Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Quantum Entanglement in Carbon-Carbon, Carbon-Phosphorus and Silicon-Silicon Bonds

Matthieu Mottet[a] Paweł Tecmer[a,b,1] Katharina Boguslawski[a,b,2], Örs Legeza[c], and Markus Reiher[a]

[a]ETH Zurich, Laboratorium für Physikalische Chemie, Vladimir-Prelog-Weg 2, CH-8093 Zurich, Switzerland

[b]Current address: Department of Chemistry and Chemical Biology, McMaster University, Hamilton, Ontario L8S 4L8, Canada

[c]Strongly Correlated Systems "Lendület" Research Group, Wigner Research Center for Physics, H-1525 Budapest, Hungary

Supporting Information

[1]Author to whom correspondence should be sent; email: tecmer@mcmaster.ca
[2]Author to whom correspondence should be sent; email: bogusl@mcmaster.ca

1 Geometries of polyatomic molecules

r_{C-C} [Å]	Atom type	Coordinates [Å]		
		x	y	z
$0.8r_e$	C	0.61273949	0.00000000	0.00000000
	C	-0.61273949	0.00000000	-0.00000000
	H	-1.08941150	-1.00326048	-0.00000000
	H	1.08941150	-0.50119911	-0.86908571
	H	1.08941150	1.00326037	-0.00000000
	H	-1.08941150	0.50119911	0.86908571
	H	-1.08941150	0.50119911	-0.86908571
	H	1.08941150	-0.50119911	0.86908571
$1.0r_e$	C	0.76592436	0.00000000	0.00000000
	C	-0.76592436	0.00000000	0.00000000
	H	-1.16726310	-1.02425417	-0.00000024
	H	1.16705857	-0.51224615	-0.88703897
	H	1.16726310	1.02425418	0.00000000
	H	-1.16705864	0.51224601	0.88703905
	H	-1.16705857	0.51224637	-0.88703885
	H	1.16705865	-0.51224622	0.88703893
$1.5r_e$	C	1.14865222	0.00000000	0.00000000
	C	-1.14865222	0.00000000	0.00000000
	H	1.38086246	-1.06476998	0.00000000
	H	1.38086246	0.53238501	-0.92211790
	H	1.38086246	0.53238501	0.92211790
	H	-1.38086246	-0.53238501	0.92211790
	H	-1.38086246	-0.53238501	-0.92211790
	H	-1.38086246	1.06476998	-0.00000000
$2.0r_e$	C	1.53153629	0.00000000	0.00000000
	C	-1.53153629	0.00000000	0.00000000
	H	-1.63161159	-1.08214099	0.00000000
	H	1.63161159	-0.54105997	-0.93714346
	H	1.63161159	1.08214099	0.00000000
	H	-1.63161159	0.54105997	0.93714346
	H	-1.63161159	0.54105997	-0.93714346
	H	1.63161159	-0.54105997	0.93714346

Table I: Optimized structures of the C_2H_6 molecule at different C–C distances (r_e = 1.53 Å).

r_{C-C} [Å]	Atom type	Coordinates [Å]		
		x	y	z
$0.8r_e$	C	0.534800	0.000000	0.000000
	C	-0.534800	0.000000	0.000000
	H	-1.164905	0.903858	0.000000
	H	-1.164905	-0.903858	0.000000
	H	1.164905	-0.903858	0.000000
	H	1.164905	0.903858	0.000000
$1.0r_e$	C	0.667370	0.000000	0.000000
	C	-0.667370	0.000000	0.000000
	H	-1.239473	0.930284	0.000000
	H	-1.239473	-0.930284	0.000000
	H	1.239473	-0.930284	0.000000
	H	1.239473	0.930284	0.000000
$1.5r_e$	C	1.002750	0.000000	0.000000
	C	-1.002750	0.000000	0.000000
	H	-1.470025	0.979073	0.000000
	H	-1.470025	-0.979073	0.000000
	H	1.470025	-0.979073	0.000000
	H	1.470025	0.979073	0.000000
$2.0r_e$	C	1.337000	0.000000	0.000000
	C	-1.337000	0.000000	0.000000
	H	-1.738106	1.007229	0.000000
	H	-1.738106	-1.007229	0.000000
	H	1.738106	-1.007229	0.000000
	H	1.738106	1.007229	0.000000

Table II: Optimized structures of the C_2H_4 molecule at different C–C distances (r_e = 1.34 Å).

r_{C-C} [Å]	Atom type	Coordinates [Å]		
		x	y	z
$0.8r_e$	C	-0.00000000	0.00000000	0.48298725
	C	0.00000000	0.00000000	-0.48298725
	H	0.00000000	0.00000000	-1.55033942
	H	-0.00000000	0.00000000	1.55033942
$1.0r_e$	C	0.00000000	0.00000000	-0.60373406
	C	0.00000000	0.00000000	0.60373406
	H	0.00000000	0.00000000	1.67487239
	H	0.00000000	0.00000000	-1.67487239
$1.5r_e$	C	-0.00000000	0.00000000	-0.90561822
	C	0.00000000	0.00000000	0.90561822
	H	0.00000000	-0.00000000	1.99229169
	H	-0.00000000	0.00000000	-1.99229168
$2.0r_e$	C	-0.00000000	0.00000000	-1.20749096
	C	0.00000000	0.00000000	1.20749096
	H	-0.00000000	0.00000000	2.11784630
	H	0.00000000	-0.00000000	-2.11784630

Table III: Optimized structures of the C_2H_2 molecule at different C–C distances (r_e = 1.21 Å).

r_{Si-Si} [Å]	Atom type	Coordinates [Å]		
		x	y	z
$0.8r_e$	Si	-0.84496638	0.00000000	-0.00000000
	Si	0.84496638	0.00000000	0.00000000
	H	2.08304824	-0.81409388	-0.00000000
	H	-2.08304824	0.81409388	-0.00000002
$1.0r_e$	Si	1.05607735	-0.00000000	0.00000000
	Si	-1.05607735	0.00000000	0.00000000
	H	1.89054607	-1.25179182	0.00000000
	H	-1.89054607	1.25179182	0.00000000
$1.65r_e$	Si	-1.74308565	-0.01023861	0.00000000
	Si	1.74308565	0.01023861	0.00000000
	H	-1.69429085	1.53446943	0.00000000
	H	1.69429085	-1.53446943	0.00000000
$2.0r_e$	Si	-2.11286754	0.00000000	0.00000000
	Si	2.11286754	0.00000000	0.00000000
	H	-2.02557026	1.54248876	-0.00000002
	H	2.02557025	-1.54248875	0.00000000

Table IV: Optimized structures of the Si_2H_2 molecule at different Si–Si distances (r_e = 2.11 Å).

r_{Si-Si} [Å]	Atom type	Coordinates [Å]		
		x	y	z
$0.8r_e$	Si	-0.00000000	0.00000000	-0.85945352
	Si	0.00000000	0.00000000	0.85945352
	H	-1.23738955	0.00000000	1.69547955
	H	1.23738955	0.00000000	1.69547955
	H	1.23738955	0.00000000	-1.69547954
	H	-1.23738955	0.00000000	-1.69547954
$1.0r_e$	Si	0.00000000	0.00000000	1.07440747
	Si	-0.00000000	0.00000000	-1.07440747
	H	1.26115194	0.00000000	-1.86009294
	H	-1.26115194	0.00000000	-1.86009294
	H	-1.26115194	0.00000000	1.86009295
	H	1.26115194	0.00000000	1.86009295
$1.5r_e$	Si	0.00000000	-0.00000000	1.61237364
	Si	0.00000000	0.00000000	-1.61237364
	H	1.29076726	0.00000000	-2.35236462
	H	-1.29076726	0.00000000	-2.35236462
	H	-1.29076726	-0.00000000	2.35236462
	H	1.29076726	-0.00000000	2.35236462

Table V: Optimized structures of the Si_2H_4 molecule at different Si–Si distances ($r_e = 2.15$ Å).

r_{C-P} [Å]	Atom type	Coordinates [Å]		
		x	y	z
$0.8r_e$	C	0.00000000	0.00000000	0.61976528
	P	-0.00000000	0.00000000	-0.61976528
	H	0.00000000	0.00000000	1.69695869
$1.0r_e$	C	0.00000000	0.00000000	0.77470660
	P	0.00000000	0.00000000	-0.77470660
	H	0.00000000	0.00000000	1.85714243
$1.5r_e$	C	0.00000000	0.00000000	1.16184630
	P	-0.00000000	-0.00000000	-1.16184630
	H	-0.00000001	-0.00000000	2.26691544
$2.0r_e$	C	0.00000000	0.00000000	1.54912840
	P	-0.00000000	0.00000000	-1.54912840
	H	-0.00000000	-0.00000001	2.67436143

Table VI: Optimized structures of the HCP molecule at different C–P distances ($r_e = 1.55$ Å).

2 Convergence of DMRG energies with respect to the number of block states (m).

In the following, the notation DMRG(x,y)[$m_{\max}, m_{\min}, m_{\text{start}}, \chi$] indicates that x electrons are correlated in y orbitals, the minimal and maximal number of active-system states was set to $m_{\min}$ and $m_{\max}$, respectively, while the minimal number of active-system states during the initialization procedure was set to m_{start}. χ is the quantum information loss and represents the truncation condition for the selection procedure of the number of renormalized active-system states.

Method	E/Hartree			
	$0.8r_e$ Å	$1.0r_e$ Å	$1.5r_e$ Å	$2.0r_e$ Å
UHF	−79.177120	−79.259002	−79.153173	−79.062759
CAS(14,14)SCF	−79.316523	−79.411086	−79.329205	−79.277434
DMRG(14,28)				
[1024,256,1024,10^{-5}]	−79.354788	−79.455364	−79.374872	−79.324648
E_{corr}	−0.177668	−0.196362	−0.221699	−0.261889
I_{tot}	1.8890	2.0416	2.4438	3.0771
[2048,512,2048,10^{-5}]	−79.355206	−79.455836	−79.375378	−79.325169
E_{corr}	−0.178086	−0.196834	−0.222205	−0.262410
I_{tot}	1.9045	2.0588	2.4638	3.0983

Table VII: Energies in Hartree atomic units and total single-orbital entropies of the C_2H_6 molecule for different inter-atomic distances for unrestricted Hartree-Fock, CASSCF and DMRG calculations at $r_e = 1.53$ Å.

Method	E/Hartree			
	$0.8r_e$ Å	$1.0r_e$ Å	$1.5r_e$ Å	$2.0r_e$ Å
UHF	−77.942930	−78.062996	−77.530114	−77.596221
CAS(14,14)SCF	−78.061880	−78.186150	−78.034195	−77.935887
DMRG(14,28)				
[1024,256,1024,10^{-5}]	−79.115652	−79.255367	−79.112357	−79.018001
E_{corr}	−1.172722	−1.192371	−1.582243	−1.421780
I_{tot}	1.7945	2.0759	3.3067	5.1610
[2048,512,2048,10^{-5}]	−79.115692	−79.255427	−79.112509	−79.018234
E_{corr}	−1.172762	−1.192431	−1.582395	−1.422013
I_{tot}	1.7958	2.0781	3.3136	5.1739

Table VIII: Energies in Hartree atomic units and total single-orbital entropies of the C_2H_4 molecule for different inter-atomic distances for unrestricted Hartree-Fock, CASSCF and DMRG calculations at $r_e = 1.34$ Å.

Method	E/Hartree			
	$0.8r_e$ Å	$1.0r_e$ Å	$1.5r_e$ Å	$2.0r_e$ Å
UHF	−76.690311	−76.848563	−76.503077	−75.919227
CAS(10,10)SCF	−76.808500	−76.997435	−76.771656	−76.578940
DMRG(10,28)				
[1024,256,1024,10^{-5}]	−76.839398	−77.037885	−76.826730	−76.626680
E_{corr}	−0.149087	−0.189322	−0.323653	−0.707453
I_{tot}	1.4317	2.0146	4.5505	7.6363
[1024,512,1024,10^{-5}]	−76.839434	−77.037919	−76.826755	−76.626698
E_{corr}	−0.149123	−0.189356	−0.323678	−0.707471
I_{tot}	1.4326	2.0154	4.5515	7.6367

Table IX: Energies in Hartree atomic units and total single-orbital entropies of the C_2H_2 molecule for different inter-atomic distances for unrestricted Hartree-Fock, CASSCF and DMRG calculations at $r_e = 1.21$ Å.

Method	E/Hartree			
	$0.8r_e$ Å	$1.0r_e$ Å	$1.5r_e$ Å	$2.0r_e$ Å
UHF	−75.248387	−75.401792	−75.213910	−74.889789
CAS(8,8)SCF	−75.473535	−75.638802	−75.448470	−75.375017
DMRG(8,26)				
[1024,256,1024,10^{-5}]	−75.480802	−75.648031	−75.483715	−75.416682
E_{corr}	−0.232415	−0.246239	−0.269805	−0.526893
I_{tot}	2.7257	3.3210	4.7453	5.6009
[2048,512,2048,10^{-5}]	−75.480831	−75.648068	−75.483756	−75.416743
E_{corr}	−0.232444	−0.246276	−0.269846	−0.526954
I_{tot}	2.7271	3.3229	4.7477	5.6028

Table X: Energies in Hartree atomic units and total single-orbital entropies of the C_2 molecule for different inter-atomic distances for unrestricted Hartree–Fock, CASSCF and DMRG calculations at $r_e = 1.24$ Å.

Method	E/Hartree			
	$0.8r_e$ Å	$1.0r_e$ Å	$1.65r_e$ Å	$2.0r_e$ Å
UHF	−578.818710	−578.907067	−578.878204	−578.739233
CAS(10,10)SCF	−578.908649	−579.025449	−578.974265	−578.935304
DMRG(10,25)				
[1024,256,1024,10^{-5}]	−578.946088	−579.054791	−579.007412	−578.969327
E_{corr}	−0.127378	−0.147724	−0.129208	−0.230094
I_{tot}	2.1644	2.6518	4.4534	3.5258
[1024,512,1024,10^{-5}]	−578.946097	−579.054801	−579.007418	−578.969341
E_{corr}	−0.127387	−0.147734	−0.129214	−0.230108
I_{tot}	2.1651	2.6526	4.4565	3.5266

Table XI: Energies in Hartree atomic units and total single-orbital entropies of the Si_2H_2 molecule for different inter-atomic distances for unrestricted Hartree-Fock, CASSCF and DMRG calculations at $r_e = 2.11$ Å.

Method	E/Hartree		
	$0.8r_e$ Å	$1.0r_e$ Å	$1.5r_e$ Å
UHF	−580.026571	−580.140382	−579.884021
CAS(12,12)SCF	−580.114218	−580.240374	−580.143295
DMRG(12,28)			
[1024,256,1024,10^{-5}]	−580.138365	−580.263966	−580.164916
E_{corr}	−0.111794	−0.123584	−0.280895
I_{tot}	1.8496	2.1695	4.0600
[1024,512,1024,10^{-5}]	−580.138395	−580.263978	−580.164927
E_{corr}	−0.111824	−0.123596	−0.280906
I_{tot}	1.8509	2.1700	4.0606

Table XII: Energies in Hartree atomic units and total single-orbital entropies of the Si_2H_4 molecule for different inter-atomic distances for unrestricted Hartree-Fock, CASSCF and DMRG calculations at $r_e = 2.15$ Å.

Method	E/Hartree			
	$0.8r_e$ Å	$1.0r_e$ Å	$1.5r_e$ Å	$2.0r_e$ Å
UHF	−378.407960	−378.543563	−378.319075	−378.235245
CAS(10,8)SCF	−378.492276	−378.648753	−378.507568	−378.436728
DMRG(10,26)				
[1024,256,1024,10^{-5}]	−378.609447	−378.773925	−378.645700	−378.576908
E_{corr}	−0.201487	−0.230362	−0.669612	−0.341663
I_{tot}	2.0007	2.6398	5.6175	8.5429
[1024,512,1024,10^{-5}]	−378.609477	−378.773945	−378.645720	−378.576924
E_{corr}	−0.201517	−0.230382	−0.669632	−0.341679
I_{tot}	2.0018	2.6406	5.6179	8.5429

Table XIII: Energies in Hartree atomic units and total single-orbital entropies of the $[CP]^-$ molecule for different inter-atomic distances for unrestricted Hartree-Fock, CASSCF and DMRG calculations at $r_e = 1.62$ Å.

Method	E/Hartree			
	$0.8r_e$ Å	$1.0r_e$ Å	$1.5r_e$ Å	$2.0r_e$ Å
UHF	−378.988230	−379.126068	−378.882948	−378.759870
CAS(10,15)SCF	−379.092148	−379.323934	−379.120606	−379.030103
DMRG(10,26)				
[1024,256,1024,10^{-5}]	−379.162320	−379.360337	−379.204213	−379.120357
E_{corr}	−0.174090	−0.234269	−0.321265	−0.360487
I_{tot}	2.4929	3.0015	5.5609	8.0375
[1024,512,1024,10^{-5}]	−379.162341	−379.360354	−379.204229	−379.120372
E_{corr}	−0.174111	−0.234286	−0.321281	−0.360502
I_{tot}	2.4942	3.0024	5.5619	8.0378

Table XIV: Energies in Hartree atomic units and total single-orbital entropies of the HCP molecule for different inter-atomic distances for unrestricted Hartree-Fock, CASSCF and DMRG calculations at $r_e = 1.55$ Å.

3 Additional entanglement diagrams

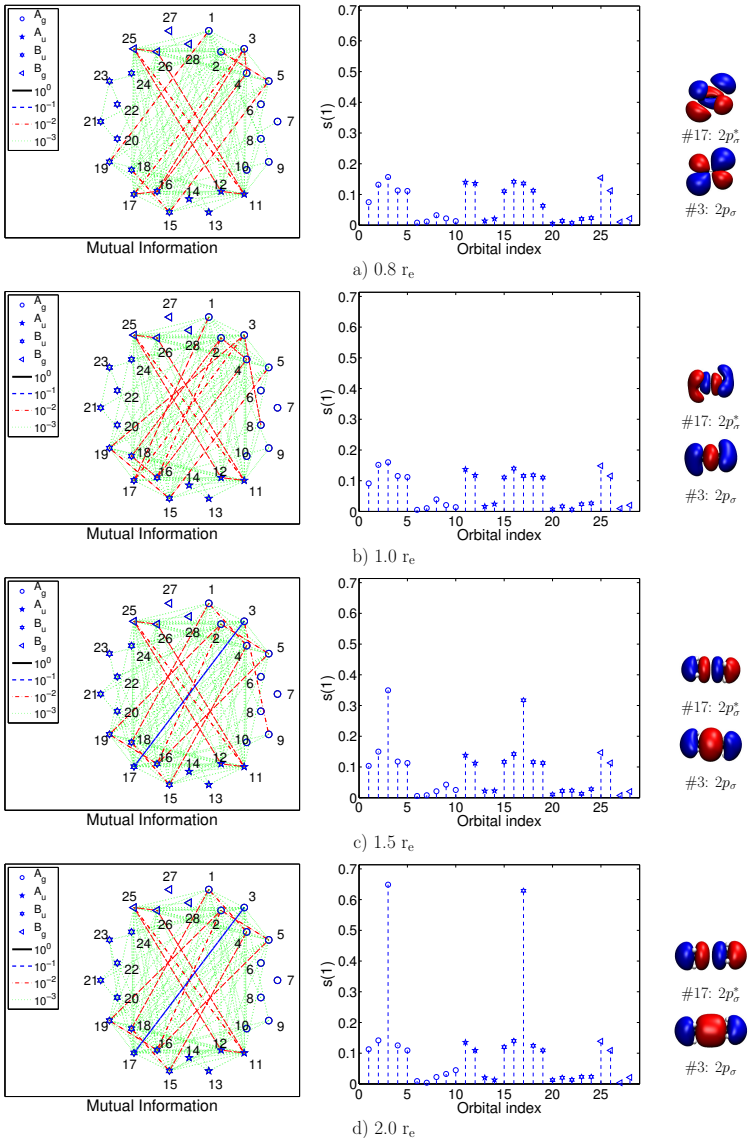
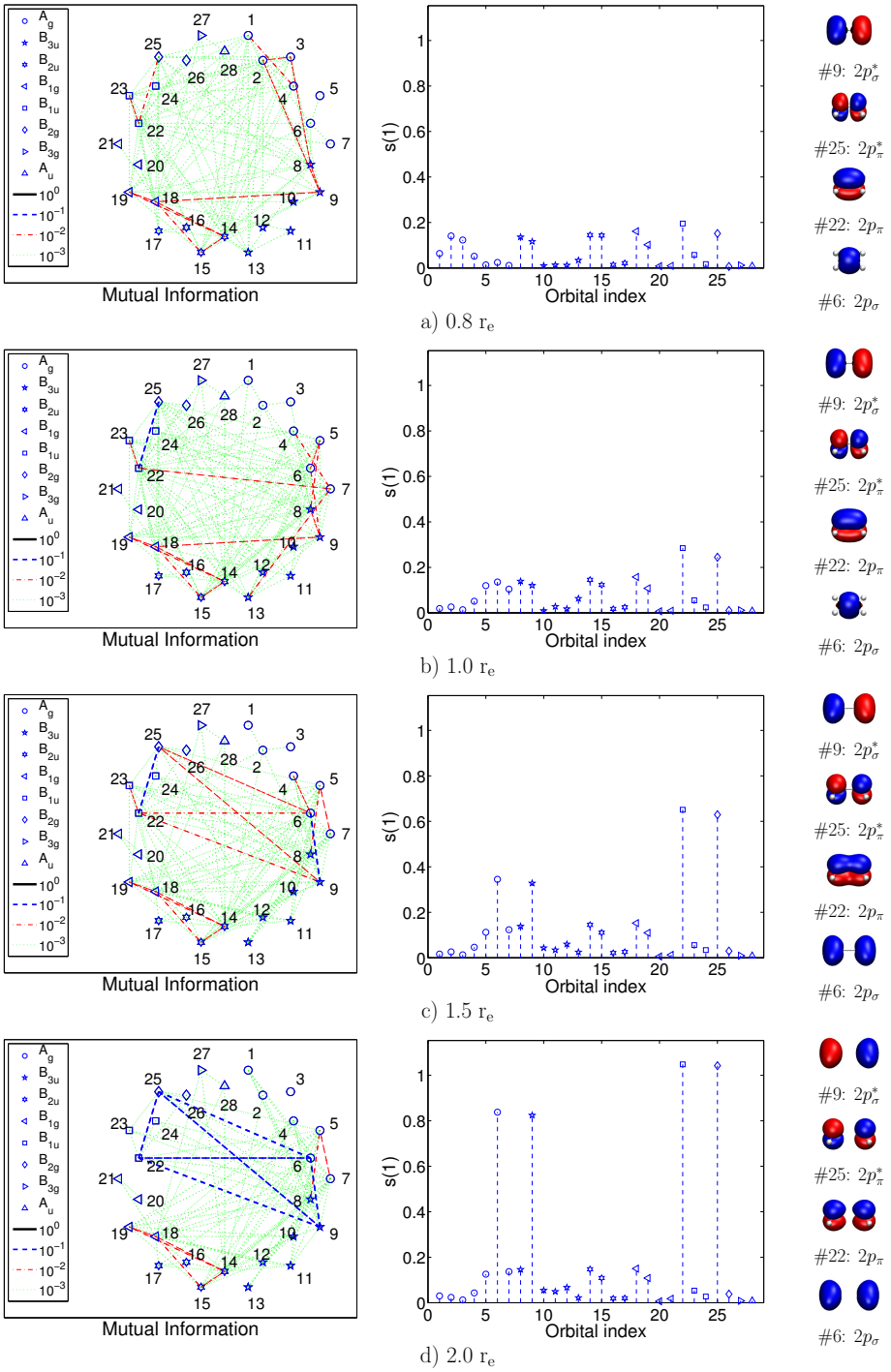


Figure 1: Mutual information and single orbital entropies $s(1)_i$ for DMRG(14,28)$[1024, 512, 1024, 10^{-5}]$ calculations for the C_2H_6 molecule at different inter-atomic distances. The orbitals are numbered and sorted according to their (CASSCF) natural occupation numbers. Strongly entangled orbitals are shown on the right-hand side. Each orbital index in the $s(1)_i$ diagram indicates one molecular orbital and corresponds to the same natural orbital as numbered in the mutual information plot (starting of index 1 and proceeding clockwise).



a) 0.8 r_e

b) 1.0 r_e

c) 1.5 r_e

d) 2.0 r_e

Figure 2: Mutual information and single orbital entropies $s(1)_i$ for DMRG(12,28)$[1024, 512, 1024, 10^{-5}]$ calculations for the C_2H_4 molecule at different inter-atomic distances. The orbitals are numbered and sorted according to their (CASSCF) natural occupation numbers. Strongly entangled orbitals are shown on the right-hand side. Each orbital index in the $s(1)_i$ diagram indicates one molecular orbital and corresponds to the same natural orbital as numbered in the mutual information plot (starting of index 1 and proceeding clockwise).

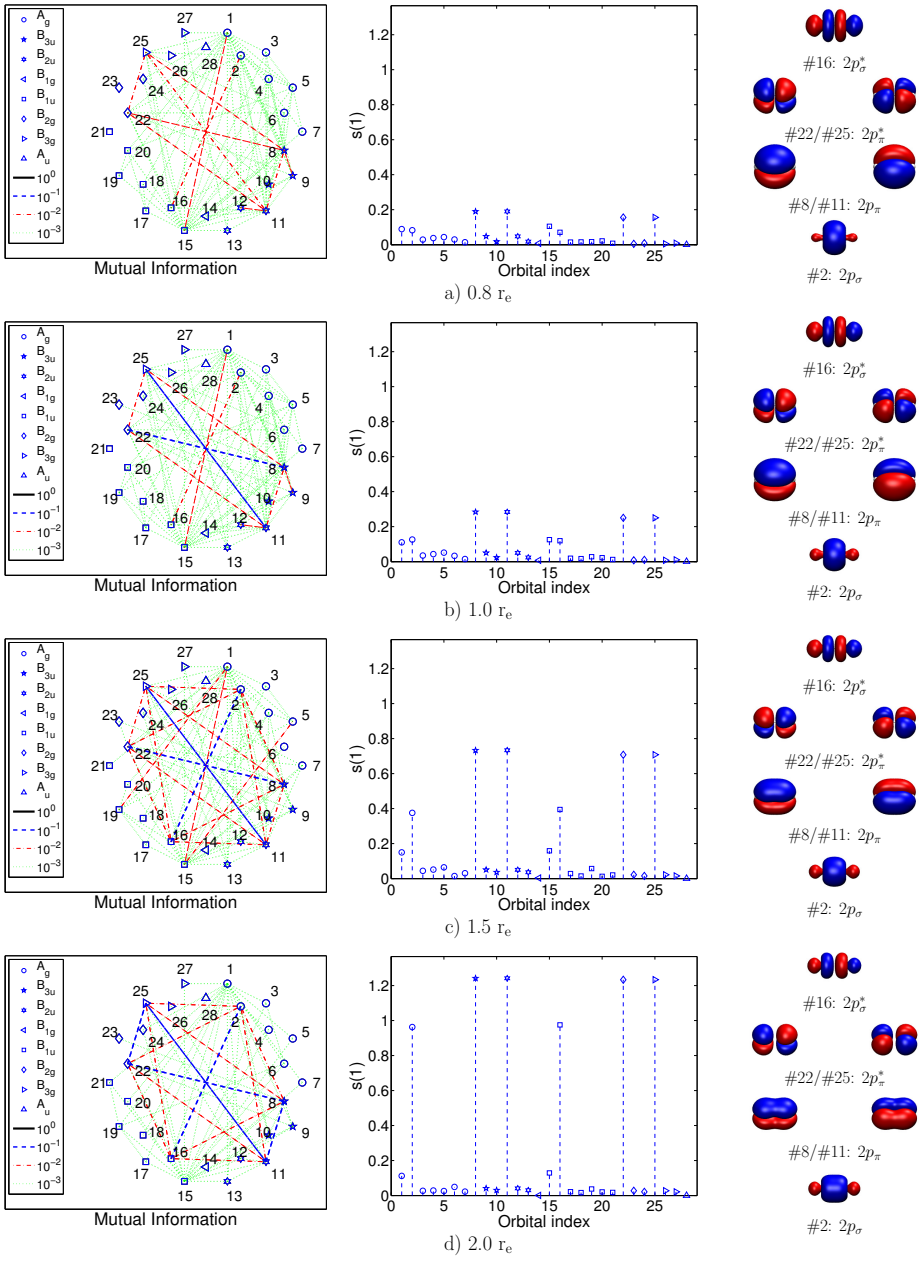


Figure 3: Mutual information and single orbital entropies $s(1)_i$ for DMRG(10,28)$[1024, 512, 1024, 10^{-5}]$ calculations for the C_2H_2 molecule at different inter-atomic distances. The orbitals are numbered and sorted according to their (CASSCF) natural occupation numbers. Strongly entangled orbitals are shown on the right-hand side. Each orbital index in the $s(1)_i$ diagram indicates one molecular orbital and corresponds to the same natural orbital as numbered in the mutual information plot (starting of index 1 and proceeding clockwise).

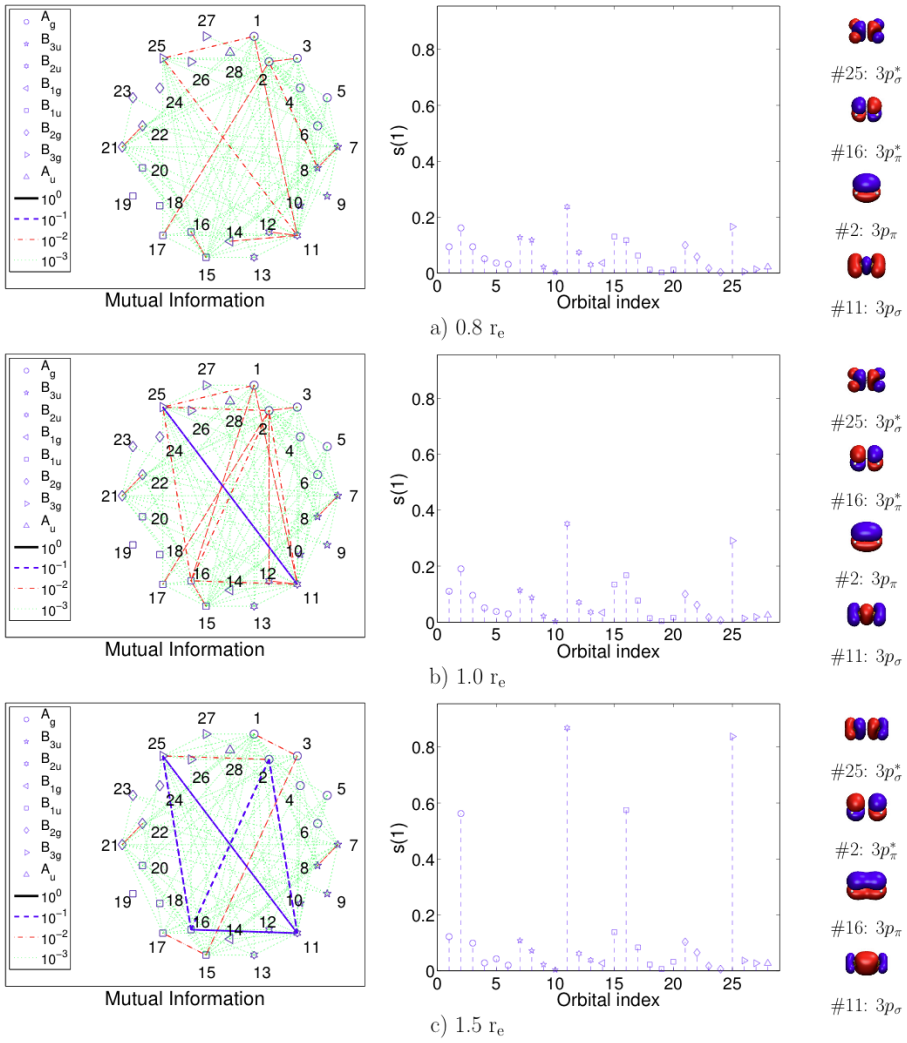
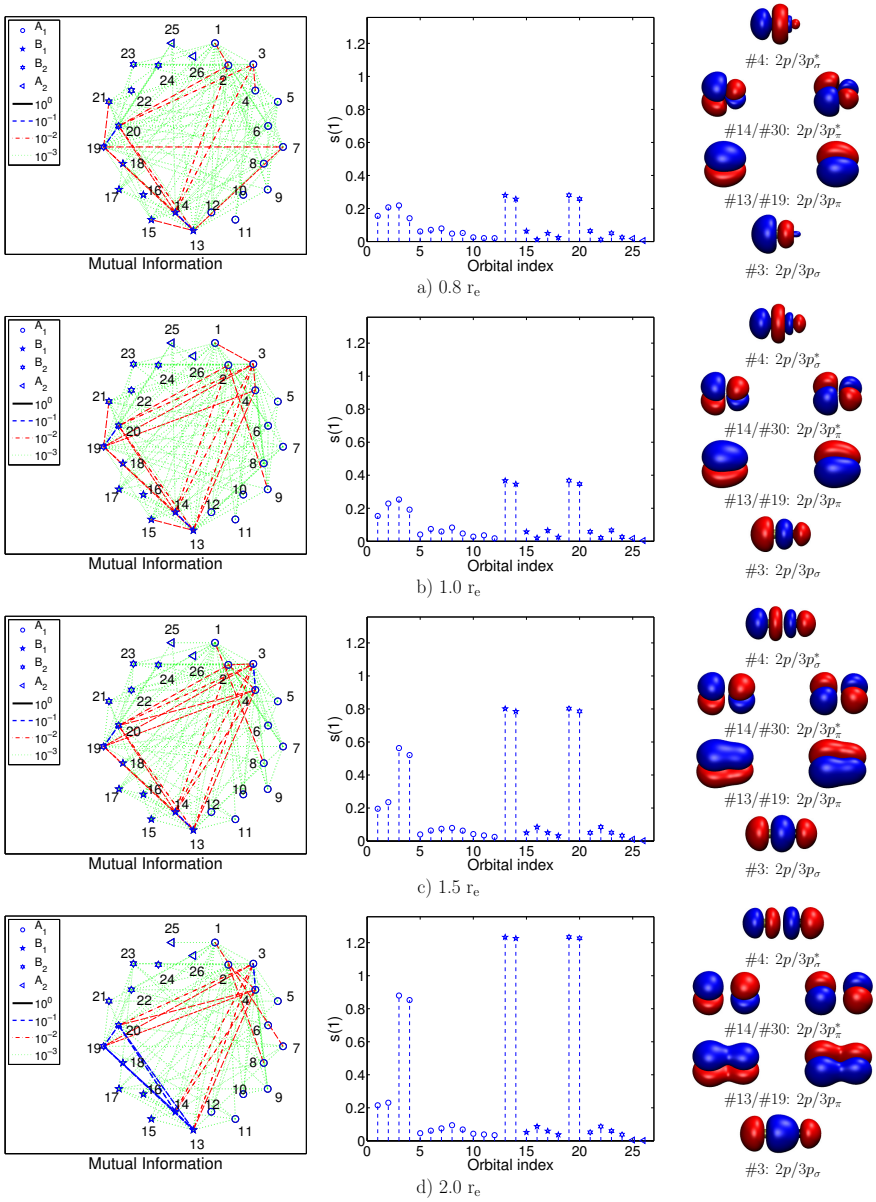


Figure 4: Mutual information and single orbital entropies $s(1)_i$ for DMRG(12,28)$[1024, 512, 1024, 10^{-5}]$ calculations for the Si_2H_4 molecule at different inter-atomic distances. The orbitals are numbered and sorted according to their (CASSCF) natural occupation numbers. Strongly entangled orbitals are shown on the right-hand side. Each orbital index in the $s(1)_i$ diagram indicates one molecular orbital and corresponds to the same natural orbital as numbered in the mutual information plot (starting of index 1 and proceeding clockwise).



a) 0.8 r_e

b) 1.0 r_e

c) 1.5 r_e

d) 2.0 r_e

Figure 5: Mutual information and single orbital entropies $s(1)_i$ for DMRG(10,26)[$1024, 512, 1024, 10^{-5}$] calculations for the $[CP]^-$ molecule at different inter-atomic distances. The orbitals are numbered and sorted according to their (CASSCF) natural occupation numbers. Strongly entangled orbitals are shown on the right-hand side. Each orbital index in the $s(1)_i$ diagram indicates one molecular orbital and corresponds to the same natural orbital as numbered in the mutual information plot (starting of index 1 and proceeding clockwise).

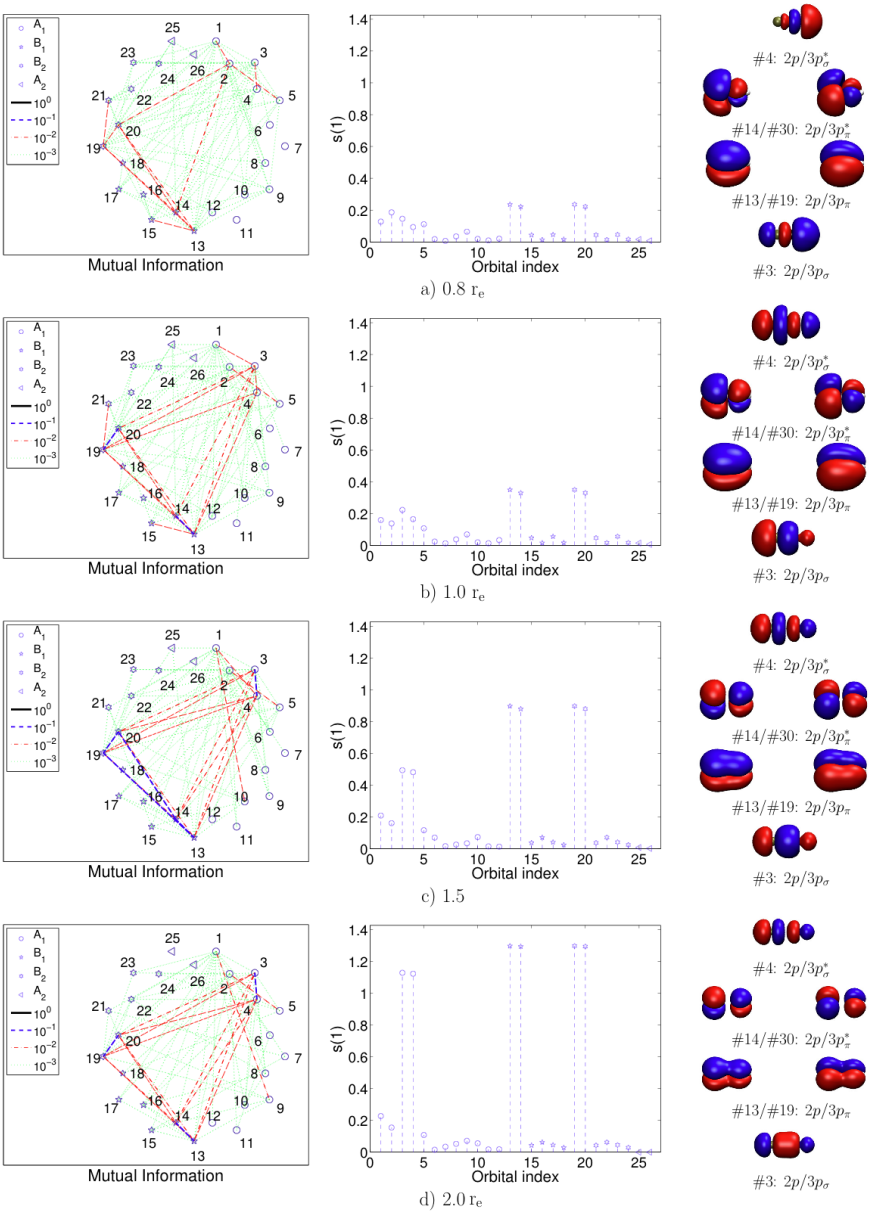


Figure 6: Mutual information and single orbital entropies $s(1)_i$ for DMRG(14,28)$[1024, 512, 1024, 10^{-5}]$ calculations for the HCP molecule at different inter-atomic distances. The orbitals are numbered and sorted according to their (CASSCF) natural occupation numbers. Strongly entangled orbitals are shown on the right-hand side. Each orbital index in the $s(1)_i$ diagram indicates one molecular orbital and corresponds to the same natural orbital as numbered in the mutual information plot (starting of index 1 and proceeding clockwise).

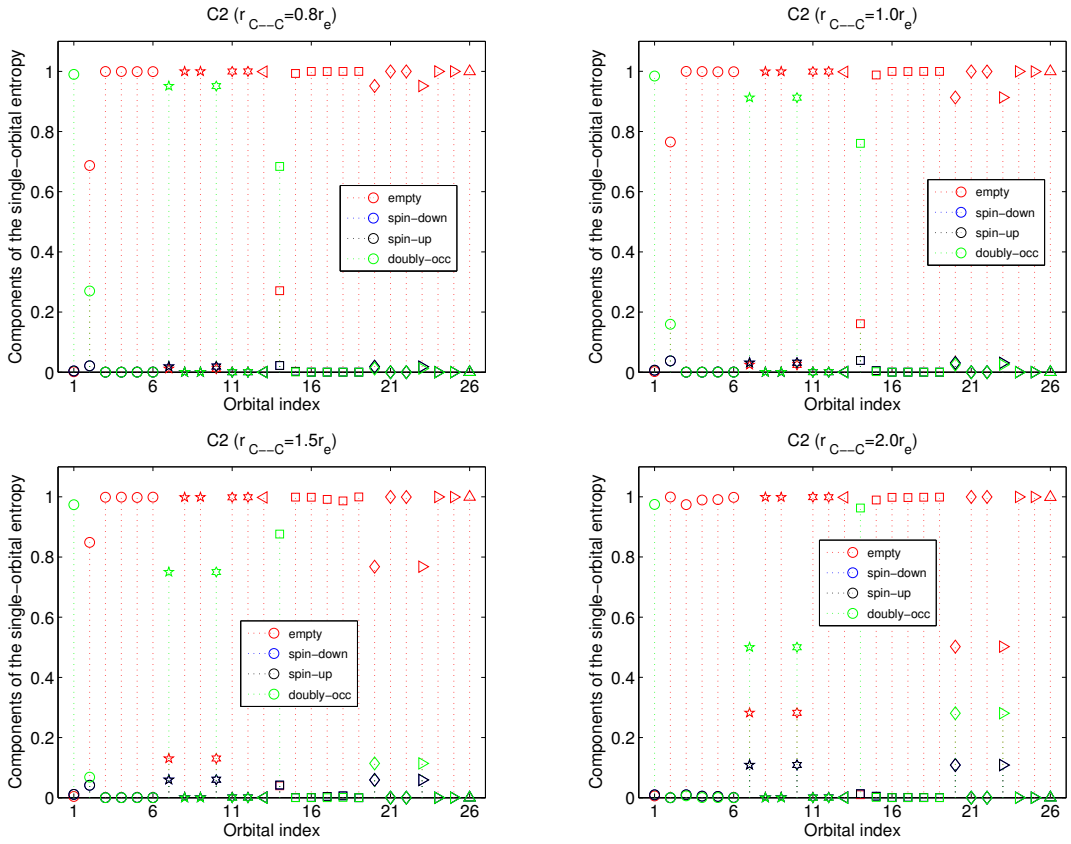


Figure 7: Each component of $s(1)_i$ analysis for the C_2 molecule at different inter-atomic distances. Each orbital index in the $s(1)_i$ diagram indicates one molecular orbital and corresponds to the same natural orbital as numbered in the mutual information plot (starting of index 1 and proceeding clockwise). Please note that $s(1)_i$ is determined as -$x \ln x$, where x is the number plotted in the figure. Symbols label refer to orbital spatial symmetries as defined in Fig. 5