Supplementary Information: Benchmarking excited-state calculations using exciton properties

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1 Formaldehyde

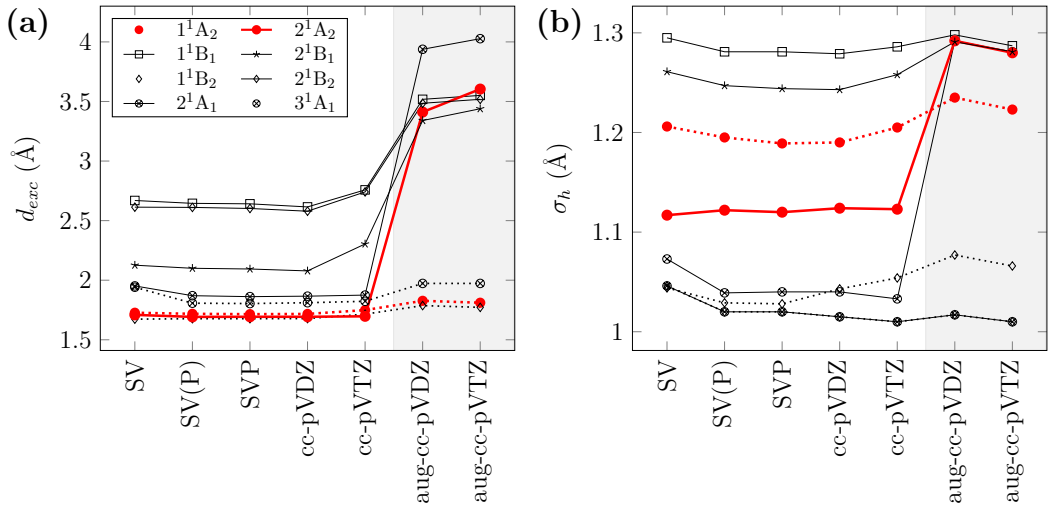

Figure 1: (a) Exciton and (b) hole sizes of the first two excited states of each symmetry point group of formaldehyde calculated at the ADC(3) level of theory in combination of seven basis sets. The legend in (a) also applies to (b).

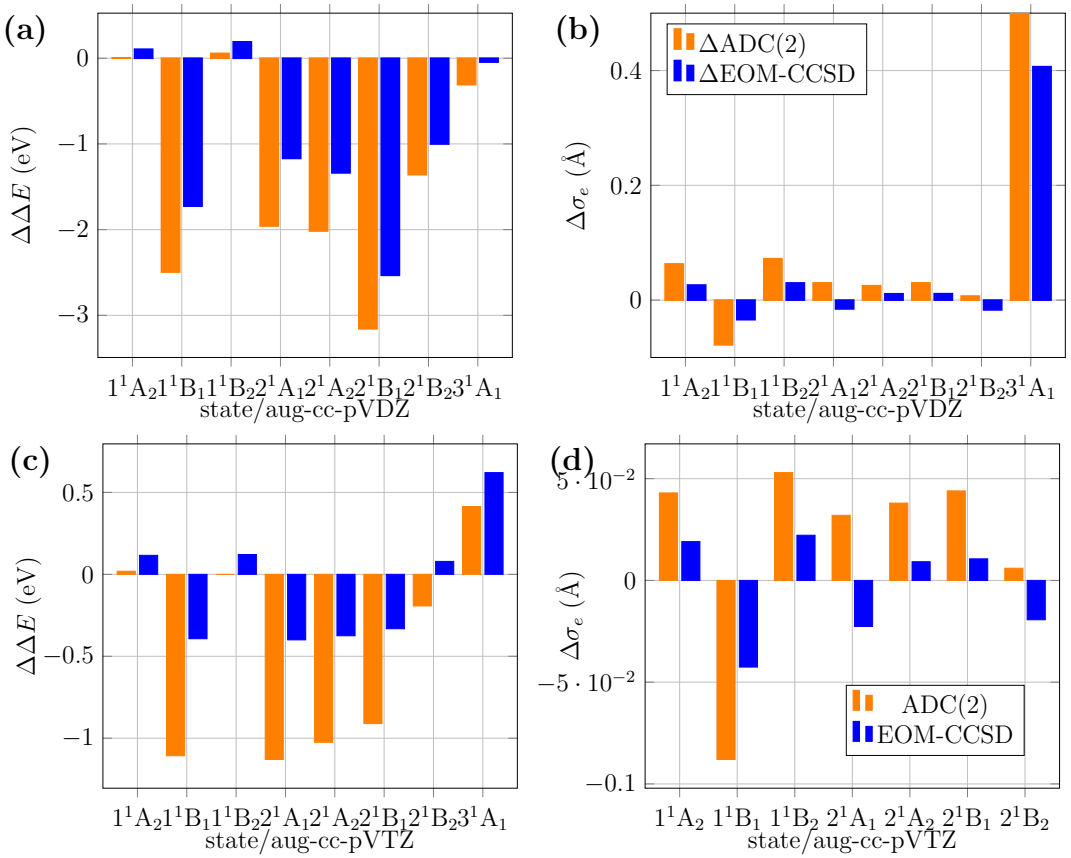

Figure 2: Differences in (a,c) excitation energies ($\Delta\Delta E$, eV), (b,d) electron sizes ($\Delta\sigma_e$, Å) for the first two singlet excited states of each point group of formaldehyde between calculations at the ADC(3) and EOM-CCSD or ADC(2) levels of theory employing the aug-cc-pVDZ and aug-cc-pVTZ basis sets.

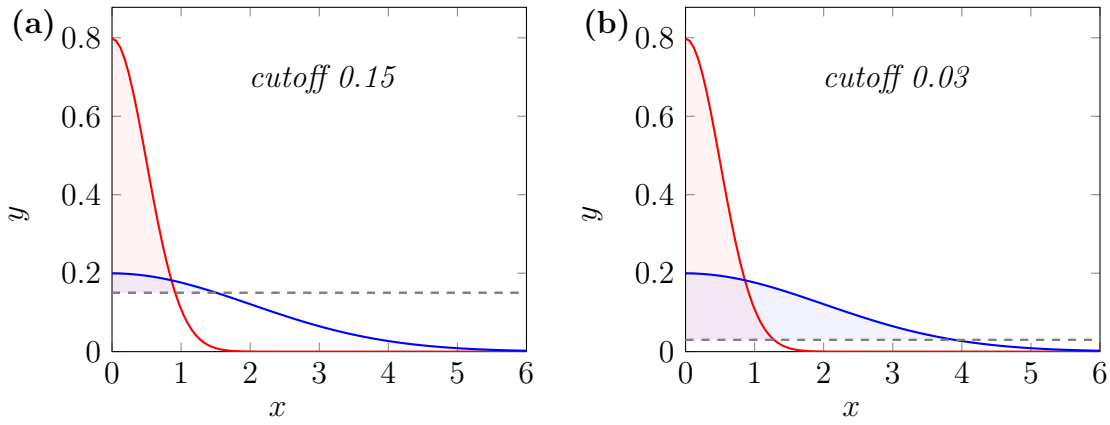

Figure 3: Why small isovalues are required for visualuzation of diffuse orbitals: Illustration using two normalized Gaussian functions. A given cutoff value determines the shape of molecular orbital as it will appear in the visualization: The electron density beyond the cutoff is not shown. If the cutoff value is too large (panel a), the more diffuse orbital will appear much smaller than it is. Lowering cutoff value below certain point will have neglectable effect on the orbital appearance.

2 4-(*N*,*N*-Dimethylamino)benzonitrile

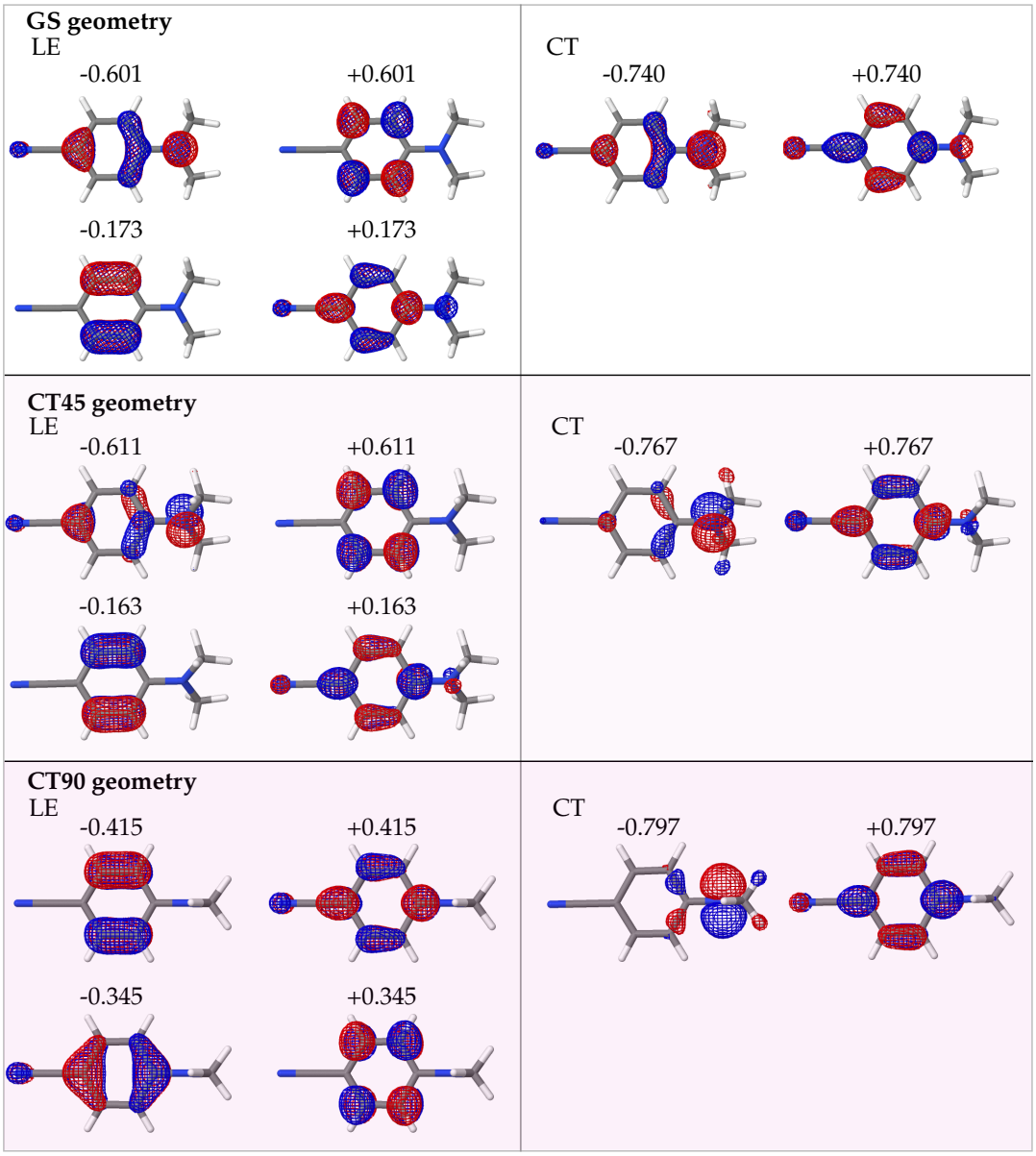

Figure 4: Natural transition orbitals of the LE and CT states of DMABN calculated for three geometries at the EOM-CCSD/cc-pVDZ level of theory, visualized with jmol-14.13.1. Negative (positive) coefficients quantify hole (electron) NTO contributions.

3 *Hexa*(thiophene)

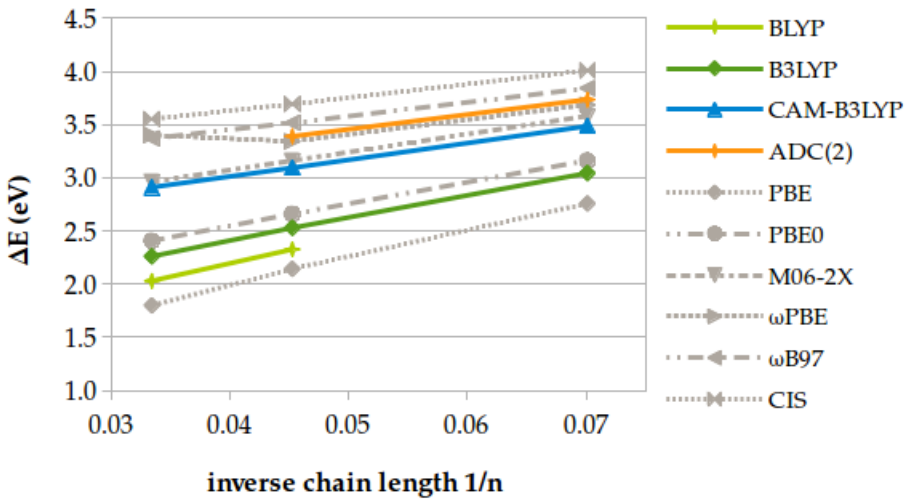

Figure 5: Excitation energies (ΔE, eV) plotted against the inverse chain length ($1/n$, 1/Å) for *tetra*-, *hexa*- and *octa*(thiophene) employing various TDDFT-TDA, CIS and ADC(2) levels of theory.

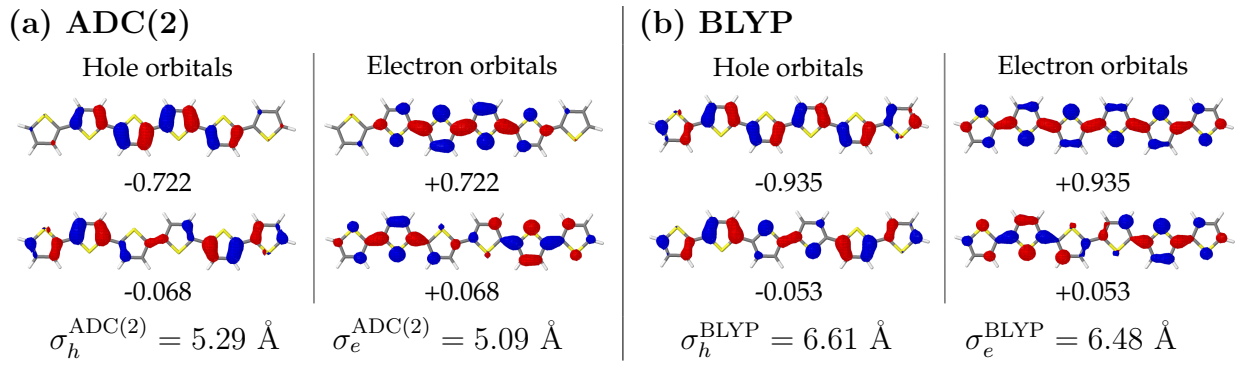

Figure 6: Natural transition orbitals for the description of the S_1 state of *hexa*(thiophene) (6T) calculated at the ADC(2) and BLYP/TDA levels of theory. Orbital cutoff 0.03, visualized with jmol-14.13.1.

Fig. 6 presents the natural transition orbitals of the S_1 state for ADC(2) and BLYP. While the patterns of orbital contributions on the individual thiophene moieties are the same for ADC(2) and BLYP, the major difference is that the outer two thiophene units are not involved in the NTO pair that describes the excited state in the case of ADC(2). This is reflected in the differences in σ_h and σ_e, which are in the order of 1.5 Å. The difference

in exciton size is significantly larger with > 5 Å. The decisive factor for this is electron-hole correlation as captured in the covariance between electron and hole quasiparticles.

Table 1: Vertical and adiabatic excitation energies of the S_1 and T_1 states of *hexa*(thiophene) in eV.

method	ΔE_{vert}	$\Delta E^{s,adia}$	$\Delta E^{t,adia}$
exp.	2.85	2.46	1.6
CAM-B3LYP/cc-pVDZ	3.05	2.80	1.62

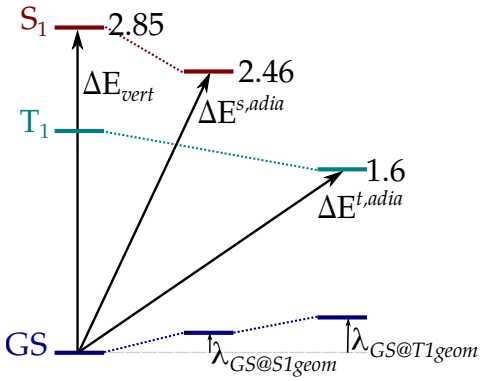

Figure 7: Jablonski diagram of *hexa*(thiophene): An overview about experimental energies in eV.

4 Magnesiumporphyrin

Table 2: First excited state of Magnesium(II)porphyrin calculated at various levels of theory employing Ahlrichs' SV basis set.

method	ΔE(eV)	f	Ω	d_{exc}	σ_h	σ_e	R_{eh}	σ_D	σ_A
exp.	2.07[a]								
ADC(3)	2.053	0.001	0.728	4.572	3.485	3.636	0.176	3.544	3.620
ADC(2)	2.397	0.013	0.772	4.617	3.361	3.672	0.140	3.484	3.634
EOM-CCSD	2.377	0.001	0.719	4.588	3.423	3.637	0.156		
BLYP	2.272	0.001	1	5.163	3.426	3.704	−0.047	-	-
B3LYP	2.398	0	1	5.017	3.449	3.681	0.011	-	-
CAM-B3LYP	2.436	0	1	4.798	3.452	3.646	0.087	-	-
CIS	2.483	0.014	1	4.680	3.533	3.666	0.155	-	-

[a] Edwards, L. Dolphin, D. H., Gouterman M., Adler, A.D., *J. Mol. Spectrosc.* **1971**, *38*, 16-32.

Table 3: Bright excited states (all degenerate) of Mg(II)porphyrin (MgP) calculated at various levels of theory employing Ahlrichs' SV(P) and TZVP basis sets.

method	state	ΔE(eV)	f	d_{exc}	σ_h	σ_e	R_{eh}
exp.	Q	2.07[a]					
BLYP/SV(P)	S_1	2.265	0	5.186	3.455	3.704	−0.048
BLYP/TZVP	S_1	2.271	0	5.198	3.465	3.718	−0.046
B3LYP/SV(P)	S_1	2.388	0.001	5.032	3.474	3.682	+0.012
B3LYP/TZVP	S_1	2.393	0	5.048	3.482	3.696	+0.011
CAM-B3LYP/SV(P)	S_1	2.423	0.004	4.806	3.475	3.648	+0.090
CAM-B3LYP/TZVP	S_1	2.430	0.001	4.827	3.482	3.662	+0.088
exp.	B	3.05[a]					
BLYP/SV(P)	S_3	3.124	0.018	5.532	3.751	3.703	−0.101
BLYP/TZVP	S_3	3.156	0.016	5.551	3.768	3.714	−0.101
B3LYP/SV(P)	S_4	3.655	0.105	5.103	3.685	3.689	+0.042
B3LYP/TZVP	S_4	3.676	0.110	5.136	3.702	3.701	+0.038
CAM-B3LYP/SV(P)	S_3	4.095	0.902	4.594	3.436	3.763	+0.188
CAM-B3LYP/TZVP	S_3	4.098	1.123	4.654	3.426	3.792	+0.172
exp.	N	3.97[a]					
BLYP/SV(P)	S_{10}	3.415	0.042	5.485	3.762	3.745	−0.068
BLYP/TZVP	S_{10}	3.441	0.064	5.471	3.752	3.765	−0.059
B3LYP/SV(P)	S_{10}	3.955	0.439	5.051	3.48	3.791	+0.037
B3LYP/TZVP	S_8	3.947	0.593	5.037	3.445	3.822	+0.042
CAM-B3LYP/SV(P)	S_7	4.442	1.178	4.923	3.555	3.711	+0.082
CAM-B3LYP/TZVP	S_7	4.402	0.992	4.928	3.601	3.713	+0.092
BLYP/SV(P)	S_{15}	3.984	1.485	5.567	3.667	3.982	−0.058
BLYP/TZVP	S_{15}	3.973	1.583	5.596	3.715	3.995	−0.052
B3LYP/SV(P)	S_{13}	4.350	1.849	5.589	3.991	3.783	−0.033
B3LYP/TZVP	S_{13}	4.340	1.722	5.631	4.049	3.789	−0.031
CAM-B3LYP/SV(P)	S_{13}	4.983	0.811	5.258	4.059	3.656	+0.074
CAM-B3LYP/TZVP	S_{12}	4.994	0.798	5.281	4.071	3.672	+0.072

[a] Edwards, L. Dolphin, D. H., Gouterman M., Adler, A.D., *J. Mol. Spectrosc.* **1971**, *38*, 16-32.

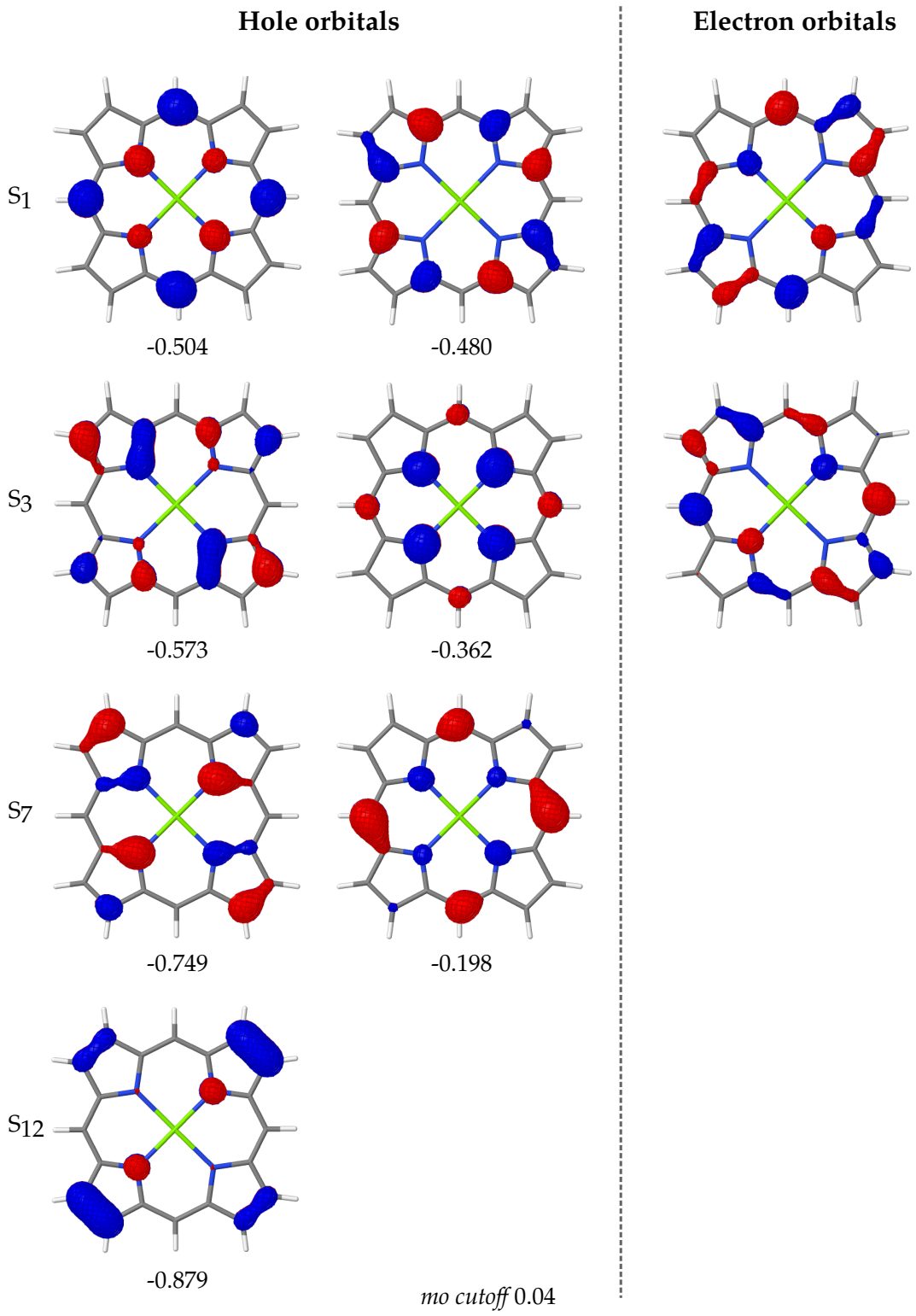

Figure 8: Natural transition orbitals of four singlet excited states of MgP computed at the CAM-B3LYP/TZVP level of theory, visualized with jmol-14.13.1.Negative coefficients quantify hole NTO contributions.

5 Raw data of plots

5.1 Figure 3: Excited states in formaldehyde

Fig. 3(a) ADC(3) vert. excitation energies (ΔE, eV)

state	SV	SV(P)	SVP	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
1^1A_2	3.822	3.954	3.986	3.967	3.92	3.963	3.902
1^1B_1	9.465	9.435	9.444	9.184	8.773	7.563	7.628
1^1B_2	9.163	9.330	9.326	9.368	9.197	9.350	9.175
2^1A_1	9.683	9.621	9.542	9.487	9.225	8.587	8.615
2^1A_2	10.234	10.181	10.171	10.145	9.954	9.111	9.027
2^1B_1	11.618	11.630	11.676	11.875	10.528	8.443	8.455
2^1B_2	12.624	12.497	12.471	12.259	11.892	10.954	10.902
3^1A_1	10.244	10.341	10.141	10.083	9.809	9.190	9.061

Fig. 3(b) ADC(3) electron sizes (σ_e, Å)

state	SV	SV(P)	SVP	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
1^1A_2	1.193	1.197	1.195	1.200	1.233	1.314	1.300
1^1B_1	1.960	1.956	1.948	1.948	2.163	3.141	3.188
1^1B_2	1.184	1.186	1.183	1.188	1.218	1.293	1.278
2^1A_1	1.490	1.430	1.420	1.423	1.445	3.559	3.701
2^1A_2	1.207	1.206	1.206	1.210	1.248	3.116	3.333
2^1B_1	1.669	1.652	1.646	1.633	1.926	3.062	3.166
2^1B_2	1.908	1.908	1.899	1.900	2.101	3.084	3.130
3^1A_1	1.488	1.382	1.375	1.380	1.405	1.612	1.607

Fig. 3(c) ADC(3) Ω values (Ω)

state	SV	SV(P)	SVP	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
1^1A_2	0.876	0.878	0.877	0.878	0.875	0.877	0.875
1^1B_1	0.898	0.895	0.892	0.893	0.895	0.905	0.903
1^1B_2	0.874	0.874	0.873	0.875	0.872	0.872	0.871
2^1A_1	0.336	0.639	0.538	0.555	0.620	0.905	0.903
2^1A_2	0.670	0.705	0.683	0.678	0.682	0.894	0.896
2^1B_1	0.913	0.909	0.908	0.909	0.905	0.908	0.906
2^1B_2	0.849	0.848	0.848	0.850	0.852	0.868	0.867
3^1A_1	0.523	0.219	0.318	0.303	0.234	0.620	0.673

5.2 Figure 4: Excited states in formaldehyde at different levels of theory

Fig. 4(a) Difference in exc. energies ($\Delta(\Delta E - exp)$, eV)

method	1^1A_2	1^1B_1	2^1B_1	2^1A_1	1^1B_2	3^1A_1
ADC(3)	-0.198	0.498	0.475	0.475	0.175	-1.639
ADC(2)	-0.179	-0.609	-0.436	-0.655	0.175	-1.225
EOM-CCSD	-0.082	0.105	0.143	0.075	0.296	-1.018

Fig. 4(b) Electron sizes (σ_e, Å)

method	1^1A_2	1^1B_1	2^1B_1	2^1A_1	1^1B_2	3^1A_1
ADC(3)	1.300	3.188	3.166	3.701	1.278	1.607
ADC(2)	1.343	3.100	3.210	3.733	1.331	3.784
EOM-CCSD	1.319	3.145	3.177	3.678	1.300	1.977

5.3 Figure 6: Excited states of DMABN

Fig. 6(a) Relative energies (E_{rel}, eV)

method/state	LE	GS	CT0	CT45	CT90	CTP
MP(2)/GS	0.443	0	0.266	0.580	0.687	1.537
MP(3)/GS	0.464	0	0.317	0.602	0.697	1.597
CCSD/GS	0.451	0	0.293	0.583	0.684	1.583
ADC(2)/ LE	4.175	4.489	4.521	4.733	5.566	6.091
ADC(2)/CT	4.891	4.746	4.524	4.281	4.109	3.928
ADC(3)/LE	4.329	4.473	4.623	4.915	5.271	5.883
ADC(3)/CT	5.193	4.938	4.844	4.875	4.869	4.648
EOM-CCSD/LE	4.466	4.645	4.767	5.034	5.520	6.142
EOM-CCSD/CT	5.366	5.149	5.041	4.864	4.660	4.504

Fig. 6(b) Dist. between *e*-*h* charge centers ($d_{h\to e}$, Å)

method/state	LE	GS	CT0	CT45	CT90	CTP
ADC(2)/LE	1.124	0.73	0.856	1.411	0.007	0.086
ADC(2)/CT	1.790	1.575	1.768	2.216	2.808	2.389
ADC(3)/LE	0.488	0.232	0.199	0.367	0.022	0.202
ADC(3)/CT	1.013	0.845	0.855	1.477	2.554	2.040
EOM-CCSD/LE	0.766	0.434	0.483	0.751	0.013	0.137
EOM-CCSD/CT	1.462	1.266	1.425	1.914	2.615	2.172

Fig. 6(c) Relative energies (E_{rel}, eV)

environm./state	LE	GS	CT0	CT45	CT90	CTP
vac/GS	0.443	0	0.266	0.580	0.687	1.537
vac/LE	4.175	4.489	4.521	4.733	5.566	6.091
vac/CT	4.891	4.746	4.524	4.281	4.109	3.928
cHex/GS	0.513	0	0.386	0.798	1.051	1.830
cHex/LE	4.083	4.449	4.494	4.657	5.914	6.348
cHex/CT	4.723	4.626	4.341	4.06	3.824	3.714
MeCN/GS	0.695	0	0.578	1.151	1.748	2.394
MeCN/LE	3.914	4.383	4.414	4.466	6.606	6.875
MeCN/CT	4.477	4.433	4.054	3.703	3.345	3.351

Fig. 6(d) Dist. between *e*-*h* charge centers ($d_{h\to e}$, **Å**)

method/state	LE	GS	CT0	CT45	CT90	CTP
vac/LE	1.124	0.73	0.856	1.411	0.007	0.086
vac/CT	1.790	1.575	1.768	2.216	2.808	2.389
cHex/LE	1.301	0.798	1.108	1.767	0.010	0.081
cHex/CT	1.918	1.656	1.900	2.324	2.897	2.479
MeCN/LE	1.565	0.911	1.449	2.054	0.051	0.093
MeCN/CT	2.070	1.768	1.997	2.389	3.034	2.609

5.4 Figure 7: Excited states of *hexa*(thiophene)

Fig. 7 complete data collection

	S_1			T_1		
method	ΔE	d_{exc}	R_{eh}	ΔE	d_{exc}	R_{eh}
ADC(2)	3.389	5.474	0.445	2.442	4.284	0.625
EOM-CCSD	3.671	4.919	0.535	2.288	3.798	0.699
CIS	3.535	4.367	0.641	1.833	3.617	0.734
BLYP/TDA	2.327	10.512	-0.289	1.722	7.424	0.143
BLYP/TDDFT	2.250	9.985	-0.239	1.676	7.068	0.213
B3LYP/TDA	2.746	7.766	0.121	1.909	5.830	0.397
B3LYP/TDDFT	2.648	7.540	0.136	1.735	5.173	0.524
CAM-B3LYP/TDA	3.204	5.448	0.480	2.108	4.502	0.599
CAM-B3LYP/TDDFT	3.092	5.392	0.476	1.689	3.731	0.730

5.5 Figure 8 and 9: Excited states of *all-trans* octatetraene

Fig. 8 and 9 complete data collection

method	state	ΔE	f_{osc}	Ω	R_2	d_{exc}	R_{eh}
ADC(2)	$2^1A_g^-$	5.981	0	0.811	0.1298	4.876	-0.317
	$1^1B_u^+$	4.622	1.677	0.861	0.0837	4.144	0.094
	$2^1B_u^-$	7.05	0	0.818	0.1269	3.964	0.214
ADC(3)	$2^1A_g^-$	3.946	0	0.205	0.7892	4.45	-0.199
	$1^1B_u^+$	4.647	1.691	0.852	0.0943	4.029	0.142
	$2^1B_u^-$	5.238	0.001	0.270	0.7177	3.799	0.267
EOM-CCSD	$2^1A_g^-$	6.132	0.000	0.693	0.1861	4.659	-0.264
	$1^1B_u^+$	5.002	1.730	0.787	0.0715	3.970	0.150
	$2^1B_u^-$	7.068	0.002	0.699	0.1931	3.805	0.271
BLYP	$2^1A_g^-$ /S_1	4.242	0	1	-	5.78	-0.491
	$1^1B_u^+$ /S_2	4.384	2.275	1	-	5.207	-0.148
	$2^1B_u^-$ /S_3	5.51	0.001	1	-	4.637	-0.032
B3LYP	$2^1A_g^-$ /S_2	4.935	0	1	-	5.522	-0.441
	$1^1B_u^+$ /S_1	4.516	2.318	1	-	4.712	-0.015
	$2^1B_u^-$ /S_4	6.215	0.001	1	-	4.401	0.063
CAM-B3LYP	$2^1A_g^-$ /S_2	5.904	0	1	-	5.077	-0.349
	$1^1B_u^+$ /S_1	4.669	2.207	1	-	4.188	0.118
	$2^1B_u^-$ /S_6	7.051	0.001	1	-	4.029	0.199

5.6 Figure 10: Electron and hole sizes of MgP

CAM-B3LYP/TZVP

state	σ_e (Å)	σ_h (Å)
S_1	3.662	3.482
S_3	3.792	3.426
S_7	3.713	3.601
S_{12}	3.672	4.071

6 Molecular geometries

6.1 Formaldehyde

```
0 1
C       0.0000000000     0.0000000000     0.5312422398
H       0.9305067687     0.0000000000     1.1108841906
H      -0.9305067687    -0.0000000000     1.1108841906
O       0.0000000000     0.0000000000    -0.6761527602
-----------------------------------------------------------------
 Molecular Point Group                 C2v   NOp =  4
 Largest Abelian Subgroup              C2v   NOp =  4
 Nuclear Repulsion Energy =    31.3165898987 hartrees
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6.2 DMABN

6.2.1 GS-optimized geometry, RIMP(2)/cc-pVDZ

```
0 1
C      -4.2238042544     2.5371414339     0.1016214622
C      -5.0046559858     1.3773007227     0.1275199922
C      -4.4105183213     0.0857705543     0.1366033689
C      -2.9914687373     0.0217269076     0.0829901811
C      -2.2102935150     1.1811879025     0.0567337079
C      -2.8167466751     2.4540310771     0.0682868785
H      -4.7097643029     3.5179382196     0.0997105098
H      -2.4805351528    -0.9426892063     0.0636272397
H      -1.1189656413     1.1004792530     0.0191208078
H      -6.0909074734     1.4884284093     0.1443469823
N      -5.1839681970    -1.0679596814     0.2166683026
C      -6.6029180813    -0.9603510887    -0.0875823613
```

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H      -7.1006782277    -0.2771772112     0.6181363524
H      -7.0635765903    -1.9509938618     0.0337478537
H      -6.8006301912    -0.6019428960    -1.1194360947
C      -4.5497469756    -2.3346853635    -0.1176591461
H      -4.1460435731    -2.3578646555    -1.1508753724
H      -5.2941075350    -3.1377896726    -0.0141151128
H      -3.7263294106    -2.5528416874     0.5806563536
C      -2.0107131234     3.6484424215     0.0391793389
N      -1.3466170354     4.6333604231     0.0156287556
-----------------------------------------------------------
 Nuclear Repulsion Energy =   543.8651238876 hartrees
```

6.2.2 LE-optimized geometry

```
0 1
C      -4.2239450000     2.5834160000     0.1648870000
C      -5.0414790000     1.3881130000     0.1500100000
C      -4.3798060000     0.1337820000     0.0017350000
C      -2.9732040000    -0.0042860000    -0.1235210000
C      -2.1570130000     1.1956600000    -0.0754540000
C      -2.8155290000     2.4497260000     0.0538990000
H      -4.6713900000     3.5725080000     0.2936990000
H      -2.5380780000    -0.9405870000    -0.4887250000
H      -1.0702800000     1.1491420000    -0.1795050000
H      -6.0712680000     1.4305730000     0.5210210000
N      -5.1651370000    -1.0250780000    -0.0269900000
C      -6.5783910000    -0.9950570000    -0.3774160000
H      -7.2007950000    -1.1565880000     0.5209030000
H      -6.7770570000    -1.8093450000    -1.0951400000
H      -6.8112790000    -0.0279630000    -0.8394800000
C      -4.6096680000    -2.3412150000     0.2541350000
H      -4.4130860000    -2.8857440000    -0.6872780000
H      -5.3459170000    -2.9112660000     0.8446640000
H      -3.6804810000    -2.2234050000     0.8253530000
C      -2.0118110000     3.6463220000     0.0784590000
N      -1.3472970000     4.6327970000     0.0996550000
-----------------------------------------------------------
Nuclear Repulsion Energy = 540.7097232319 hartrees
```

6.2.3 CT0-optimzied geometry

```
0 1
C       0.0000000000     0.0000000000    -2.6615190000
C       0.0000000000    -1.2492790000    -1.9186200000
C       0.0000000000    -1.2409680000    -0.5277250000
```

```
C       0.0000000000     0.0000000000     0.1875590000
C       0.0000000000     1.2409680000    -0.5277250000
C       0.0000000000     1.2492790000    -1.9186200000
H       0.0000000000    -2.1991070000    -2.4619550000
H       0.0000000000    -2.1975170000     0.0036480000
N       0.0000000000     0.0000000000     1.6416560000
H       0.0000000000     2.1975170000     0.0036480000
H       0.0000000000     2.1991070000    -2.4619550000
C       0.0000000000     0.0000000000    -4.0754240000
N       0.0000000000     0.0000000000    -5.2776190000
C       0.0000000000     1.2541370000     2.3630320000
C       0.0000000000    -1.2541370000     2.3630320000
H       0.0000000000     1.0527040000     3.4419060000
H       0.8936890000     1.8492650000     2.0961940000
H      -0.8936890000     1.8492650000     2.0961940000
H       0.0000000000    -1.0527040000     3.4419060000
H      -0.8936890000    -1.8492650000     2.0961940000
H       0.8936890000    -1.8492650000     2.0961940000
-----------------------------------------------------------------
 Nuclear Repulsion Energy =   538.8760943895 hartrees
```

6.2.4 CT45-optimzied geometry

```
0 1
C       0.0000000000     0.0000000000    -1.8130580000
C      -1.1810370000     0.3968040000    -1.0755870000
C      -1.1839580000     0.3917200000     0.3121890000
C       0.0000000000     0.0000000000     1.0210900000
C       1.1839580000    -0.3917200000     0.3121890000
C       1.1810370000    -0.3968040000    -1.0755870000
H      -2.0837680000     0.6871520000    -1.6233860000
H      -2.0750820000     0.7298530000     0.8539250000
N       0.0000000000     0.0000000000     2.4756580000
H       2.0750820000    -0.7298530000     0.8539250000
H       2.0837680000    -0.6871520000    -1.6233860000
C       0.0000000000     0.0000000000    -3.2324600000
C      -1.1293400000    -0.5696850000     3.1820750000
C       1.1293400000     0.5696850000     3.1820750000
H      -1.2610230000    -1.6146000000     2.8465800000
H      -0.9735880000    -0.5128550000     4.2681250000
H      -2.0465910000    -0.0197980000     2.9028450000
H       1.2610230000     1.6146000000     2.8465800000
H       0.9735880000     0.5128550000     4.2681250000
H       2.0465910000     0.0197980000     2.9028450000
N       0.0000000000     0.0000000000    -4.4314770000
```

```
---------------------------------------------------------------
 Nuclear Repulsion Energy =   538.8013412198 hartrees
```

6.2.5 CT90-optimzied geometry

```
0 1
C       0.0000000000     0.0000000000    -2.6648305000
C      -1.2418610000     0.0000000000    -1.9234329000
C      -1.2544926000     0.0000000000    -0.5399182000
C       0.0000000000     0.0000000000     0.1700945000
C       1.2544926000     0.0000000000    -0.5399182000
C       1.2418610000     0.0000000000    -1.9234329000
H      -2.1915906000     0.0000000000    -2.4704347000
H      -2.2028833000     0.0000000000     0.0113680000
N       0.0000000000     0.0000000000     1.5988591000
H       2.2028833000     0.0000000000     0.0113680000
H       2.1915906000     0.0000000000    -2.4704347000
C       0.0000000000     0.0000000000    -4.0850693000
C       0.0000000000    -1.2444562000     2.3667175000
C       0.0000000000     1.2444562000     2.3667175000
H       0.0000000000    -2.0826498000     1.6619428000
H       0.8962944000    -1.2629128000     3.0126713000
H      -0.8962944000    -1.2629128000     3.0126713000
H       0.0000000000     2.0826498000     1.6619428000
H      -0.8962944000     1.2629128000     3.0126713000
H       0.8962944000     1.2629128000     3.0126713000
N       0.0000000000     0.0000000000    -5.2834495000
---------------------------------------------------------------
 Nuclear Repulsion Energy =   537.5640027081 hartrees
```

6.2.6 CTP-optimzied geometry

```
0 1
C      -0.1593856000    -0.0239940000    -2.5992895000
C      -0.2525990000    -1.2478831000    -1.8478120000
C       0.0539879000    -1.2917647000    -0.4999242000
C       0.6101824000    -0.1204125000     0.1682048000
C       0.5412997000     1.1471966000    -0.5505607000
C       0.2303310000     1.1707141000    -1.8980256000
H      -0.5692284000    -2.1633982000    -2.3616022000
H      -0.0325840000    -2.2368463000     0.0528680000
N       0.1775598000    -0.0039784000     1.5519813000
H       0.8286452000     2.0743553000    -0.0366587000
H       0.2856193000     2.1163605000    -2.4503985000
C      -0.4826838000     0.0118175000    -3.9854735000
```

```
N      -0.7557588000     0.0421609000    -5.1498566000
C       1.1566677000    -0.1658945000     2.6114743000
C      -1.2125834000     0.2783596000     1.8994749000
H       0.6889015000    -0.0571525000     3.6010115000
H       1.6192083000    -1.1593450000     2.4898069000
H       1.9466070000     0.5873422000     2.4541050000
H      -1.5965842000    -0.5412313000     2.5324857000
H      -1.2524081000     1.2196797000     2.4760709000
H      -1.7830937000     0.3604942000     0.9658383000
-----------------------------------------------------------
 Nuclear Repulsion Energy =   541.4274985661 hartrees
```

6.3 All*trans*(1,3,5,7)octatetraene

```
0 1
C       0.0000000000     0.0000000000     0.0000000000
C       0.0000000000     0.0000000000     1.3408760000
C       1.2013090760     0.0000000000     2.1472399038
C       1.2025319191     0.0000000000     3.4946193489
C       2.3979216302    -0.0000000000     4.3004646368
C       2.3991444733     0.0000000000     5.6478440819
C       3.6004535493    -0.0000000000     6.4542079857
C       3.6004535493     0.0000000000     7.7950839857
H       0.2555450518     0.0000000000     4.0185492877
H       3.3449084975    -0.0000000000     3.7765346980
H       2.1472511388     0.0000000000     1.6217079820
H      -0.9411267057     0.0000000000     1.8726678842
H       1.4532024105     0.0000000000     6.1733760037
H       4.5415802550    -0.0000000000     5.9224161016
H       4.5193910546     0.0000000000     8.3583199258
H       2.6740087425     0.0000000000     8.3504725409
H      -0.9189375054    -0.0000000000    -0.5632359401
H       0.9264448068     0.0000000000    -0.5553885552
-----------------------------------------------------------
 Nuclear Repulsion Energy =   298.5276699980 hartrees
```

6.4 *Hexa*(thiophene)

6.4.1 Unsymmetric sturcture

```
0 1
S       9.7534506739    -1.0803308794    -0.0010174001
C       8.5136408308     0.1216952824     0.0003752512
C       9.0558709957     1.3845792117     0.0019794985
C      10.4854009942     1.3732690251     0.0020672984
```

```
C      10.9926008285     0.1034569589     0.0005407231
H       8.4498811148     2.2973892908     0.0031229180
H      11.1066011118     2.2742789440     0.0032608278
H      12.0418007884    -0.2036661781     0.0002524642
S       5.8634209381     0.9436326284     0.0000760272
C       4.6053307836    -0.2403422074    -0.0009423514
C       5.1287106177    -1.5108802757    -0.0013364296
C       6.5544106161    -1.5231804618    -0.0008621807
C       7.0998507807    -0.2624185330    -0.0001740665
S       1.9426006824    -1.0154398599     0.0011780402
C       0.7060128399     0.1911493015    -0.0008428994
C       1.2519210045     1.4522302303    -0.0031040212
C       2.6772310028     1.4393900442    -0.0033610212
C       3.2005108370     0.1686039759    -0.0012733905
H       0.6496201239     2.3671603089    -0.0047099317
H     -11.1067994818    -2.2738181566     0.0037410116
S      -1.9425690525     1.0151706473    -0.0001635438
C      -2.6772793730    -1.4396392568     0.0015205607
C      -5.1285889878     1.5107610631     0.0053943491
S      -5.8634893082    -0.9436788410    -0.0023732394
C     -10.9925991985    -0.1030201715    -0.0021406096
C      -8.5136592009    -0.1215144950     0.0006140052
C      -7.0998291508     0.2624673204     0.0014714399
C      -9.0560193657    -1.3843484242     0.0034513710
C      -6.5542889862     1.5231812492     0.0052671292
H      -8.4501294849    -2.2972085033     0.0070346815
H      -7.1572388669     2.4376413279     0.0083655187
H      -3.2962494909    -2.3433291760     0.0024915013
C      -4.6053091537     0.2401929948     0.0017530698
H      -0.6496894941    -2.3674695215     0.0009872292
C      -1.2519593746    -1.4525194429     0.0008153286
C      -0.7060172100    -0.1914515141    -0.0000474006
S      -9.7533390440     1.0806316668    -0.0042857704
C     -10.4855993642    -1.3728782376     0.0018133711
C      -3.2005092071    -0.1688311885     0.0011243800
H     -12.0417991584     0.2042109655    -0.0039698398
H      -4.5099488698     2.4147509824     0.0085533986
H       3.2961811208     2.3430999635    -0.0052367318
H       7.1574304968    -2.4376005405    -0.0010700192
H       4.5101404997    -2.4149201950    -0.0020692791
-----------------------------------------------------------------
 Molecular Point Group                C1    NOp =  1
 Largest Abelian Subgroup             C1    NOp =  1
 Nuclear Repulsion Energy =  3223.0521845029 hartrees
```

6.4.2 Symmetric GS-optimized sturcture

```
0 1
S       9.7533953941    -1.0804811024    -0.0000000000
C       8.5136500611     0.1216048980     0.0000000000
C       9.0559456837     1.3844637654     0.0000000000
C      10.4855003476     1.3730737090     0.0000000000
C      10.9926000932     0.1032388059     0.0000000000
H       8.4500070080     2.2972990236     0.0000000000
H      11.1067008840     2.2740486694     0.0000000000
H      12.0418002769    -0.2039382907    -0.0000000000
S       5.8634553109     0.9436559681     0.0000000000
C       4.6053201370    -0.2402678043    -0.0000000000
C       5.1286510953    -1.5108214223    -0.0000000000
C       6.5543507941    -1.5231814076    -0.0000000000
C       7.0998400280    -0.2624430161    -0.0000000000
S       1.9425850236    -1.0153053358    -0.0000000000
C       0.7060152806     0.1913004418     0.0000000000
C       1.2519413293     1.4523755080     0.0000000000
C       2.6772563655     1.4395147371     0.0000000000
C       3.2005103068     0.1687173819     0.0000000000
H       0.6496559275     2.3673170253     0.0000000000
H     -11.1067008840    -2.2740486694    -0.0000000000
S      -1.9425850236     1.0153053358     0.0000000000
C      -2.6772563655    -1.4395147371    -0.0000000000
C      -5.1286510953     1.5108214223     0.0000000000
S      -5.8634553109    -0.9436559681    -0.0000000000
C     -10.9926000932    -0.1032388059    -0.0000000000
C      -8.5136500611    -0.1216048980    -0.0000000000
C      -7.0998400280     0.2624430161     0.0000000000
C      -9.0559456837    -1.3844637654    -0.0000000000
C      -6.5543507941     1.5231814076     0.0000000000
H      -8.4500070080    -2.2972990236    -0.0000000000
H      -7.1573367593     2.4376221091     0.0000000000
H      -3.2962174751    -2.3432150517    -0.0000000000
C      -4.6053201370     0.2402678043     0.0000000000
H      -0.6496559275    -2.3673170253    -0.0000000000
C      -1.2519413293    -1.4523755080    -0.0000000000
C      -0.7060152806    -0.1913004418    -0.0000000000
S      -9.7533953941     1.0804811024     0.0000000000
C     -10.4855003476    -1.3730737090    -0.0000000000
C      -3.2005103068    -0.1687173819    -0.0000000000
H     -12.0418002769     0.2039382907     0.0000000000
H      -4.5100479165     2.4148376965     0.0000000000
H       3.2962174751     2.3432150517     0.0000000000
```

```
H       7.1573367593    -2.4376221091    -0.0000000000
H       4.5100479165    -2.4148376965    -0.0000000000
-----------------------------------------------------------------
 Molecular Point Group                C2h   NOp =  4
 Largest Abelian Subgroup             C2h   NOp =  4
 Nuclear Repulsion Energy =  3223.0537996195 hartrees
```

6.4.3 Symmetric S1-optimized sturcture

```
0 1
S       9.7396647779    -1.1005267950     0.0000000000
C       8.4875083998     0.1224485549    -0.0000000000
C       9.0523406028     1.3827049348    -0.0000000000
C      10.4705874553     1.3629494815    -0.0000000000
C      10.9843886772     0.0966215330    -0.0000000000
H       8.4590706848     2.2966379100    -0.0000000000
H      11.0894310226     2.2594134956    -0.0000000000
H      12.0287055435    -0.2062105793     0.0000000000
S       5.8489378169     0.9864426702    -0.0000000000
C       4.5738429697    -0.2233279246     0.0000000000
C       5.1306746319    -1.5034332314     0.0000000000
C       6.5296642885    -1.5059149313     0.0000000000
C       7.0965464851    -0.2393034372     0.0000000000
S       1.9363707058    -1.0654707283     0.0000000000
C       0.6818124838     0.1709444103    -0.0000000000
C       1.2647227158     1.4508486478    -0.0000000000
C       2.6518361748     1.4347463734    -0.0000000000
C       3.2083678172     0.1473590174    -0.0000000000
H       0.6679011312     2.3622108748    -0.0000000000
H     -11.0894310226    -2.2594134956     0.0000000000
S      -1.9363707058     1.0654707283    -0.0000000000
C      -2.6518361748    -1.4347463734     0.0000000000
C      -5.1306746319     1.5034332314    -0.0000000000
S      -5.8489378169    -0.9864426702     0.0000000000
C     -10.9843886772    -0.0966215330     0.0000000000
C      -8.4875083998    -0.1224485549     0.0000000000
C      -7.0965464851     0.2393034372    -0.0000000000
C      -9.0523406028    -1.3827049348     0.0000000000
C      -6.5296642885     1.5059149313    -0.0000000000
H      -8.4590706848    -2.2966379100     0.0000000000
H      -7.1295231195     2.4156425583    -0.0000000000
H      -3.2669439285    -2.3340336613     0.0000000000
C      -4.5738429697     0.2233279246    -0.0000000000
H      -0.6679011312    -2.3622108748     0.0000000000
C      -1.2647227158    -1.4508486478     0.0000000000
```

```
C      -0.6818124838    -0.1709444103     0.0000000000
S      -9.7396647779     1.1005267950    -0.0000000000
C     -10.4705874553    -1.3629494815     0.0000000000
C      -3.2083678172    -0.1473590174     0.0000000000
H     -12.0287055435     0.2062105793    -0.0000000000
H      -4.5232958027     2.4078109258    -0.0000000000
H       3.2669439285     2.3340336613    -0.0000000000
H       7.1295231195    -2.4156425583     0.0000000000
H       4.5232958027    -2.4078109258     0.0000000000
 ---------------------------------------------------------------
 Molecular Point Group                C2h   NOp =  4
 Largest Abelian Subgroup             C2h   NOp =  4
 Nuclear Repulsion Energy =  3218.6501723953 hartrees
```

6.4.4 T_1-optimized structure

```
0 1
S         9.7455670339   -1.0961957368    0.0000000000
C         8.4937724009    0.1227517301    0.0000000000
C         9.0519515651    1.3806083941    0.0000000000
C        10.4734300629    1.3664304974    0.0000000000
C        10.9885908505    0.1030195039    0.0000000000
H         8.4559642493    2.2927587261    0.0000000000
H        11.0888375191    2.2650219924    0.0000000000
H        12.0330446729   -0.1988671087    0.0000000000
S         5.8487868190    0.9799917097    0.0000000000
C         4.5736520381   -0.2301732733    0.0000000000
C         5.1320814235   -1.5079476896    0.0000000000
C         6.5347821270   -1.5082856303    0.0000000000
C         7.0965450766   -0.2448845981    0.0000000000
S         1.9347430341   -1.0834599773    0.0000000000
C         0.6740933272    0.1612199274    0.0000000000
C         1.2734810799    1.4536830036    0.0000000000
C         2.6483720881    1.4310250544    0.0000000000
C         3.2093649412    0.1347905790    0.0000000000
H         0.6784763189    2.3659043052    0.0000000000
H       -11.0888375191   -2.2650219924    0.0000000000
S        -1.9347430341    1.0834599773    0.0000000000
C        -2.6483720881   -1.4310250544    0.0000000000
C        -5.1320814235    1.5079476896    0.0000000000
S        -5.8487868190   -0.9799917097    0.0000000000
C       -10.9885908505   -0.1030195039    0.0000000000
C        -8.4937724009   -0.1227517301    0.0000000000
C        -7.0965450766    0.2448845981    0.0000000000
C        -9.0519515651   -1.3806083941    0.0000000000
```

```
C        -6.5347821270    1.5082856303    0.0000000000
H        -8.4559642493   -2.2927587261    0.0000000000
H        -7.1354050882    2.4174676421    0.0000000000
H        -3.2675257093   -2.3277538296    0.0000000000
C        -4.5736520381    0.2301732733    0.0000000000
H        -0.6784763189   -2.3659043052    0.0000000000
C        -1.2734810799   -1.4536830036    0.0000000000
C        -0.6740933272   -0.1612199274    0.0000000000
S        -9.7455670339    1.0961957368    0.0000000000
C       -10.4734300629   -1.3664304974    0.0000000000
C        -3.2093649412   -0.1347905790    0.0000000000
H       -12.0330446729    0.1988671087    0.0000000000
H        -4.5261446924    2.4129551808    0.0000000000
H         3.2675257093    2.3277538296    0.0000000000
H         7.1354050882   -2.4174676421    0.0000000000
H         4.5261446924   -2.4129551808    0.0000000000
 ---------------------------------------------------------------
 Molecular Point Group                C2h   NOp =  4
 Largest Abelian Subgroup             C2h   NOp =  4
 Nuclear Repulsion Energy =  3216.8005202756 hartrees
```

6.5 Magnesium(II)porphyrin

6.5.1 Unsymmetric sturcture

```
0 1
Mg     -0.0000095021    -0.0000199530    -0.0001184041
N      -1.1943128162    -1.6885336039    -0.0003932493
C      -2.5943543029    -1.7223067128     0.0014546935
C      -0.7597673502    -3.0198631975    -0.0021701050
C      -3.4236283008    -0.5869641022     0.0015411108
H      -4.5013153060    -0.7717031615     0.0025737812
C       0.5869626396    -3.4236261728    -0.0015033515
H       0.7717077299    -4.5013123235    -0.0023277783
C       1.7223053803    -2.5943443375    -0.0006242040
N       1.6885395096    -1.1943016985     0.0001989085
C       3.0198719079    -0.7597630388     0.0014656203
C       3.4236358387     0.5869646813     0.0010624218
H       4.5013218910     0.7717113944     0.0016029409
C       2.5943497726     1.7223044654     0.0003775555
N       1.1943071019     1.6885322452    -0.0000222424
C       0.7597645757     3.0198628104    -0.0005918040
C      -0.5869666422     3.4236358622    -0.0010888395
H      -0.7717072503     4.5013229233    -0.0017002133
C      -1.7223057724     2.5943588111    -0.0012744018
```

```
N      -1.6885273342     1.1943158543     0.0000446136
C      -3.0198554705     0.7597672695     0.0012799371
C       3.0448673235     3.1087419292     0.0000548021
H       4.0832234733     3.4291097352     0.0003081417
C       1.9169471167     3.9064948860    -0.0005070412
H       1.8731194302     4.9922656165    -0.0008861258
C      -3.1087459989     3.0448738665    -0.0005510255
H      -3.4291189159     4.0832282726    -0.0011916969
C      -3.9064927738     1.9169510244     0.0006617618
H      -4.9922632402     1.8731212094     0.0013903088
C       3.1087457851    -3.0448654780    -0.0000101563
H       3.4291124151    -4.0832218847    -0.0005431359
C       3.9065027274    -1.9169496136     0.0009845429
H       4.9922735168    -1.8731271387     0.0016720124
C      -3.0448718759    -3.1087492497     0.0006833969
H      -4.0832261107    -3.4291215940     0.0017479067
C      -1.9169530752    -3.9064992670    -0.0009449378
H      -1.8731278633    -4.9922698099    -0.0018213615
 ---------------------------------------------------------------
 Molecular Point Group                C1    NOp =  1
 Largest Abelian Subgroup             C1    NOp =  1
 Nuclear Repulsion Energy =  2092.9079950301 hartrees
```

6.5.2 Symmetric sturcture

```
0 1
Mg      0.0000000000     0.0000000000     0.0000000000
N       2.0682164000     0.0000000000     0.0000000000
C       2.9042329000    -1.1235395000     0.0000000000
C       2.9042329000     1.1235395000     0.0000000000
C       2.4561944000    -2.4561944000     0.0000000000
H       3.2293499000    -3.2293499000     0.0000000000
C       2.4561944000     2.4561944000     0.0000000000
H       3.2293499000     3.2293499000     0.0000000000
C       1.1235395000     2.9042329000     0.0000000000
N       0.0000000000     2.0682164000     0.0000000000
C      -1.1235395000     2.9042329000     0.0000000000
C      -2.4561944000     2.4561944000     0.0000000000
H      -3.2293499000     3.2293499000     0.0000000000
C      -2.9042329000     1.1235395000     0.0000000000
N      -2.0682164000     0.0000000000     0.0000000000
C      -2.9042329000    -1.1235395000     0.0000000000
C      -2.4561944000    -2.4561944000     0.0000000000
H      -3.2293499000    -3.2293499000     0.0000000000
C      -1.1235395000    -2.9042329000     0.0000000000
```

```
N       0.0000000000    -2.0682164000     0.0000000000
C       1.1235395000    -2.9042329000     0.0000000000
C      -4.2963151000     0.6907623000     0.0000000000
H      -5.1574655000     1.3535132000     0.0000000000
C      -4.2963151000    -0.6907623000     0.0000000000
H      -5.1574655000    -1.3535132000     0.0000000000
C      -0.6907623000    -4.2963151000     0.0000000000
H      -1.3535132000    -5.1574655000     0.0000000000
C       0.6907623000    -4.2963151000     0.0000000000
H       1.3535132000    -5.1574655000     0.0000000000
C       0.6907623000     4.2963151000     0.0000000000
H       1.3535132000     5.1574655000     0.0000000000
C      -0.6907623000     4.2963151000     0.0000000000
H      -1.3535132000     5.1574655000     0.0000000000
C       4.2963151000    -0.6907623000     0.0000000000
H       5.1574655000    -1.3535132000     0.0000000000
C       4.2963151000     0.6907623000     0.0000000000
H       5.1574655000     1.3535132000     0.0000000000
-----------------------------------------------------------------
 Molecular Point Group                 D2h   NOp =  8
 Largest Abelian Subgroup              D2h   NOp =  8
 Nuclear Repulsion Energy =  2092.9081454570 hartrees
```