pyridine-Pyridine TS	-3.533	-2.667	-2.666	-0.084
49 Benzene-Pyridine TS	-3.433	-2.490	-2.489	-0.075
50 Benzene-Ethyne CH-π	-2.152	-2.377	-2.378	-0.155
51 Ethyne-Ethyne TS	-0.811	-1.328	-1.329	0.061
52 Benzene-AcOH OH-π	-3.235	-3.916	-3.914	-0.059
53 Benzene-AcNH2 NH-π	-2.828	-3.693	-3.692	-0.006
54 Benzene-Water OH-π	-2.027	-2.789	-2.786	-0.083
55 Benzene-MeOH OH-π	-3.496	-3.356	-3.354	-0.039

56 Benzene-MeNH2 NH-π	-3.510	-2.422	-2.420	-0.084
57 Benzene-Peptide NH-π	-4.686	-4.168	-4.166	-0.097
58 Pyridine-Pyridine CH-N	-2.444	-3.608	-3.605	-0.099
59 Ethyne-Water CH-O	-0.553	-2.759	-2.757	-0.064
60 Ethyne-AcOH OH π	-1.813	-4.420	-4.422	-0.026
61 Pentane-AcOH	-4.107	-2.021	-2.020	0.008
62 Pentane-AcNH2	-4.657	-2.502	-2.500	0.009
63 Benzene-AcOH	-4.070	-2.810	-2.807	-0.021
64 Peptide-Ethene	-2.884	-2.334	-2.331	-0.042
65 Pyridine-Ethyne	-1.199	-3.727	-3.727	-0.049
66 MeNH2-Pyridine	-3.619	-3.153	-3.149	-0.080

Table 2: Dimers in the S66 set with an absolute deviation to the PNO-CCSD[F12]/aTZ results larger 0.2 kcal/mol

Dimer	|Lit.-PNO-CCSD[F12]/aTZ|
24 Benzene-Benzene π-π	0.357
25 Pyridine-Pyridine π-π	0.386
26 Uracil-Uracil π-π	0.545
27 Benzene-Pyridine π-π	0.371
28 Benzene-Uracil π-π	0.519
29 Pyridine-Uracil π-π	0.499
30 Benzene-Ethene	0.241
31 Uracil-Ethene	0.272
32 Uracil-Ethyne	0.258
33 Pyridine-Ethene	0.255
34 Pentane-Pentane	0.281
38 Cyclopentane-Cyclopentane	0.224
39 Benzene-Cyclopentane	0.306
40 Benzene-Neopentane	0.231
41 Uracil-Pentane	0.388
42 Uracil-Cyclopentane	0.328
43 Uracil-Neopentane	0.262
46 Peptide-Pentane	0.315
47 Benzene-Benzene TS	0.209
48 Pyridine-Pyridine TS	0.218
49 Benzene-Pyridine TS	0.211
52 Benzene-AcOH OH π	0.204
55 Benzene-MeOH OH π	0.246
56 Benzene-$MeNH_2$ NH π	0.227
57 Benzene-Peptide NH π	0.289
61 Pentane-AcOH	0.219
62 Pentane-$AcNH_2$	0.247
63 Benzene-AcOH	0.286
66 $MeNH_2$-Pyridine	0.207