An assessment of initial guesses for self-consistent field calculations. Superposition of Atomic Potentials: simple yet efficient. Supporting information

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The performance of the GWH, CORE, SAD, SADNO, HUCKEL, GSZ, LDA-X, CAP-X, and CHA-X guesses are shown in

- tables S1 and S2 at HF/STO-3G level of theory
- tables S3 and S4 at revTPSSh/STO-3G level of theory
- tables S5 and S6 at HF/pcseg-0 level of theory
- tables S7 and S8 at revTPSSh/pcseg-0 level of theory
- tables S9 and S10 at HF/pcseg-1 level of theory
- tables S11 and S12 at revTPSSh/pcseg-1 level of theory
- tables S13 and S14 at HF/aug-pcseg-2 level of theory
- tables S15 and S16 at revTPSSh/aug-pcseg-2 level of theory

for the neutral singlets and non-singlet calculations, respectively. The wave functions have been calculated using Q-Chem with stability analysis, while the guess analysis has been performed with Erkale. The results are ordered in each table from most challenging molecule to least challenging molecule, as determined by the largest f value afforded by any of the 9 guesses studied in the present work. On each row, the value for the best guess(es) is shown in bold. The last row of each table counts the number of molecules for which the guess in question was ranked best.

Table S1: Neutral singlet molecules, HF/STO-3G: fraction f of electron density covered.

Molecule	**GWH**	**CORE**	**SAD**	**SADNO**	**HUCKEL**	**GSZ**	**LDA-X**	**CAP-X**	**CHA-X**
CuMe	0.868	0.852	0.868	**0.927**	0.861	0.826	0.803	0.779	0.802
CuCN	0.846	0.853	0.861	**0.937**	0.865	0.861	0.806	0.806	0.806
Ni(C5H5)NO	0.741	0.778	0.878	**0.950**	0.814	0.870	0.924	0.909	0.925
ED15	0.709	0.736	0.876	**0.960**	0.773	0.931	0.947	0.945	0.944
Ni(C3H5)2	0.710	0.737	0.875	**0.960**	0.774	0.933	0.937	0.934	0.935
ED03	0.732	0.762	0.882	0.951	0.912	**0.961**	0.933	0.929	0.930
Ni(PH3)2	0.839	0.837	0.900	0.940	0.917	0.945	0.962	0.961	**0.963**
Cr(NO)4	0.714	0.733	0.881	0.941	0.896	0.923	0.963	**0.963**	0.961
Mn(C5H5)(CO)3	0.668	0.728	0.874	**0.963**	0.792	0.802	0.944	0.946	0.948
Cr(C6H6)(CO)3	0.656	0.723	0.872	**0.964**	0.752	0.810	0.939	0.942	0.940
MnCp(CO)3	0.668	0.727	0.873	**0.964**	0.791	0.803	0.943	0.945	0.948
Mn(NO)3CO	0.713	0.726	0.880	0.930	0.902	0.921	0.963	**0.964**	0.962
ED02	0.698	0.730	0.875	0.948	0.895	0.940	0.964	**0.964**	0.963
Co(C3H5)(CO)3	0.693	0.715	0.877	0.963	0.845	0.853	0.963	0.965	**0.965**
ED01	0.679	0.703	0.872	0.946	0.856	0.939	0.966	**0.968**	0.964
PR15	0.738	0.746	0.878	**0.969**	0.815	0.919	0.935	0.933	0.935
Fe(CO)2(NO)2	0.713	0.747	0.879	0.940	0.911	0.933	0.969	**0.970**	0.968
Fe(C4H6)(CO)3	0.683	0.704	0.874	**0.970**	0.824	0.822	0.955	0.956	0.957
Fe(C4H4)(CO)3	0.689	0.736	0.875	**0.970**	0.820	0.833	0.962	0.963	0.965
VCp(CO)4	0.646	0.709	0.873	**0.971**	0.781	0.794	0.942	0.946	0.944

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Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Fe(C5Me5)(P5)	0.771	0.755	0.896	**0.971**	0.767	0.832	0.903	0.906	0.902
Fe(CO)3(tmm)	0.680	0.702	0.874	**0.971**	0.828	0.826	0.959	0.962	0.964
Fe(CO)4(C2H4)	0.712	0.700	0.875	0.962	0.864	0.861	0.968	0.971	**0.972**
PR05	0.677	0.705	0.874	0.954	0.890	0.899	0.968	**0.972**	0.972
Co(CO)3(NO)	0.713	0.746	0.879	0.960	0.912	0.944	0.972	**0.972**	0.970
Fe(C2H4)(CO)4	0.701	0.700	0.875	0.964	0.865	0.864	0.970	0.973	**0.974**
ED04	0.702	0.712	0.873	**0.974**	0.713	0.886	0.962	0.960	0.959
Mn(CO)5CN	0.673	0.716	0.872	0.956	0.883	0.905	0.972	**0.975**	0.974
ED05	0.674	0.716	0.874	0.956	0.893	0.900	0.973	0.975	**0.976**
ED14	0.718	0.731	0.878	**0.976**	0.748	0.840	0.917	0.923	0.913
Mn(CO)4NO	0.685	0.725	0.876	0.949	0.907	0.919	0.973	**0.976**	0.975
PR12	0.688	0.684	0.871	0.965	0.831	0.838	0.973	**0.977**	0.974
PR04	0.692	0.722	0.873	**0.977**	0.735	0.892	0.956	0.956	0.958
Ni(CO)4	0.713	0.750	0.881	0.958	0.916	0.959	**0.977**	0.976	0.973
PR03	0.713	0.750	0.881	0.958	0.916	0.959	**0.977**	0.976	0.974
Cr(C6H6)2	0.632	0.737	0.870	0.972	0.636	0.889	**0.979**	0.961	0.960
PR14	0.696	0.709	0.877	**0.979**	0.719	0.822	0.949	0.943	0.938
PR02	0.685	0.727	0.876	0.953	0.898	0.925	0.977	**0.980**	0.980
Fe(CO)5	0.685	0.727	0.876	0.953	0.899	0.925	0.978	**0.980**	0.980
CoH(CO)4	0.700	0.739	0.879	0.959	0.907	0.933	0.979	**0.980**	0.980
Ni(acac)2	0.736	0.740	0.878	**0.981**	0.817	0.918	0.929	0.929	0.929
ocs	0.844	0.844	0.915	**0.982**	0.944	0.934	0.976	0.975	0.979
beta-lactim	0.725	0.713	0.873	**0.983**	0.796	0.933	0.978	0.977	0.982
dithiotane	0.839	0.845	0.915	**0.983**	0.902	0.938	0.980	0.979	0.982
ED40a	0.639	0.651	0.872	**0.984**	0.745	0.961	0.977	0.976	0.975
acetaldehyde	0.714	0.724	0.872	0.980	0.797	0.926	0.982	0.982	**0.984**
oxetane	0.698	0.715	0.871	**0.985**	0.760	0.948	0.979	0.978	0.981

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Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
methanol	0.736	0.766	0.880	0.982	0.864	0.962	0.984	0.984	**0.985**
AcCl	0.828	0.833	0.916	**0.985**	0.903	0.868	0.955	0.954	0.963
ch3ph2	0.765	0.782	0.898	**0.986**	0.834	0.936	0.983	0.982	0.984
ethanol	0.704	0.730	0.876	**0.986**	0.793	0.944	0.978	0.977	0.980
ccl2o	0.895	0.868	0.947	**0.986**	0.971	0.954	0.982	0.981	0.985
oxirane	0.725	0.752	0.874	0.982	0.800	0.962	0.985	0.984	**0.986**
nh3	0.733	0.799	0.874	0.984	0.978	0.967	**0.986**	0.986	0.986
cs2	0.858	0.839	0.928	0.983	0.942	0.977	0.986	0.985	**0.987**
Sc(acac)3	0.697	0.704	0.884	**0.987**	0.797	0.850	0.981	0.983	0.971
acetic	0.757	0.769	0.885	0.980	0.869	0.951	0.985	0.985	**0.987**
clcof	0.871	0.838	0.938	0.984	0.965	0.939	0.983	0.983	**0.987**
ketene	0.725	0.752	0.873	0.985	0.820	0.963	0.985	0.985	**0.987**
n2h4	0.703	0.753	0.874	0.984	0.980	0.969	0.987	0.986	**0.987**
Zn(CH3)2	0.782	0.798	0.874	0.952	0.854	0.951	**0.988**	0.987	0.987
PR06	0.666	0.701	0.873	0.960	0.851	0.894	0.986	**0.988**	0.986
FeCp2	0.678	0.751	0.874	**0.988**	0.689	0.909	0.971	0.971	0.970
cis-c2f2cl2	0.846	0.834	0.946	**0.988**	0.943	0.898	0.978	0.977	0.982
trans-c2f2cl2	0.845	0.823	0.946	**0.988**	0.943	0.911	0.977	0.977	0.982
clcn	0.830	0.862	0.922	0.987	0.926	0.945	0.986	0.985	**0.988**
c2h5f	0.738	0.758	0.892	**0.988**	0.798	0.906	0.981	0.980	0.983
ED27	0.732	0.750	0.888	**0.988**	0.752	0.920	0.976	0.975	0.976
sio	0.902	0.881	0.890	0.986	0.942	0.974	**0.988**	0.988	0.988
ED28	0.721	0.742	0.886	**0.989**	0.741	0.901	0.973	0.973	0.973
ch3nh2	0.685	0.730	0.870	**0.989**	0.864	0.951	0.979	0.979	0.981
dioxetane	0.768	0.780	0.881	0.978	0.889	0.970	0.987	0.987	**0.989**
ch2c	0.720	0.729	0.816	**0.989**	0.671	0.955	0.984	0.983	0.984
PMe3	0.715	0.741	0.885	**0.989**	0.747	0.916	0.977	0.976	0.978

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Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
cs	0.905	0.868	0.897	0.987	0.920	0.982	0.989	0.989	**0.989**
c2cl6	0.913	0.892	0.961	**0.989**	0.978	0.952	0.980	0.979	0.985
c2h3f	0.753	0.764	0.891	**0.989**	0.808	0.942	0.983	0.982	0.984
PR01	0.663	0.710	0.873	0.966	0.858	0.912	0.987	**0.990**	0.988
ch3f	0.782	0.804	0.903	0.986	0.871	0.969	0.990	0.989	**0.990**
ch2nh	0.703	0.732	0.859	0.986	0.854	0.978	0.990	0.989	**0.990**
ccl2	0.951	0.933	0.946	0.988	0.983	0.981	0.989	0.989	**0.990**
oxadiazole	0.768	0.724	0.870	0.982	0.848	0.971	0.990	0.989	**0.990**
formamide	0.724	0.746	0.885	0.981	0.940	0.958	0.989	0.989	**0.990**
h2o	0.827	0.863	0.893	0.973	0.963	0.980	**0.991**	0.990	0.991
PR40	0.713	0.722	0.896	**0.991**	0.790	0.908	0.979	0.979	0.980
MnO3F	0.812	0.815	0.888	0.946	0.934	0.975	**0.991**	0.990	0.988
furan	0.701	0.722	0.872	**0.991**	0.729	0.975	0.986	0.985	0.987
hccf	0.771	0.809	0.890	0.991	0.774	0.984	0.991	0.991	**0.991**
dioxetan2one	0.766	0.750	0.890	0.976	0.917	0.938	0.989	0.988	**0.991**
ch2clf	0.889	0.883	0.940	0.988	0.948	0.920	0.990	0.989	**0.991**
Cr(CO)6	0.663	0.710	0.873	0.966	0.859	0.915	0.988	**0.991**	0.989
c2cl4	0.877	0.866	0.957	**0.991**	0.955	0.955	0.979	0.978	0.982
s2o	0.885	0.892	0.933	0.984	0.987	0.970	0.990	0.990	**0.991**
nh2oh	0.757	0.786	0.880	0.976	0.967	0.978	0.991	0.991	**0.991**
TiCl2Me2	0.807	0.789	0.928	**0.992**	0.879	0.843	0.984	0.986	0.988
ccl2h2	0.909	0.903	0.952	**0.992**	0.957	0.959	0.989	0.988	0.990
thiophene	0.736	0.769	0.893	**0.992**	0.761	0.901	0.965	0.963	0.967
hoclo	0.882	0.890	0.928	0.971	0.981	0.976	**0.992**	0.991	0.992
PhSH	0.729	0.747	0.885	**0.992**	0.726	0.875	0.920	0.920	0.921
nh2cl	0.866	0.883	0.934	0.987	0.986	0.966	0.991	0.991	**0.992**
formic-anhydride	0.751	0.775	0.888	0.977	0.928	0.950	0.990	0.990	**0.992**

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Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ccl3h	0.890	0.898	0.959	0.990	0.979	0.969	0.990	0.989	**0.992**
ED30	0.708	0.717	0.878	**0.992**	0.750	0.820	0.976	0.979	0.971
clno	0.882	0.884	0.922	0.985	0.986	0.923	0.988	0.986	**0.992**
PCy3	0.663	0.682	0.871	**0.992**	0.661	0.783	0.963	0.964	0.962
hoclo2	0.878	0.872	0.926	0.969	0.979	0.979	**0.992**	0.992	0.992
glyoxal	0.786	0.769	0.876	0.977	0.882	0.975	0.991	0.991	**0.992**
CrO2(NO3)2	0.760	0.733	0.890	0.962	0.936	0.939	**0.992**	0.992	0.990
tetrahedrane	0.663	0.704	0.863	**0.993**	0.583	0.969	0.983	0.982	0.984
ccl4	0.945	0.908	0.963	0.989	0.984	0.978	0.991	0.990	**0.993**
cyclobutene	0.643	0.670	0.859	**0.993**	0.635	0.950	0.975	0.974	0.977
cf2cl2	0.886	0.872	0.955	0.986	0.979	0.949	0.991	0.990	**0.993**
cclh3	0.852	0.867	0.935	**0.993**	0.910	0.944	0.986	0.986	0.988
silole	0.703	0.700	0.877	**0.993**	0.681	0.891	0.954	0.953	0.959
oxirene	0.748	0.800	0.862	0.977	0.789	0.986	0.993	0.992	**0.993**
hnnn	0.738	0.727	0.870	0.981	0.973	0.967	0.992	0.992	**0.993**
fccf	0.831	0.848	0.910	0.986	0.837	0.993	0.992	0.993	**0.993**
cyclobutane	0.634	0.643	0.863	**0.993**	0.639	0.931	0.968	0.967	0.972
dioxirane	0.806	0.806	0.876	0.974	0.875	0.976	0.993	0.992	**0.993**
ED31	0.685	0.693	0.871	**0.993**	0.643	0.816	0.964	0.966	0.954
c2clh5	0.802	0.817	0.919	**0.993**	0.846	0.831	0.975	0.973	0.978
PhSeH	0.793	0.808	0.911	**0.993**	0.796	0.902	0.936	0.936	0.937
c2cl2	0.866	0.901	0.944	**0.993**	0.894	0.941	0.975	0.974	0.978
CrF6	0.787	0.795	0.922	0.969	0.952	**0.993**	0.993	0.993	0.991
c2f4	0.792	0.825	0.928	0.983	0.925	0.986	0.992	0.992	**0.993**
cyclobutadiene	0.658	0.702	0.850	**0.993**	0.608	0.974	0.985	0.984	0.986
t-hcoh	0.779	0.782	0.856	0.982	0.854	0.983	0.993	0.993	**0.994**
formic	0.791	0.801	0.890	0.977	0.936	0.981	0.993	0.993	**0.994**

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Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Ni(PF3)4	0.878	0.849	0.939	0.973	0.966	0.979	0.993	**0.994**	0.992
c-hcoh	0.777	0.779	0.856	0.982	0.868	0.987	0.993	0.993	**0.994**
CrO2Cl2	0.811	0.794	0.926	0.970	0.940	0.912	0.994	**0.994**	0.992
c2clh3	0.819	0.826	0.919	**0.994**	0.857	0.862	0.949	0.947	0.955
TiCl3Me	0.817	0.801	0.947	0.992	0.930	0.835	0.991	0.993	**0.994**
si2h6	0.797	0.786	0.909	0.992	0.784	0.985	0.992	0.993	**0.994**
c2f6	0.825	0.816	0.936	0.982	0.963	0.980	0.992	0.992	**0.994**
cyclopropene	0.630	0.684	0.857	**0.994**	0.626	0.967	0.983	0.982	0.985
ED40b	0.786	0.801	0.914	**0.994**	0.838	0.875	0.984	0.985	0.985
nccn	0.707	0.682	0.852	0.987	0.814	0.985	0.993	0.993	**0.994**
hocl	0.892	0.913	0.939	0.982	0.987	0.975	0.994	0.993	**0.994**
ch2f2	0.852	0.867	0.921	0.983	0.933	0.982	0.994	0.993	**0.994**
t-hono	0.799	0.753	0.883	0.976	0.972	0.977	0.994	0.994	**0.994**
ch2-sing	0.753	0.591	0.783	0.775	0.644	0.992	0.994	0.994	**0.994**
h2co	0.757	0.768	0.873	0.977	0.883	0.985	0.994	0.994	**0.994**
cyclopropane	0.634	0.653	0.865	**0.994**	0.636	0.944	0.974	0.973	0.976
n-pentane	0.628	0.662	0.865	**0.994**	0.657	0.869	0.968	0.968	0.970
cyclopentadiene	0.643	0.688	0.860	**0.994**	0.618	0.958	0.978	0.977	0.980
n-butane	0.629	0.665	0.864	**0.994**	0.661	0.910	0.968	0.967	0.971
hcno	0.773	0.798	0.880	0.981	0.887	0.985	0.994	0.993	**0.994**
hcof	0.836	0.824	0.906	0.980	0.942	0.990	0.994	0.994	**0.994**
honc	0.780	0.812	0.864	0.983	0.911	0.906	0.994	0.993	**0.995**
propane	0.625	0.670	0.864	**0.995**	0.669	0.925	0.969	0.968	0.972
c2clh	0.833	0.857	0.921	**0.995**	0.835	0.886	0.970	0.969	0.974
c2h6	0.628	0.700	0.863	**0.995**	0.681	0.933	0.972	0.971	0.974
hooh	0.797	0.849	0.885	0.971	0.971	0.988	0.995	0.994	**0.995**
pyrrole	0.672	0.663	0.870	**0.995**	0.718	0.969	0.983	0.983	0.985

Table S1– *Continued on next page*

Table S1– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
so2	0.868	0.870	0.922	0.982	0.982	0.987	**0.995**	0.995	0.994
nh2f	0.805	0.824	0.900	0.978	0.972	0.983	0.995	0.994	**0.995**
c-n2h2	0.764	0.682	0.858	0.984	0.975	0.992	0.995	0.994	**0.995**
sih4	0.750	0.771	0.905	0.992	0.778	0.987	0.994	0.994	**0.995**
borole	0.659	0.675	0.846	**0.995**	0.615	0.915	0.983	0.982	0.984
t-n2h2	0.766	0.688	0.858	0.985	0.871	0.989	0.995	0.994	**0.995**
propene	0.634	0.668	0.860	**0.995**	0.682	0.944	0.976	0.975	0.978
ch4	0.617	0.727	0.862	**0.995**	0.718	0.940	0.976	0.976	0.977
hnco	0.751	0.746	0.883	0.983	0.926	0.988	0.995	0.994	**0.995**
allene	0.640	0.656	0.855	**0.995**	0.642	0.974	0.984	0.983	0.985
fno	0.863	0.828	0.897	0.979	0.977	0.993	**0.995**	0.995	0.995
c-hono	0.798	0.749	0.883	0.976	0.974	0.985	0.995	0.995	**0.995**
hclo4	0.881	0.860	0.927	0.967	0.977	0.988	**0.995**	0.995	0.995
hocn	0.772	0.755	0.874	0.979	0.893	0.974	0.995	0.995	**0.996**
chf3	0.901	0.893	0.933	0.982	0.966	0.989	0.995	0.995	**0.996**
propyne	0.645	0.669	0.855	**0.996**	0.631	0.954	0.982	0.982	0.984
alf	0.929	0.911	0.906	0.988	0.972	0.987	0.996	0.995	**0.996**
t-butadiene	0.641	0.662	0.857	**0.996**	0.655	0.950	0.978	0.978	0.980
b2h6	0.561	0.605	0.834	**0.996**	0.545	0.933	0.977	0.977	0.980
n2o4	0.779	0.773	0.893	0.974	0.969	0.984	0.995	0.995	**0.996**
f2co	0.836	0.819	0.924	0.980	0.956	0.995	0.996	0.996	**0.996**
benzene	0.650	0.706	0.862	**0.996**	0.604	0.967	0.983	0.982	0.984
CrO2F2	0.820	0.807	0.904	0.963	0.923	**0.996**	0.995	0.995	0.993
hnc	0.796	0.760	0.844	0.994	0.880	0.980	**0.996**	0.996	0.996
c2h4	0.635	0.748	0.855	**0.996**	0.670	0.967	0.983	0.983	0.984
ph3	0.817	0.829	0.913	0.982	0.935	0.996	0.996	0.996	**0.996**
hf	0.917	0.931	0.934	0.979	0.971	0.995	**0.997**	0.996	0.996

Table S1– *Continued on next page*

Table S1– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
sih3f	0.835	0.838	0.924	0.988	0.884	0.994	0.996	0.996	**0.997**
VOCl3	0.821	0.796	0.945	0.982	0.956	0.928	0.995	0.996	**0.997**
cf4	0.889	0.843	0.941	0.982	0.970	0.993	0.996	0.996	**0.997**
p4	0.990	0.884	0.921	0.985	0.844	0.994	0.996	0.996	**0.997**
hcn	0.732	0.752	0.848	0.987	0.811	0.990	0.997	0.997	**0.997**
bhf2	0.882	0.881	0.920	0.986	0.930	0.995	0.996	0.997	**0.997**
bh3	0.606	0.771	0.801	**0.997**	0.586	0.977	0.991	0.991	0.991
hof	0.842	0.870	0.906	0.974	0.980	0.990	0.997	0.997	**0.997**
pf3	0.902	0.883	0.942	0.984	0.980	0.993	**0.998**	0.998	0.998
hno	0.789	0.786	0.869	0.979	0.961	0.996	0.998	0.998	**0.998**
cf2	0.918	0.886	0.911	0.984	0.969	**0.998**	0.997	0.998	0.998
h2s	0.885	0.893	0.936	0.983	0.977	**0.998**	0.997	0.997	0.997
VOF3	0.823	0.818	0.918	0.974	0.936	0.992	**0.998**	0.998	0.998
clf	0.923	0.938	0.954	0.982	0.994	0.992	0.998	0.998	**0.998**
bf3	0.921	0.940	0.936	0.985	0.962	0.998	0.998	0.998	**0.998**
n2o	0.769	0.749	0.882	0.981	0.975	0.991	0.998	0.998	**0.998**
ScF3	0.928	0.946	0.937	0.983	0.969	0.996	**0.998**	0.998	0.998
so3	0.846	0.856	0.924	0.977	0.977	0.998	**0.998**	0.998	0.998
alcl	0.948	0.939	0.933	0.991	0.981	0.995	0.998	0.998	**0.999**
c2h2	0.589	0.806	0.845	**0.999**	0.613	0.990	0.993	0.992	0.993
co2	0.738	0.830	0.893	0.981	0.939	**0.999**	0.999	0.999	0.999
alh3	0.763	0.785	0.881	0.996	0.817	0.998	0.998	0.999	**0.999**
bh	0.819	0.592	0.698	0.666	0.711	0.997	0.999	**0.999**	0.999
sf6	0.899	0.906	0.953	0.983	0.983	0.996	0.999	0.999	**0.999**
alh	0.886	0.898	0.862	0.860	0.900	0.986	**0.999**	0.999	0.999
TiCl4	0.846	0.816	0.962	0.992	0.972	0.982	0.998	0.999	**0.999**
pf5	0.875	0.885	0.952	0.985	0.980	0.998	0.999	0.999	**0.999**

Table S1– *Continued on next page*

Table S1– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
VF5	0.833	0.838	0.930	0.979	0.955	0.989	0.999	**0.999**	0.999
TiF4	0.813	0.809	0.934	0.983	0.955	0.998	0.999	**0.999**	0.999
bf	0.925	0.846	0.866	0.986	0.958	0.996	**0.999**	0.999	0.999
alf3	0.947	0.957	0.938	0.987	0.967	0.998	**0.999**	0.999	0.999
p2	0.928	0.880	0.913	0.993	0.865	0.999	0.999	0.999	**0.999**
sif4	0.897	0.868	0.948	0.986	0.976	0.999	0.999	0.999	**0.999**
alcl3	0.904	0.893	0.966	0.995	0.982	0.998	0.999	0.999	**1.000**
hcl	0.952	0.956	0.969	0.992	0.990	0.999	1.000	**1.000**	1.000
co	0.862	0.799	0.854	0.988	0.928	0.994	**1.000**	1.000	1.000
f2	0.889	0.944	0.927	0.975	0.996	0.999	**1.000**	1.000	1.000
cl2	0.941	0.962	0.968	0.988	0.995	0.999	1.000	1.000	**1.000**
n2	0.792	0.742	0.852	0.993	0.855	0.999	**1.000**	1.000	1.000
h2	**1.000**	**1.000**	0.829	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**
Best	1	1	0	82	1	7	27	23	**87**

Table S2: Non-neutral and/or non-singlet molecules, HF/STO-3G: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ch	0.738	0.853	0.732	0.750	0.647	0.892	0.842	0.973	**0.973**
cn	0.731	0.771	0.813	0.965	0.795	0.971	**0.973**	0.972	0.972
Cu(acac)2	0.742	0.745	0.880	**0.973**	0.822	0.904	0.927	0.927	0.928
cch	0.640	0.730	0.810	**0.975**	0.605	0.947	0.967	0.967	0.968
t-hooo	0.839	0.803	0.876	0.957	0.966	0.947	0.976	0.976	**0.976**
h2cn	0.725	0.709	0.836	0.967	0.809	0.957	0.976	0.976	**0.977**
ch2ch	0.628	0.706	0.834	**0.979**	0.680	0.955	0.970	0.970	0.971
hcnh	0.725	0.748	0.843	0.978	0.840	0.976	0.980	0.980	**0.981**
h2ccn	0.705	0.683	0.845	0.977	0.774	0.911	0.980	0.979	**0.981**
no2	0.791	0.770	0.884	0.960	0.958	0.981	0.982	0.982	**0.982**

Table S2– *Continued on next page*

Table S2– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
bn3pi	0.811	0.744	0.774	0.892	0.805	**0.982**	0.907	0.973	0.918
ch3nh	0.689	0.723	0.851	0.979	0.826	0.953	0.982	0.981	**0.983**
c-hooo	0.842	0.799	0.878	0.961	0.971	0.963	**0.985**	0.984	0.985
so	0.892	0.890	0.914	0.983	0.982	0.973	0.985	0.985	**0.985**
n2h	0.756	0.725	0.847	0.972	0.901	0.980	0.987	0.986	**0.987**
no	0.830	0.805	0.860	0.974	0.975	**0.988**	0.930	0.930	0.932
V(NMe2)4	0.681	0.685	0.872	**0.988**	0.805	0.842	0.975	0.975	0.973
allyl	0.640	0.685	0.850	**0.989**	0.671	0.956	0.974	0.974	0.976
ch2nh2	0.692	0.742	0.863	**0.989**	0.860	0.967	0.983	0.982	0.984
clo	0.918	0.934	0.934	0.947	**0.989**	0.964	0.981	0.959	0.983
hco	0.786	0.784	0.859	0.976	0.865	0.990	0.990	0.990	**0.990**
h2no	0.759	0.775	0.879	0.964	0.960	0.982	0.992	0.992	**0.992**
cyclopropyl	0.635	0.671	0.855	**0.992**	0.647	0.952	0.977	0.976	0.979
ch2-trip	0.756	0.845	0.793	0.992	0.707	0.988	0.992	0.992	**0.992**
hoo	0.829	0.813	0.876	0.962	0.969	0.989	0.993	0.993	**0.993**
nh2	0.800	0.745	0.833	0.876	0.965	0.988	0.994	0.994	**0.994**
s2	0.933	0.921	0.934	0.985	0.991	0.993	0.994	0.994	**0.994**
Ti(BH4)3	0.636	0.637	0.869	**0.994**	0.648	0.859	0.983	0.984	0.983
o2	0.863	0.847	0.876	0.979	0.989	0.994	**0.994**	0.994	0.994
ch3	0.679	0.784	0.834	**0.995**	0.745	0.969	0.986	0.986	0.987
sif	0.919	0.904	0.905	0.956	0.941	0.955	0.966	0.953	**0.996**
cf	0.891	0.839	0.866	0.938	0.946	0.944	0.932	0.936	**0.996**
ssh	0.907	0.894	0.936	0.980	0.983	0.994	0.996	**0.996**	0.996
oh	0.901	0.889	0.855	0.879	0.969	0.886	0.996	**0.997**	0.995
sih	0.848	0.859	0.868	0.974	0.833	0.932	0.981	0.946	**0.997**
nh	0.886	0.913	0.787	0.916	0.969	0.998	0.998	0.998	**0.998**
hs	0.900	0.892	0.921	0.934	0.984	**0.998**	0.941	0.944	0.968

Table S2– *Continued on next page*

Table S2– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Best	0	0	0	9	1	3	3	2	**19**

Table S3: Neutral singlet molecules, revTPSSh/STO-3G: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
CuCN	0.834	0.849	0.861	**0.945**	0.867	0.868	0.817	0.816	0.817
CuMe	0.852	0.849	0.867	**0.955**	0.867	0.810	0.801	0.798	0.801
Ni(C3H5)2	0.716	0.738	0.876	**0.961**	0.779	0.933	0.951	0.947	0.947
ED15	0.715	0.738	0.876	**0.961**	0.778	0.933	0.955	0.952	0.951
ED03	0.734	0.763	0.880	0.947	0.909	**0.963**	0.944	0.940	0.941
Ni(PH3)2	0.839	0.837	0.901	0.942	0.919	0.946	0.965	0.964	**0.965**
Cr(C6H6)(CO)3	0.659	0.725	0.872	**0.966**	0.749	0.809	0.945	0.947	0.945
MnCp(CO)3	0.671	0.730	0.873	**0.969**	0.784	0.802	0.948	0.950	0.953
Mn(C5H5)(CO)3	0.671	0.731	0.874	**0.969**	0.785	0.801	0.949	0.951	0.953
PR15	0.739	0.746	0.877	**0.971**	0.812	0.919	0.937	0.935	0.937
Zn(CH3)2	0.788	0.800	0.877	0.952	0.860	0.944	**0.971**	0.970	0.970
VCp(CO)4	0.650	0.712	0.873	**0.972**	0.776	0.794	0.947	0.950	0.949
Fe(C5Me5)(P5)	0.771	0.756	0.896	**0.973**	0.770	0.831	0.903	0.907	0.903
Ni(C5H5)NO	0.740	0.778	0.879	**0.974**	0.815	0.875	0.924	0.913	0.928
Co(C3H5)(CO)3	0.698	0.718	0.878	0.971	0.844	0.855	0.971	0.973	**0.975**
ED14	0.719	0.734	0.878	**0.977**	0.748	0.841	0.918	0.924	0.914
Fe(CO)4(C2H4)	0.717	0.704	0.875	**0.977**	0.859	0.863	0.971	0.974	0.976
Fe(C2H4)(CO)4	0.706	0.704	0.876	**0.978**	0.860	0.866	0.973	0.976	0.977
Ni(acac)2	0.737	0.742	0.878	**0.978**	0.815	0.918	0.933	0.933	0.933
PR12	0.693	0.689	0.871	0.969	0.824	0.841	0.975	**0.978**	0.977
PR05	0.681	0.709	0.874	0.964	0.881	0.900	0.975	0.979	**0.979**
ED04	0.703	0.713	0.872	**0.979**	0.714	0.888	0.977	0.975	0.974
PR14	0.697	0.709	0.876	**0.980**	0.717	0.822	0.955	0.944	0.941

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Fe(C4H6)(CO)3	0.686	0.707	0.874	**0.980**	0.820	0.822	0.958	0.960	0.961
Cr(C6H6)2	0.634	0.737	0.870	0.972	0.637	0.891	**0.981**	0.963	0.962
PR04	0.693	0.723	0.873	**0.981**	0.734	0.890	0.964	0.967	0.969
Fe(C4H4)(CO)3	0.694	0.739	0.875	**0.982**	0.816	0.832	0.964	0.965	0.968
ED40a	0.641	0.652	0.872	**0.982**	0.742	0.961	0.977	0.976	0.975
Mn(CO)5CN	0.677	0.719	0.872	0.967	0.875	0.907	0.979	**0.983**	0.982
Fe(CO)3(tmm)	0.686	0.706	0.874	**0.983**	0.824	0.825	0.962	0.964	0.967
dithiotane	0.839	0.846	0.915	0.982	0.901	0.939	0.981	0.980	**0.983**
ocs	0.839	0.838	0.914	0.979	0.938	0.939	0.980	0.979	**0.983**
oxetane	0.698	0.715	0.871	**0.983**	0.759	0.949	0.979	0.978	0.981
ED05	0.678	0.721	0.875	0.966	0.881	0.902	0.980	0.982	**0.983**
AcCl	0.828	0.833	0.915	**0.984**	0.901	0.870	0.959	0.957	0.967
beta-lactim	0.725	0.713	0.872	0.981	0.793	0.938	0.981	0.980	**0.984**
Sc(acac)3	0.699	0.706	0.883	0.984	0.793	0.850	0.982	**0.984**	0.971
ethanol	0.704	0.731	0.875	**0.985**	0.791	0.945	0.978	0.978	0.980
ED02	0.699	0.736	0.876	0.973	0.890	0.945	0.984	**0.985**	0.985
ch3ph2	0.767	0.784	0.898	0.985	0.832	0.938	0.984	0.983	**0.985**
methanol	0.735	0.766	0.879	0.980	0.862	0.962	0.984	0.984	**0.985**
acetaldehyde	0.714	0.724	0.871	0.979	0.796	0.930	0.984	0.983	**0.986**
sio	0.892	0.876	0.888	0.981	0.936	0.971	**0.986**	0.985	0.985
cis-c2f2cl2	0.848	0.835	0.945	**0.986**	0.943	0.900	0.980	0.979	0.984
trans-c2f2cl2	0.845	0.824	0.945	**0.986**	0.943	0.912	0.980	0.979	0.984
nh3	0.733	0.799	0.874	0.983	0.977	0.967	0.986	0.986	**0.986**
FeCp2	0.679	0.750	0.873	**0.986**	0.689	0.911	0.980	0.981	0.981
oxirane	0.723	0.751	0.873	0.980	0.799	0.963	0.985	0.985	**0.986**
c2h5f	0.737	0.758	0.891	**0.987**	0.796	0.909	0.982	0.981	0.984
n2h4	0.703	0.754	0.874	0.982	0.979	0.969	0.987	0.986	**0.987**

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
c2h3f	0.752	0.763	0.889	0.987	0.806	0.949	0.987	0.986	**0.988**
ED27	0.734	0.751	0.888	**0.988**	0.750	0.922	0.977	0.977	0.978
ccl2o	0.896	0.868	0.946	0.984	0.969	0.957	0.985	0.985	**0.988**
PR02	0.689	0.731	0.877	0.971	0.895	0.929	0.985	0.988	**0.988**
c2cl6	0.914	0.893	0.960	**0.988**	0.977	0.953	0.981	0.981	0.986
ED28	0.722	0.743	0.886	**0.988**	0.740	0.902	0.975	0.975	0.974
ch3nh2	0.685	0.730	0.870	**0.988**	0.863	0.952	0.980	0.979	0.981
Mn(CO)4NO	0.689	0.727	0.877	0.958	0.891	0.923	0.985	**0.988**	0.988
Fe(CO)5	0.689	0.731	0.877	0.971	0.895	0.930	0.986	0.988	**0.988**
PMe3	0.717	0.742	0.885	**0.989**	0.745	0.917	0.978	0.977	0.979
acetic	0.757	0.769	0.883	0.977	0.865	0.953	0.987	0.987	**0.989**
dioxetane	0.766	0.779	0.880	0.975	0.887	0.970	0.988	0.987	**0.989**
PR40	0.715	0.723	0.895	**0.989**	0.788	0.909	0.980	0.980	0.980
furan	0.699	0.721	0.871	**0.989**	0.727	0.976	0.987	0.986	0.988
ketene	0.722	0.753	0.872	0.983	0.815	0.966	0.988	0.987	**0.989**
TiCl2Me2	0.808	0.789	0.927	0.989	0.876	0.847	0.986	0.988	**0.989**
cs2	0.853	0.844	0.928	0.981	0.938	0.981	0.989	0.988	**0.989**
clcof	0.870	0.839	0.936	0.981	0.962	0.941	0.986	0.986	**0.990**
h2o	0.826	0.861	0.891	0.971	0.960	0.979	**0.990**	0.990	0.990
ch2c	0.719	0.730	0.817	**0.990**	0.665	0.956	0.985	0.984	0.986
c2cl4	0.878	0.867	0.957	**0.990**	0.955	0.957	0.981	0.981	0.984
clcn	0.830	0.862	0.921	0.986	0.927	0.950	0.989	0.988	**0.990**
thiophene	0.735	0.768	0.893	**0.990**	0.760	0.903	0.967	0.966	0.970
ch3f	0.781	0.804	0.901	0.983	0.870	0.970	0.990	0.989	**0.990**
ch2nh	0.702	0.732	0.858	0.984	0.853	0.978	0.990	0.989	**0.990**
PhSH	0.729	0.747	0.885	**0.991**	0.725	0.877	0.922	0.922	0.923
ED30	0.708	0.717	0.877	**0.991**	0.748	0.820	0.977	0.980	0.972

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ED01	0.683	0.707	0.872	0.961	0.848	0.955	0.990	**0.991**	0.986
nh2oh	0.757	0.785	0.879	0.974	0.964	0.978	0.991	0.990	**0.991**
formamide	0.723	0.745	0.884	0.979	0.936	0.960	0.990	0.990	**0.991**
ccl2h2	0.909	0.903	0.951	0.991	0.957	0.961	0.990	0.989	**0.991**
ch2clf	0.888	0.883	0.939	0.986	0.947	0.922	0.990	0.990	**0.992**
PCy3	0.664	0.683	0.870	**0.992**	0.660	0.784	0.964	0.965	0.963
cs	0.901	0.864	0.896	0.983	0.918	0.986	0.992	0.992	**0.992**
nh2cl	0.866	0.883	0.934	0.985	0.985	0.967	0.991	0.991	**0.992**
cclh3	0.852	0.867	0.934	**0.992**	0.909	0.946	0.987	0.987	0.988
tetrahedrane	0.664	0.705	0.863	**0.992**	0.583	0.970	0.984	0.982	0.985
c2clh5	0.802	0.817	0.918	**0.993**	0.844	0.833	0.976	0.974	0.980
PR06	0.670	0.705	0.873	0.965	0.844	0.897	0.990	**0.993**	0.992
c2cl2	0.864	0.899	0.944	**0.993**	0.895	0.946	0.978	0.978	0.981
oxadiazole	0.766	0.724	0.869	0.978	0.845	0.975	0.992	0.992	**0.993**
PR01	0.668	0.714	0.873	0.969	0.851	0.916	0.990	**0.993**	0.992
PhSeH	0.793	0.808	0.911	**0.993**	0.796	0.903	0.937	0.937	0.938
cyclobutene	0.644	0.671	0.859	**0.993**	0.634	0.951	0.976	0.975	0.978
ED31	0.685	0.693	0.871	**0.993**	0.642	0.817	0.964	0.966	0.955
ccl3h	0.890	0.899	0.959	0.989	0.978	0.971	0.991	0.991	**0.993**
CrO2(NO3)2	0.760	0.735	0.888	0.958	0.931	0.943	**0.993**	0.993	0.990
silole	0.705	0.700	0.877	**0.993**	0.681	0.891	0.956	0.954	0.960
CoH(CO)4	0.704	0.743	0.879	0.966	0.905	0.937	0.991	0.993	**0.993**
cyclobutane	0.635	0.644	0.863	**0.993**	0.638	0.932	0.969	0.968	0.972
cyclobutadiene	0.659	0.702	0.850	**0.993**	0.609	0.974	0.985	0.985	0.987
c2clh3	0.818	0.826	0.919	**0.993**	0.856	0.864	0.952	0.950	0.958
dioxetan2one	0.766	0.751	0.888	0.973	0.912	0.941	0.991	0.991	**0.993**
ED40b	0.787	0.802	0.914	**0.993**	0.837	0.877	0.985	0.985	0.986

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
s2o	0.891	0.896	0.932	0.981	0.984	0.974	0.993	0.992	**0.993**
formic-anhydride	0.749	0.772	0.886	0.974	0.924	0.954	0.992	0.992	**0.993**
ccl2	0.950	0.931	0.944	0.984	0.982	0.985	0.992	0.992	**0.993**
cyclopropene	0.632	0.685	0.857	**0.994**	0.626	0.968	0.984	0.983	0.985
glyoxal	0.787	0.769	0.875	0.974	0.880	0.977	0.992	0.992	**0.994**
hoclo	0.883	0.886	0.927	0.966	0.976	0.980	**0.994**	0.994	0.993
oxirene	0.747	0.798	0.861	0.975	0.788	0.987	0.993	0.993	**0.994**
c-hcoh	0.770	0.774	0.854	0.977	0.864	0.985	0.993	0.993	**0.994**
ccl4	0.945	0.908	0.962	0.988	0.983	0.979	0.992	0.991	**0.994**
Cr(CO)6	0.668	0.715	0.873	0.969	0.852	0.919	0.991	**0.994**	0.993
CrO2Cl2	0.812	0.796	0.924	0.966	0.937	0.917	0.994	**0.994**	0.992
c2clh	0.833	0.856	0.921	**0.994**	0.835	0.890	0.974	0.972	0.977
t-hcoh	0.773	0.776	0.855	0.977	0.848	0.981	0.994	0.993	**0.994**
cf2cl2	0.886	0.873	0.954	0.984	0.977	0.950	0.992	0.991	**0.994**
hccf	0.768	0.808	0.889	0.988	0.775	0.988	0.994	0.994	**0.994**
dioxirane	0.804	0.804	0.875	0.970	0.872	0.978	0.993	0.993	**0.994**
alf	0.918	0.906	0.903	0.982	0.966	0.985	0.994	0.994	**0.994**
ch2-sing	0.754	0.594	0.782	0.774	0.643	0.992	0.994	0.994	**0.994**
hocl	0.891	0.913	0.938	0.979	0.985	0.976	0.994	0.993	**0.994**
cyclopropane	0.636	0.654	0.865	**0.994**	0.636	0.945	0.975	0.974	0.977
MnO3F	0.819	0.812	0.887	0.942	0.930	0.984	**0.994**	0.993	0.991
n-pentane	0.629	0.663	0.865	**0.994**	0.656	0.870	0.969	0.969	0.971
so2	0.875	0.874	0.920	0.977	0.976	0.986	**0.994**	0.994	0.994
h2co	0.755	0.767	0.871	0.975	0.883	0.986	0.994	0.994	**0.994**
pyrrole	0.671	0.662	0.869	**0.994**	0.717	0.970	0.984	0.983	0.985
hnnn	0.743	0.731	0.870	0.982	0.975	0.968	0.994	0.993	**0.994**
n-butane	0.630	0.666	0.864	**0.994**	0.660	0.912	0.969	0.968	0.971

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
hooh	0.796	0.851	0.884	0.967	0.967	0.988	0.994	0.994	**0.994**
propane	0.627	0.672	0.864	**0.995**	0.667	0.926	0.970	0.969	0.973
cyclopentadiene	0.644	0.687	0.860	**0.995**	0.617	0.959	0.979	0.978	0.981
borole	0.660	0.675	0.845	**0.995**	0.615	0.915	0.983	0.983	0.985
c-n2h2	0.764	0.684	0.857	0.982	0.973	0.992	0.994	0.994	**0.995**
c2h6	0.630	0.701	0.863	**0.995**	0.680	0.934	0.973	0.972	0.974
si2h6	0.800	0.789	0.908	0.991	0.783	0.986	0.993	0.994	**0.995**
t-n2h2	0.766	0.690	0.857	0.982	0.870	0.989	0.994	0.994	**0.995**
formic	0.784	0.797	0.888	0.974	0.931	0.982	0.994	0.994	**0.995**
TiCl3Me	0.819	0.802	0.945	0.989	0.926	0.840	0.993	0.994	**0.995**
nh2f	0.806	0.824	0.899	0.976	0.969	0.983	0.995	0.994	**0.995**
Fe(CO)2(NO)2	0.716	0.748	0.879	0.951	0.914	0.938	0.993	**0.995**	0.994
propene	0.635	0.669	0.859	**0.995**	0.681	0.946	0.977	0.976	0.979
ch2f2	0.850	0.865	0.919	0.980	0.931	0.984	0.995	0.994	**0.995**
nccn	0.707	0.682	0.851	0.985	0.814	0.987	0.994	0.994	**0.995**
ch4	0.619	0.729	0.862	**0.995**	0.717	0.941	0.977	0.977	0.977
Cr(NO)4	0.715	0.734	0.881	0.962	0.883	0.942	**0.995**	0.995	0.992
Co(CO)3(NO)	0.716	0.749	0.880	0.968	0.913	0.950	0.994	**0.995**	0.994
hoclo2	0.878	0.867	0.925	0.964	0.973	0.985	**0.995**	0.995	0.995
honc	0.776	0.808	0.863	0.980	0.909	0.907	0.995	0.994	**0.995**
allene	0.642	0.658	0.855	**0.996**	0.640	0.975	0.985	0.984	0.986
b2h6	0.564	0.608	0.834	**0.996**	0.544	0.935	0.979	0.979	0.981
sih4	0.754	0.774	0.905	0.992	0.776	0.988	0.995	0.995	**0.996**
hnc	0.792	0.758	0.843	0.992	0.877	0.979	**0.996**	0.995	0.996
Ni(CO)4	0.717	0.753	0.882	0.962	0.915	0.964	**0.996**	0.995	0.993
PR03	0.716	0.753	0.882	0.962	0.915	0.965	**0.996**	0.995	0.994
benzene	0.652	0.706	0.862	**0.996**	0.604	0.968	0.983	0.983	0.985

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
t-butadiene	0.643	0.663	0.857	**0.996**	0.654	0.951	0.979	0.979	0.981
hf	0.915	0.929	0.933	0.978	0.969	0.994	**0.996**	0.996	0.996
Mn(NO)3CO	0.715	0.724	0.881	0.932	0.897	0.929	0.994	**0.996**	0.995
propyne	0.647	0.669	0.855	**0.996**	0.630	0.955	0.983	0.982	0.985
c2h4	0.637	0.749	0.855	**0.996**	0.670	0.967	0.984	0.983	0.985
fccf	0.825	0.841	0.908	0.983	0.838	0.996	0.996	0.996	**0.996**
ScF3	0.920	0.938	0.932	0.976	0.962	0.992	**0.996**	0.996	0.996
sih3f	0.834	0.839	0.922	0.986	0.882	0.994	0.996	0.996	**0.996**
hocn	0.770	0.753	0.873	0.977	0.891	0.976	0.996	0.996	**0.997**
clno	0.883	0.884	0.921	0.981	0.983	0.927	0.993	0.992	**0.997**
bh3	0.608	0.773	0.801	**0.997**	0.586	0.978	0.991	0.991	0.992
hnco	0.749	0.747	0.881	0.980	0.919	0.990	0.996	0.996	**0.997**
c2f4	0.792	0.820	0.926	0.980	0.924	0.991	0.996	0.996	**0.997**
t-hono	0.799	0.755	0.881	0.972	0.968	0.980	0.997	0.996	**0.997**
ph3	0.820	0.831	0.913	0.981	0.932	0.996	0.996	0.997	**0.997**
hcno	0.771	0.795	0.879	0.977	0.885	0.990	0.997	0.996	**0.997**
c2f6	0.828	0.816	0.934	0.979	0.960	0.985	0.995	0.995	**0.997**
hcof	0.830	0.821	0.904	0.976	0.939	0.994	0.997	0.997	**0.997**
hcn	0.732	0.751	0.847	0.986	0.811	0.991	0.997	0.997	**0.997**
hof	0.842	0.871	0.905	0.970	0.977	0.990	0.997	0.997	**0.997**
VOCl3	0.824	0.799	0.943	0.979	0.952	0.933	0.997	0.997	**0.997**
hno	0.790	0.786	0.867	0.975	0.958	0.996	0.997	0.997	**0.998**
chf3	0.898	0.889	0.931	0.979	0.962	0.992	0.997	0.997	**0.998**
CrO2F2	0.821	0.806	0.901	0.957	0.917	**0.998**	0.994	0.994	0.991
c-hono	0.798	0.751	0.881	0.972	0.969	0.988	0.998	0.997	**0.998**
hclo4	0.886	0.855	0.925	0.962	0.972	0.992	0.998	**0.998**	0.997
alf3	0.939	0.949	0.935	0.982	0.959	0.995	**0.998**	0.998	0.997

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
so3	0.853	0.860	0.922	0.973	0.972	0.997	**0.998**	0.998	0.997
p4	0.989	0.887	0.920	0.982	0.842	0.995	0.998	0.997	**0.998**
c2h2	0.589	0.806	0.845	**0.998**	0.614	0.990	0.993	0.993	0.993
h2s	0.886	0.894	0.936	0.982	0.976	**0.998**	0.997	0.998	0.998
clf	0.923	0.939	0.953	0.981	0.993	0.992	0.998	0.998	**0.998**
VOF3	0.826	0.818	0.914	0.968	0.929	0.996	**0.998**	0.998	0.997
bhf2	0.875	0.873	0.917	0.981	0.923	0.997	0.998	0.998	**0.998**
alcl	0.944	0.937	0.932	0.989	0.979	0.995	0.998	0.998	**0.999**
n2o4	0.781	0.777	0.891	0.969	0.964	0.989	0.998	0.998	**0.999**
pf3	0.906	0.883	0.940	0.980	0.976	0.994	**0.999**	0.999	0.999
f2co	0.834	0.817	0.921	0.977	0.951	0.998	0.999	0.999	**0.999**
cf4	0.894	0.843	0.939	0.979	0.966	0.996	0.998	0.998	**0.999**
bh	0.821	0.596	0.697	0.666	0.713	0.998	0.999	**0.999**	0.999
TiF4	0.818	0.807	0.930	0.977	0.947	0.999	**0.999**	0.999	0.998
n2o	0.768	0.749	0.881	0.977	0.973	0.991	0.999	0.999	**0.999**
alh3	0.766	0.788	0.880	0.995	0.816	0.997	0.999	0.999	**0.999**
Ni(PF3)4	0.882	0.850	0.938	0.971	0.963	0.983	0.999	**0.999**	0.997
VF5	0.838	0.836	0.926	0.972	0.947	0.994	**0.999**	0.999	0.998
hcl	0.951	0.955	0.968	0.992	0.989	**0.999**	0.999	0.999	0.999
co	0.856	0.795	0.852	0.985	0.925	0.993	**1.000**	0.999	0.999
alh	0.887	0.899	0.861	0.860	0.898	0.986	**1.000**	0.999	0.999
CrF6	0.803	0.790	0.919	0.964	0.946	**1.000**	0.991	0.991	0.988
bf3	0.913	0.932	0.932	0.980	0.955	0.999	0.999	1.000	**1.000**
p2	0.927	0.882	0.912	0.992	0.865	0.999	1.000	1.000	**1.000**
cf2	0.912	0.879	0.909	0.977	0.965	0.999	1.000	1.000	**1.000**
fno	0.857	0.827	0.896	0.975	0.974	0.999	**1.000**	1.000	1.000
bf	0.914	0.840	0.864	0.980	0.952	0.995	**1.000**	1.000	1.000

Table S3– *Continued on next page*

Table S3– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
TiCl4	0.849	0.819	0.960	0.989	0.968	0.986	0.999	1.000	**1.000**
co2	0.728	0.821	0.891	0.976	0.931	0.999	1.000	1.000	**1.000**
sif4	0.904	0.869	0.945	0.982	0.970	0.999	**1.000**	1.000	1.000
pf5	0.879	0.886	0.949	0.982	0.975	0.999	**1.000**	1.000	1.000
sf6	0.905	0.907	0.951	0.980	0.979	0.998	1.000	1.000	**1.000**
alcl3	0.904	0.892	0.965	0.993	0.979	0.999	1.000	1.000	**1.000**
cl2	0.941	0.963	0.968	0.987	0.994	1.000	1.000	1.000	**1.000**
f2	0.889	0.946	0.926	0.973	0.996	1.000	**1.000**	1.000	1.000
n2	0.792	0.745	0.851	0.992	0.855	1.000	**1.000**	1.000	1.000
h2	**1.000**	**1.000**	0.829	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**	**1.000**
Best	1	1	0	75	1	6	30	17	**98**

Table S4: Non-neutral and/or non-singlet molecules, revTPSSh/STO-3G: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
cf	0.881	0.835	0.864	0.934	0.942	0.955	0.933	0.953	**0.968**
Cu(acac)2	0.743	0.746	0.879	**0.969**	0.822	0.900	0.922	0.922	0.923
sif	0.909	0.878	0.904	0.951	0.968	0.972	0.959	**0.972**	0.954
ch3nh	0.690	0.725	0.851	0.979	0.825	0.955	0.984	0.983	**0.985**
V(NMe2)4	0.682	0.685	0.871	**0.986**	0.800	0.843	0.975	0.975	0.973
ch	0.748	0.864	0.731	0.736	0.612	0.888	0.985	0.884	**0.987**
sih	0.849	0.860	0.868	0.979	0.842	**0.990**	0.949	0.981	0.933
h2ccn	0.698	0.681	0.848	0.984	0.777	0.919	0.988	0.988	**0.990**
h2cn	0.710	0.713	0.840	0.979	0.812	0.968	0.989	0.989	**0.990**
so	0.897	0.887	0.915	0.987	0.986	0.977	0.990	0.990	**0.990**
ch2nh2	0.687	0.738	0.863	**0.990**	0.857	0.968	0.985	0.985	0.986
clo	0.915	0.932	0.934	0.942	**0.991**	0.954	0.987	0.959	0.988

Table S4– *Continued on next page*

Table S4– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Ti(BH4)3	0.640	0.641	0.869	**0.992**	0.645	0.862	0.985	0.986	0.985
ch2ch	0.645	0.715	0.837	**0.993**	0.681	0.967	0.985	0.984	0.985
cyclopropyl	0.637	0.671	0.855	**0.993**	0.646	0.953	0.979	0.978	0.980
hcnh	0.724	0.746	0.846	0.988	0.844	0.986	0.993	0.993	**0.993**
nh2	0.800	0.745	0.832	0.875	0.962	0.988	0.993	0.993	**0.993**
ch2-trip	0.758	0.845	0.793	0.992	0.706	0.989	0.993	0.993	**0.993**
t-hooo	0.827	0.805	0.879	0.967	0.978	0.961	0.994	0.993	**0.994**
h2no	0.765	0.781	0.880	0.969	0.965	0.982	0.994	0.994	**0.994**
bn3pi	0.813	0.747	0.774	0.898	0.818	0.975	0.922	0.992	**0.995**
allyl	0.641	0.687	0.852	**0.995**	0.668	0.962	0.981	0.980	0.983
cch	0.657	0.752	0.816	**0.995**	0.596	0.965	0.988	0.988	0.989
ch3	0.680	0.784	0.834	**0.995**	0.744	0.970	0.987	0.987	0.987
oh	0.901	0.888	0.854	0.878	0.967	0.966	**0.996**	0.887	0.995
n2h	0.765	0.728	0.849	0.982	0.912	0.989	0.996	0.996	**0.996**
c-hooo	0.831	0.802	0.879	0.966	0.977	0.975	**0.996**	0.996	0.996
cn	0.762	0.780	0.818	0.979	0.829	0.990	0.996	0.996	**0.997**
hco	0.783	0.779	0.859	0.976	0.866	0.995	0.997	0.997	**0.997**
hoo	0.820	0.817	0.876	0.968	0.974	0.990	0.997	0.997	**0.997**
nh	0.886	0.913	0.787	0.915	0.968	**0.998**	0.998	0.998	0.998
hs	0.936	0.940	0.921	0.941	0.972	0.967	**0.999**	0.960	0.994
ssh	0.905	0.896	0.936	0.983	0.986	0.995	0.999	0.999	**0.999**
no	0.827	0.796	0.862	0.980	0.984	0.996	**0.999**	0.934	0.934
s2	0.935	0.925	0.935	0.990	0.997	0.999	1.000	1.000	**1.000**
no2	0.790	0.781	0.886	0.972	0.968	0.999	1.000	1.000	**1.000**
o2	0.871	0.852	0.876	0.982	0.994	0.999	**1.000**	1.000	1.000
Best	0	0	0	9	1	2	5	1	**19**

Table S5: Neutral singlet molecules, HF/pcseg-0: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Mn(NO)3CO	0.590	0.645	0.892	0.948	**0.953**	0.914	0.948	0.950	0.949
Fe(CO)2(NO)2	0.596	0.655	0.890	0.953	0.955	0.929	0.957	**0.959**	0.957
b2h6	0.509	0.545	0.878	0.959	0.961	0.897	0.962	0.961	**0.965**
Ni(C5H5)NO	0.625	0.663	0.892	0.959	**0.965**	0.872	0.961	0.961	0.961
Fe(C2H4)(CO)4	0.586	0.632	0.890	0.964	0.964	0.848	0.960	0.964	**0.965**
Fe(CO)4(C2H4)	0.584	0.630	0.890	0.964	**0.965**	0.844	0.958	0.962	0.963
Fe(C4H4)(CO)3	0.597	0.631	0.892	**0.965**	0.962	0.820	0.940	0.946	0.951
Cr(NO)4	0.592	0.634	0.893	0.951	0.960	0.907	0.962	0.965	**0.965**
Fe(C4H6)(CO)3	0.576	0.643	0.890	**0.966**	0.964	0.819	0.946	0.953	0.954
Mn(C5H5)(CO)3	0.589	0.635	0.893	0.963	**0.966**	0.794	0.937	0.944	0.945
Mn(CO)5CN	0.580	0.630	0.887	0.953	**0.966**	0.898	0.955	0.960	0.958
Fe(CO)3(tmm)	0.592	0.613	0.891	**0.966**	0.963	0.810	0.934	0.942	0.947
MnCp(CO)3	0.588	0.633	0.893	0.963	**0.966**	0.794	0.934	0.941	0.943
Co(C3H5)(CO)3	0.599	0.644	0.890	0.966	**0.967**	0.840	0.960	0.964	0.966
PR05	0.574	0.633	0.890	0.955	**0.967**	0.889	0.958	0.962	0.960
VCp(CO)4	0.570	0.624	0.895	0.962	**0.967**	0.782	0.926	0.938	0.934
Mn(CO)4NO	0.590	0.656	0.890	0.955	0.965	0.913	0.965	**0.967**	0.966
ED05	0.593	0.657	0.890	0.956	0.967	0.890	0.965	0.968	**0.968**
PR04	0.588	0.649	0.893	**0.970**	0.964	0.877	0.938	0.940	0.944
ch4	0.405	0.618	0.881	0.966	**0.972**	0.907	0.965	0.964	0.965
ED15	0.623	0.648	0.890	0.959	0.966	0.932	0.970	0.971	**0.972**
Ni(C3H5)2	0.622	0.648	0.889	0.957	0.966	0.933	0.971	0.971	**0.972**
ED14	0.577	0.624	0.899	0.956	**0.973**	0.840	0.929	0.933	0.931
Co(CO)3(NO)	0.615	0.678	0.889	0.963	0.964	0.948	0.971	**0.973**	0.971
ED04	0.610	0.659	0.891	**0.973**	0.962	0.876	0.953	0.954	0.961
Cr(C6H6)(CO)3	0.580	0.637	0.893	0.963	**0.973**	0.800	0.931	0.947	0.953

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
PR12	0.562	0.622	0.890	0.960	0.973	0.823	0.970	**0.974**	0.972
tetrahedrane	0.511	0.612	0.890	0.971	0.971	0.944	0.972	0.971	**0.974**
PR02	0.598	0.623	0.891	0.962	0.967	0.921	0.971	**0.974**	0.973
propyne	0.471	0.590	0.881	0.972	0.972	0.929	0.972	0.971	**0.974**
Fe(CO)5	0.598	0.623	0.890	0.962	0.967	0.922	0.972	**0.974**	0.974
cyclopropene	0.489	0.586	0.883	0.974	0.974	0.941	0.973	0.972	**0.975**
ch3nh2	0.478	0.608	0.885	0.969	**0.975**	0.929	0.972	0.971	0.973
PR14	0.555	0.594	0.900	0.965	**0.976**	0.807	0.952	0.958	0.927
oxetane	0.512	0.621	0.895	0.970	**0.976**	0.931	0.972	0.971	0.974
propene	0.476	0.584	0.885	0.972	**0.976**	0.919	0.966	0.965	0.968
c2h6	0.485	0.591	0.887	0.971	**0.976**	0.906	0.960	0.959	0.962
allene	0.465	0.584	0.880	0.971	0.972	0.948	0.975	0.974	**0.976**
cyclobutene	0.524	0.586	0.887	0.971	**0.976**	0.927	0.966	0.965	0.969
ED40a	0.600	0.655	0.886	0.967	0.956	0.939	**0.976**	0.975	0.973
ethanol	0.467	0.621	0.895	0.971	**0.976**	0.927	0.971	0.970	0.973
MnO3F	0.648	0.700	0.895	0.946	0.961	0.944	0.975	0.975	**0.976**
cyclopropane	0.511	0.561	0.890	0.973	**0.976**	0.920	0.964	0.963	0.966
c2h4	0.487	0.553	0.878	0.974	**0.976**	0.938	0.974	0.973	0.974
PR15	0.592	0.641	0.893	0.966	0.966	0.918	0.976	**0.976**	0.976
ch2c	0.528	0.639	0.839	0.965	0.965	0.930	0.976	0.975	**0.977**
FeCp2	0.597	0.661	0.897	**0.977**	0.960	0.900	0.956	0.958	0.960
CoH(CO)4	0.619	0.677	0.890	0.966	0.968	0.931	0.975	**0.977**	0.977
Ni(acac)2	0.582	0.637	0.897	0.950	0.968	0.914	**0.977**	0.962	0.974
propane	0.470	0.579	0.889	0.972	**0.978**	0.901	0.958	0.957	0.961
PR40	0.618	0.650	0.915	**0.978**	0.974	0.883	0.955	0.959	0.967
cyclopentadiene	0.534	0.608	0.889	0.975	**0.978**	0.935	0.969	0.968	0.971
beta-lactim	0.495	0.633	0.895	0.971	0.975	0.930	0.975	0.974	**0.978**

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Fe(C5Me5)(P5)	0.641	0.680	0.918	**0.978**	0.970	0.823	0.898	0.901	0.897
t-butadiene	0.475	0.590	0.883	0.977	**0.978**	0.926	0.968	0.968	0.970
cyclobutadiene	0.525	0.610	0.879	0.976	**0.978**	0.950	0.976	0.975	0.978
n-butane	0.450	0.582	0.891	0.974	**0.978**	0.892	0.957	0.956	0.960
cyclobutane	0.517	0.564	0.891	0.973	**0.979**	0.910	0.959	0.958	0.962
borole	0.514	0.596	0.877	0.977	**0.979**	0.894	0.973	0.972	0.975
c2h5f	0.489	0.642	0.911	0.975	**0.979**	0.909	0.975	0.974	0.977
acetaldehyde	0.484	0.618	0.893	0.968	0.973	0.913	0.977	0.976	**0.979**
n-pentane	0.449	0.584	0.891	0.974	**0.979**	0.857	0.957	0.957	0.959
Cr(C6H6)2	0.581	0.652	0.898	**0.979**	0.972	0.883	0.963	0.966	0.968
oxirane	0.517	0.641	0.894	0.969	0.973	0.944	0.979	0.978	**0.980**
methanol	0.506	0.634	0.895	0.969	0.974	0.944	0.979	0.979	**0.980**
CuCN	0.750	0.751	0.860	0.930	0.973	**0.980**	0.947	0.941	0.949
ED31	0.533	0.595	0.901	0.981	**0.981**	0.790	0.960	0.959	0.940
benzene	0.533	0.624	0.891	0.980	**0.981**	0.944	0.973	0.973	0.975
furan	0.520	0.639	0.896	0.978	0.980	0.956	0.980	0.979	**0.981**
pyrrole	0.505	0.628	0.894	0.979	**0.981**	0.947	0.975	0.975	0.977
PMe3	0.572	0.654	0.909	0.977	**0.981**	0.899	0.971	0.970	0.972
ED02	0.618	0.662	0.885	0.950	0.965	0.939	0.979	**0.981**	0.981
nh3	0.442	0.646	0.877	0.965	0.973	0.946	**0.981**	0.981	0.981
Sc(acac)3	0.532	0.603	0.906	0.978	**0.982**	0.836	0.975	0.978	0.963
bh3	0.509	0.689	0.830	0.966	0.967	0.939	0.981	0.981	**0.982**
PR06	0.585	0.640	0.890	0.958	0.974	0.883	0.978	0.981	**0.982**
ED28	0.559	0.649	0.911	0.978	**0.982**	0.884	0.967	0.967	0.966
ch3ph2	0.620	0.689	0.922	0.978	**0.982**	0.921	0.978	0.977	0.980
ED27	0.564	0.657	0.913	0.979	**0.982**	0.905	0.971	0.970	0.971
PCy3	0.493	0.578	0.901	0.978	**0.982**	0.752	0.954	0.956	0.953

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ED30	0.547	0.617	0.904	0.980	**0.982**	0.800	0.969	0.973	0.963
PR01	0.578	0.641	0.889	0.959	0.975	0.898	0.979	**0.982**	0.981
silole	0.582	0.673	0.907	0.980	**0.983**	0.875	0.947	0.945	0.951
c2h3f	0.519	0.652	0.909	0.979	0.980	0.939	0.982	0.981	**0.983**
PhSH	0.571	0.677	0.911	0.982	**0.983**	0.859	0.913	0.913	0.915
AcCl	0.605	0.708	0.931	0.980	**0.983**	0.859	0.953	0.951	0.960
Ni(PH3)2	0.740	0.767	0.908	0.961	0.972	0.968	0.983	**0.983**	0.983
acetic	0.506	0.648	0.904	0.973	0.976	0.937	0.982	0.981	**0.983**
dithiotane	0.660	0.728	0.933	0.980	**0.983**	0.925	0.975	0.974	0.978
TiCl2Me2	0.683	0.727	0.934	0.983	**0.983**	0.831	0.916	0.931	0.948
Cr(CO)6	0.578	0.648	0.889	0.959	0.974	0.901	0.980	**0.984**	0.983
thiophene	0.601	0.688	0.916	0.983	**0.984**	0.885	0.959	0.958	0.962
ketene	0.511	0.649	0.893	0.974	0.977	0.948	0.983	0.982	**0.984**
ch2nh	0.477	0.619	0.874	0.972	0.974	0.956	0.984	0.983	**0.984**
Zn(CH3)2	0.685	0.696	0.885	0.949	0.980	0.960	**0.984**	0.984	0.984
n2h4	0.446	0.622	0.883	0.971	0.977	0.954	0.983	0.983	**0.984**
c2h2	0.514	0.590	0.869	0.979	0.974	0.965	**0.984**	0.984	0.984
dioxetane	0.516	0.635	0.901	0.970	0.974	0.955	0.983	0.983	**0.985**
c2clh5	0.592	0.700	0.933	0.982	**0.985**	0.845	0.970	0.968	0.973
CuMe	0.751	0.761	0.864	0.929	0.976	0.965	0.985	0.984	**0.985**
c2clh3	0.620	0.712	0.933	0.984	**0.985**	0.862	0.949	0.946	0.955
ocs	0.646	0.756	0.930	0.985	**0.985**	0.921	0.972	0.971	0.976
ch3f	0.534	0.663	0.917	0.975	0.978	0.952	0.985	0.984	**0.985**
PhSeH	0.670	0.727	0.928	0.984	**0.986**	0.891	0.931	0.931	0.932
cclh3	0.653	0.734	0.944	0.984	**0.986**	0.939	0.983	0.983	0.985
cs2	0.740	0.783	0.943	0.986	**0.986**	0.970	0.985	0.984	0.985
ED40b	0.638	0.700	0.933	0.983	**0.987**	0.868	0.980	0.980	0.981

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
formamide	0.495	0.647	0.899	0.974	0.978	0.944	0.986	0.985	**0.987**
clcn	0.650	0.754	0.933	0.986	0.983	0.944	0.985	0.984	**0.987**
clcof	0.629	0.746	0.949	**0.987**	0.986	0.933	0.982	0.981	0.986
CrO2(NO3)2	0.584	0.643	0.904	0.966	0.976	0.900	0.987	0.987	**0.987**
c2clh	0.642	0.743	0.935	**0.988**	0.984	0.882	0.972	0.970	0.975
VOCl3	0.731	0.772	0.949	0.983	**0.988**	0.895	0.966	0.970	0.978
oxadiazole	0.539	0.650	0.892	0.978	0.981	0.960	0.987	0.986	**0.988**
ED01	0.588	0.649	0.887	0.954	0.973	0.920	0.986	**0.988**	0.987
ccl2o	0.682	0.770	0.956	0.988	**0.988**	0.951	0.982	0.981	0.985
oxirene	0.505	0.677	0.884	0.968	0.968	0.969	0.988	0.987	**0.988**
ch2clf	0.638	0.739	0.950	0.985	0.986	0.915	0.987	0.986	**0.989**
TiCl3Me	0.718	0.767	0.950	0.988	**0.989**	0.814	0.956	0.961	0.971
Ni(CO)4	0.628	0.687	0.888	0.967	0.974	0.968	0.988	**0.989**	0.988
cis-c2f2cl2	0.677	0.758	0.957	**0.989**	0.988	0.896	0.976	0.975	0.981
PR03	0.629	0.687	0.888	0.967	0.974	0.968	0.988	**0.989**	0.988
trans-c2f2cl2	0.676	0.755	0.957	**0.989**	0.988	0.908	0.976	0.975	0.981
hccf	0.534	0.693	0.909	0.984	0.980	0.976	0.989	0.989	**0.989**
dioxetan2one	0.515	0.650	0.909	0.974	0.976	0.927	0.987	0.987	**0.989**
ccl2h2	0.698	0.768	0.960	0.988	0.989	0.955	0.988	0.987	**0.989**
glyoxal	0.538	0.687	0.893	0.977	0.979	0.963	0.988	0.988	**0.990**
clno	0.665	0.732	0.931	0.986	**0.990**	0.918	0.981	0.980	0.988
h2co	0.519	0.648	0.888	0.974	0.977	0.967	0.990	0.989	**0.990**
c2cl6	0.723	0.778	0.968	0.989	**0.990**	0.944	0.980	0.979	0.985
formic-anhydride	0.561	0.651	0.905	0.977	0.978	0.940	0.989	0.988	**0.990**
hnnn	0.513	0.616	0.884	0.973	0.974	0.953	0.989	0.989	**0.990**
dioxirane	0.515	0.670	0.894	0.969	0.975	0.964	0.990	0.989	**0.990**
CrO2Cl2	0.710	0.746	0.932	0.973	0.989	0.887	0.981	0.982	**0.990**

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
nh2cl	0.639	0.743	0.939	0.984	0.988	0.959	0.990	0.989	**0.991**
nh2oh	0.474	0.648	0.890	0.971	0.976	0.967	0.990	0.990	**0.991**
cs	0.701	0.760	0.911	0.990	**0.991**	0.978	0.990	0.990	0.990
nccn	0.547	0.689	0.873	0.982	0.978	0.973	0.990	0.989	**0.991**
c2cl2	0.693	0.784	0.955	**0.991**	0.988	0.940	0.976	0.976	0.979
c2cl4	0.732	0.785	0.966	**0.991**	0.990	0.952	0.979	0.978	0.982
h2o	0.489	0.689	0.896	0.969	0.974	0.970	**0.991**	0.991	0.991
s2o	0.702	0.766	0.943	0.986	0.990	0.964	0.990	0.990	**0.991**
si2h6	0.678	0.717	0.943	0.986	0.989	0.969	0.989	0.990	**0.991**
hnc	0.529	0.646	0.858	0.981	0.978	0.962	**0.991**	0.990	0.991
ch2-sing	0.505	0.523	0.795	0.758	0.972	0.971	**0.992**	0.991	0.991
c-hcoh	0.538	0.656	0.868	0.973	0.978	0.972	0.991	0.991	**0.992**
ccl3h	0.722	0.800	0.966	0.989	0.990	0.966	0.990	0.989	**0.992**
honc	0.524	0.685	0.880	0.976	0.974	0.888	0.991	0.990	**0.992**
TiCl4	0.746	0.783	0.962	0.991	**0.992**	0.917	0.982	0.985	0.990
t-hcoh	0.537	0.659	0.868	0.972	0.973	0.968	0.992	0.991	**0.992**
formic	0.532	0.698	0.904	0.976	0.978	0.969	0.991	0.991	**0.992**
hcno	0.527	0.676	0.897	0.978	0.978	0.975	0.992	0.991	**0.992**
sih4	0.660	0.704	0.937	0.982	0.986	0.968	0.991	0.991	**0.992**
cf2cl2	0.675	0.746	0.964	0.989	0.989	0.946	0.989	0.989	**0.992**
ch2f2	0.538	0.692	0.934	0.980	0.981	0.972	0.991	0.991	**0.992**
fccf	0.560	0.724	0.927	0.986	0.983	0.985	0.992	0.992	**0.992**
ED03	0.655	0.704	0.883	0.944	0.974	0.978	0.991	**0.992**	0.991
c-n2h2	0.508	0.572	0.869	0.976	0.980	0.977	0.992	0.992	**0.992**
hnco	0.531	0.676	0.899	0.980	0.981	0.976	0.992	0.992	**0.992**
hcn	0.532	0.640	0.865	0.979	0.975	0.975	**0.993**	0.992	0.992
t-n2h2	0.509	0.576	0.869	0.976	0.972	0.976	0.992	0.992	**0.993**

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ccl4	0.744	0.784	0.970	0.989	0.990	0.976	0.991	0.990	**0.993**
ccl2	0.719	0.793	0.954	0.990	**0.993**	0.982	0.991	0.991	0.993
c2f4	0.581	0.758	0.942	0.986	0.985	0.981	0.992	0.992	**0.993**
hocn	0.525	0.697	0.891	0.976	0.975	0.965	0.993	0.992	**0.993**
sio	0.706	0.780	0.897	0.989	**0.993**	0.968	0.988	0.987	0.988
hoclo	0.628	0.740	0.936	0.977	0.984	0.974	**0.994**	0.993	0.994
nh2f	0.507	0.675	0.910	0.976	0.981	0.972	0.993	0.993	**0.994**
c2f6	0.556	0.681	0.950	0.986	0.985	0.976	0.992	0.992	**0.994**
hcof	0.551	0.717	0.920	0.981	0.981	0.982	0.994	0.993	**0.994**
n2o4	0.514	0.633	0.909	0.978	0.980	0.974	0.993	0.992	**0.994**
hocl	0.650	0.758	0.944	0.983	0.990	0.972	0.994	0.994	**0.994**
hoclo2	0.616	0.727	0.935	0.975	0.981	0.975	**0.995**	0.994	0.995
t-hono	0.522	0.617	0.896	0.977	0.981	0.970	0.995	0.994	**0.995**
sih3f	0.643	0.726	0.942	0.983	0.986	0.981	0.994	0.994	**0.995**
alf	0.713	0.801	0.910	0.990	0.994	0.980	0.994	0.994	**0.995**
chf3	0.560	0.738	0.945	0.984	0.983	0.983	0.994	0.994	**0.995**
CrF6	0.624	0.720	0.931	0.977	0.984	0.973	0.995	**0.995**	0.995
ph3	0.668	0.732	0.937	0.981	0.984	0.981	0.995	0.995	**0.995**
hooh	0.494	0.664	0.897	0.972	0.979	0.981	0.995	0.995	**0.995**
c-hono	0.519	0.614	0.897	0.978	0.982	0.977	**0.996**	0.995	0.996
bhf2	0.564	0.726	0.931	0.986	0.984	0.987	0.995	0.995	**0.996**
n2o	0.516	0.684	0.897	0.980	0.980	0.979	0.996	0.995	**0.996**
f2co	0.548	0.718	0.937	0.985	0.984	0.989	0.996	0.995	**0.996**
so2	0.635	0.735	0.930	0.982	0.986	0.983	**0.996**	0.996	0.996
co2	0.555	0.752	0.909	0.984	0.984	0.988	0.996	0.996	**0.996**
p4	0.779	0.798	0.941	0.986	0.991	0.986	0.996	0.995	**0.996**
CrO2F2	0.642	0.735	0.913	0.969	0.986	0.984	0.997	**0.997**	0.996

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
hno	0.524	0.659	0.880	0.979	0.981	0.986	0.997	0.996	**0.997**
hclo4	0.609	0.719	0.935	0.974	0.980	0.980	0.996	0.996	**0.997**
Ni(PF3)4	0.616	0.713	0.946	0.980	0.986	0.980	0.996	**0.997**	0.995
cf4	0.595	0.678	0.953	0.987	0.985	0.989	0.996	0.996	**0.997**
fno	0.567	0.675	0.911	0.983	0.987	0.990	**0.997**	0.997	0.997
VOF3	0.625	0.726	0.927	0.980	0.984	0.960	0.995	0.996	**0.997**
co	0.563	0.677	0.864	0.985	0.988	0.983	**0.997**	0.997	0.997
hof	0.517	0.698	0.917	0.977	0.985	0.983	0.997	0.997	**0.997**
alh3	0.704	0.679	0.912	0.988	0.988	0.986	0.997	0.997	**0.997**
h2s	0.695	0.766	0.950	0.985	0.986	0.988	0.997	0.997	**0.997**
alcl	0.775	0.824	0.939	0.993	0.995	0.988	0.997	0.997	**0.998**
bf3	0.581	0.762	0.945	0.990	0.987	0.992	0.997	0.997	**0.998**
hf	0.537	0.739	0.938	0.984	0.983	0.991	**0.998**	0.998	0.998
cf2	0.567	0.730	0.922	0.985	0.988	0.992	0.998	0.998	**0.998**
bh	0.609	0.546	0.711	0.856	0.978	0.979	**0.998**	0.997	0.997
n2	0.588	0.616	0.864	0.986	0.989	0.990	**0.998**	0.998	0.998
pf3	0.613	0.730	0.949	0.986	0.990	0.987	0.998	0.998	**0.998**
VF5	0.618	0.727	0.939	0.986	0.987	0.955	0.996	0.997	**0.998**
bf	0.589	0.719	0.873	0.985	0.988	0.988	**0.998**	0.998	0.998
so3	0.612	0.703	0.935	0.981	0.986	0.992	**0.998**	0.998	0.998
alh	0.782	0.735	0.875	0.890	0.993	0.973	0.998	0.998	**0.999**
TiF4	0.615	0.710	0.940	0.991	0.990	0.979	0.997	0.998	**0.999**
sf6	0.603	0.742	0.962	0.987	0.989	0.991	0.998	0.998	**0.999**
clf	0.669	0.776	0.958	0.986	0.994	0.990	0.998	0.998	**0.999**
ScF3	0.622	0.699	0.943	0.994	0.992	0.994	0.999	**0.999**	0.999
p2	0.769	0.784	0.929	0.994	0.997	0.993	0.999	0.999	**0.999**
pf5	0.591	0.726	0.961	0.989	0.990	0.993	0.998	0.998	**0.999**

Table S5– *Continued on next page*

Table S5– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
sif4	0.614	0.712	0.956	0.990	0.989	0.994	0.999	0.999	**0.999**
alcl3	0.761	0.829	0.974	0.996	0.995	0.995	0.999	0.999	**0.999**
alf3	0.654	0.801	0.946	0.992	0.990	0.994	**0.999**	0.999	0.999
hcl	0.718	0.797	0.971	0.992	0.991	0.994	**0.999**	0.999	0.999
f2	0.545	0.713	0.936	0.980	0.992	0.997	1.000	1.000	**1.000**
h2	0.546	0.973	0.855	0.950	0.950	0.973	**1.000**	0.999	0.999
cl2	0.737	0.803	0.972	0.992	0.996	0.996	1.000	1.000	**1.000**
Best	0	0	0	15	62	1	23	20	**101**

Table S6: Non-neutral and/or non-singlet molecules, HF/pcseg-0: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ch	0.501	0.557	0.739	0.877	**0.937**	0.862	0.851	0.868	0.843
cch	0.504	0.693	0.833	0.962	0.945	0.931	0.966	0.965	**0.966**
ch2ch	0.493	0.603	0.856	0.960	0.960	0.934	0.968	0.968	**0.969**
Ti(BH4)3	0.608	0.614	0.897	**0.972**	0.924	0.809	0.959	0.963	0.967
cyclopropyl	0.515	0.576	0.880	0.970	**0.973**	0.929	0.968	0.967	0.970
bn3pi	0.568	0.643	0.789	0.900	0.901	0.970	**0.973**	0.907	0.938
cn	0.532	0.674	0.829	0.959	0.944	0.962	**0.974**	0.973	0.973
allyl	0.475	0.598	0.874	0.971	**0.974**	0.933	0.968	0.967	0.969
Cu(acac)2	0.575	0.641	0.896	0.954	**0.974**	0.926	0.940	0.925	0.954
cf	0.583	0.680	0.874	0.942	**0.976**	0.943	0.954	0.966	0.946
h2cn	0.494	0.616	0.853	0.957	0.959	0.942	0.976	0.975	**0.976**
ch3nh	0.474	0.604	0.867	0.957	0.964	0.934	0.976	0.975	**0.977**
t-hooo	0.516	0.657	0.889	0.959	0.967	0.940	0.977	0.977	**0.977**
ch2nh2	0.477	0.624	0.876	0.970	0.974	0.946	0.979	0.978	**0.979**
h2ccn	0.527	0.615	0.866	0.967	0.967	0.898	0.978	0.978	**0.980**
ch3	0.458	0.661	0.849	0.969	0.974	0.941	**0.980**	0.979	0.980

Table S6– *Continued on next page*

Table S6– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
V(NMe2)4	0.511	0.574	0.893	0.974	**0.981**	0.839	0.957	0.969	0.948
clo	0.676	0.777	0.939	0.982	0.964	0.956	0.963	0.972	**0.982**
hcnh	0.508	0.634	0.860	0.970	0.965	0.963	0.983	0.982	**0.983**
c-hooo	0.517	0.655	0.892	0.964	0.972	0.955	**0.986**	0.985	0.985
sif	0.702	0.782	0.909	**0.986**	0.950	0.962	0.981	0.970	0.974
n2h	0.524	0.598	0.859	0.969	0.967	0.971	0.988	0.988	**0.988**
ch2-trip	0.510	0.693	0.803	0.973	0.975	0.968	**0.990**	0.990	0.990
no2	0.546	0.644	0.900	0.975	0.977	0.983	0.991	0.991	**0.991**
h2no	0.489	0.653	0.889	0.967	0.973	0.969	0.992	0.992	**0.992**
nh2	0.490	0.611	0.836	0.861	0.972	0.973	**0.992**	0.992	0.992
so	0.680	0.761	0.922	0.987	**0.992**	0.971	0.989	0.989	0.989
hco	0.540	0.663	0.874	0.979	0.978	0.981	**0.994**	0.993	0.994
hoo	0.517	0.655	0.888	0.967	0.974	0.982	**0.995**	0.995	0.995
no	0.552	0.674	0.872	0.917	0.928	0.937	0.946	0.954	**0.995**
ssh	0.729	0.780	0.947	0.985	0.988	0.988	0.997	0.997	**0.997**
oh	0.530	0.661	0.858	0.921	0.974	0.989	**0.998**	0.997	0.969
nh	0.550	0.655	0.789	0.957	0.978	0.990	**0.998**	0.998	0.998
sih	0.745	0.727	0.879	0.972	0.944	0.917	0.984	**0.999**	0.998
o2	0.558	0.680	0.889	0.984	0.991	0.993	**0.999**	0.999	0.999
hs	0.731	0.773	0.930	0.942	0.932	0.965	0.961	0.958	**0.999**
s2	0.745	0.797	0.945	0.993	0.996	0.995	0.999	0.999	**0.999**
Best	0	0	0	2	7	0	11	1	**16**

Table S7: Neutral singlet molecules, revTPSSh/pcseg-0: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
b2h6	0.512	0.550	0.876	0.957	0.959	0.902	0.966	0.965	**0.968**
ch4	0.409	0.621	0.880	0.964	**0.970**	0.909	0.966	0.965	0.966

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Mn(CO)5CN	0.577	0.631	0.888	0.965	**0.971**	0.901	0.959	0.963	0.961
MnCp(CO)3	0.588	0.636	0.894	**0.971**	0.969	0.792	0.937	0.944	0.946
Co(C3H5)(CO)3	0.599	0.646	0.891	**0.971**	0.968	0.842	0.963	0.967	0.969
Mn(C5H5)(CO)3	0.589	0.638	0.894	**0.971**	0.969	0.792	0.940	0.948	0.949
PR05	0.573	0.634	0.891	0.965	**0.971**	0.892	0.964	0.967	0.966
Ni(C5H5)NO	0.626	0.666	0.892	0.967	**0.971**	0.876	0.968	0.968	0.968
VCp(CO)4	0.570	0.627	0.895	0.966	**0.972**	0.783	0.930	0.942	0.938
Fe(C2H4)(CO)4	0.585	0.635	0.891	**0.972**	0.967	0.851	0.965	0.968	0.969
Fe(CO)4(C2H4)	0.583	0.633	0.891	**0.972**	0.967	0.848	0.962	0.966	0.967
ED04	0.610	0.661	0.891	**0.972**	0.963	0.876	0.953	0.955	0.964
Fe(CO)2(NO)2	0.599	0.655	0.892	**0.972**	0.970	0.935	0.970	0.972	0.970
Fe(C4H6)(CO)3	0.577	0.645	0.891	**0.973**	0.966	0.820	0.950	0.957	0.958
PR04	0.590	0.651	0.893	**0.973**	0.967	0.877	0.939	0.941	0.946
ED05	0.591	0.655	0.892	0.967	0.971	0.893	0.971	0.973	**0.973**
Fe(C4H4)(CO)3	0.598	0.634	0.893	**0.973**	0.966	0.820	0.942	0.948	0.954
ED14	0.579	0.626	0.898	0.954	**0.973**	0.842	0.934	0.937	0.936
Mn(CO)4NO	0.590	0.654	0.892	0.966	0.971	0.916	0.971	**0.974**	0.973
ch3nh2	0.479	0.611	0.884	0.967	0.974	0.930	0.972	0.971	**0.974**
Fe(CO)3(tmm)	0.592	0.616	0.892	**0.974**	0.964	0.810	0.937	0.946	0.951
ethanol	0.469	0.624	0.894	0.970	**0.974**	0.929	0.972	0.971	0.974
c2h6	0.488	0.595	0.885	0.969	**0.974**	0.908	0.962	0.961	0.964
Mn(NO)3CO	0.595	0.648	0.894	0.969	**0.975**	0.921	0.966	0.969	0.968
FeCp2	0.598	0.664	0.896	**0.975**	0.963	0.903	0.962	0.964	0.966
PR40	0.621	0.653	0.913	**0.975**	0.972	0.887	0.957	0.961	0.970
cyclopropane	0.513	0.564	0.889	0.971	**0.975**	0.922	0.966	0.964	0.968
oxetane	0.513	0.624	0.894	0.968	0.974	0.933	0.973	0.972	**0.975**
propene	0.478	0.587	0.884	0.972	**0.975**	0.922	0.967	0.966	0.970

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Cr(C6H6)(CO)3	0.580	0.639	0.894	0.967	**0.975**	0.799	0.936	0.952	0.958
tetrahedrane	0.512	0.617	0.889	0.970	0.969	0.946	0.974	0.973	**0.976**
cyclobutene	0.525	0.590	0.886	0.971	**0.976**	0.930	0.968	0.967	0.970
c2h4	0.488	0.557	0.876	0.973	0.975	0.941	0.975	0.974	**0.976**
propyne	0.473	0.594	0.880	0.972	0.972	0.932	0.974	0.973	**0.976**
ED15	0.624	0.649	0.889	0.960	0.968	0.936	0.975	0.975	**0.976**
cyclopropene	0.489	0.591	0.881	0.972	0.973	0.944	0.975	0.974	**0.976**
PR14	0.555	0.595	0.899	0.965	**0.976**	0.808	0.953	0.959	0.928
propane	0.471	0.582	0.888	0.971	**0.976**	0.903	0.959	0.958	0.962
Ni(C3H5)2	0.624	0.650	0.888	0.958	0.968	0.937	0.975	0.976	**0.977**
PR02	0.595	0.624	0.892	0.970	0.969	0.924	0.975	**0.977**	0.977
n-butane	0.451	0.585	0.890	0.972	**0.977**	0.895	0.959	0.958	0.961
PR12	0.562	0.625	0.891	0.966	0.977	0.828	0.973	**0.977**	0.976
cyclobutane	0.519	0.567	0.890	0.972	**0.978**	0.912	0.960	0.959	0.964
Fe(CO)5	0.595	0.624	0.892	0.970	0.969	0.925	0.975	**0.978**	0.977
c2h5f	0.491	0.644	0.909	0.973	0.977	0.913	0.976	0.975	**0.978**
n-pentane	0.451	0.587	0.891	0.973	**0.978**	0.860	0.958	0.958	0.961
t-butadiene	0.478	0.592	0.882	0.976	**0.978**	0.928	0.970	0.969	0.972
cyclopentadiene	0.534	0.612	0.889	0.975	**0.978**	0.938	0.971	0.970	0.973
borole	0.514	0.599	0.876	0.977	**0.978**	0.896	0.975	0.974	0.976
ED40a	0.601	0.659	0.884	0.962	0.954	0.942	**0.978**	0.976	0.975
allene	0.468	0.588	0.880	0.971	0.972	0.952	0.977	0.976	**0.978**
CuCN	0.750	0.748	0.860	0.932	0.975	**0.979**	0.951	0.945	0.953
ch2c	0.529	0.643	0.840	0.966	0.967	0.933	0.979	0.977	**0.979**
Cr(C6H6)2	0.581	0.653	0.897	**0.979**	0.972	0.886	0.966	0.969	0.971
Co(CO)3(NO)	0.615	0.675	0.891	0.975	0.970	0.951	0.978	**0.979**	0.978
cyclobutadiene	0.526	0.615	0.878	0.975	0.978	0.953	0.978	0.977	**0.979**

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Sc(acac)3	0.534	0.602	0.904	0.976	**0.979**	0.838	0.976	0.979	0.965
Fe(C5Me5)(P5)	0.643	0.682	0.918	**0.980**	0.971	0.824	0.899	0.902	0.898
PMe3	0.574	0.657	0.909	0.976	**0.980**	0.901	0.972	0.971	0.973
benzene	0.533	0.628	0.890	0.979	**0.980**	0.947	0.975	0.975	0.977
beta-lactim	0.498	0.636	0.894	0.969	0.974	0.935	0.978	0.977	**0.980**
methanol	0.507	0.636	0.893	0.967	0.972	0.946	0.980	0.979	**0.980**
acetaldehyde	0.486	0.621	0.891	0.966	0.972	0.918	0.979	0.978	**0.981**
Ni(acac)2	0.583	0.636	0.896	0.950	0.967	0.915	**0.981**	0.965	0.977
pyrrole	0.506	0.631	0.893	0.979	**0.981**	0.949	0.977	0.976	0.979
ch3ph2	0.622	0.693	0.920	0.977	0.981	0.924	0.979	0.978	**0.981**
PR15	0.594	0.644	0.891	0.963	0.967	0.917	0.981	**0.981**	0.981
oxirane	0.518	0.644	0.892	0.967	0.970	0.946	0.980	0.979	**0.981**
CoH(CO)4	0.618	0.676	0.892	0.972	0.970	0.933	0.979	**0.981**	0.981
ED28	0.561	0.652	0.911	0.977	**0.981**	0.886	0.968	0.969	0.968
nh3	0.446	0.649	0.875	0.963	0.971	0.946	**0.981**	0.980	0.981
ED31	0.534	0.597	0.901	0.981	**0.981**	0.791	0.962	0.960	0.941
ED27	0.565	0.659	0.913	0.978	**0.981**	0.907	0.972	0.971	0.972
TiCl2Me2	0.686	0.729	0.932	0.979	**0.981**	0.835	0.922	0.937	0.954
PCy3	0.493	0.579	0.901	0.977	**0.982**	0.753	0.956	0.957	0.955
AcCl	0.607	0.711	0.930	0.978	**0.982**	0.861	0.956	0.954	0.963
ED30	0.547	0.618	0.904	0.980	**0.982**	0.801	0.971	0.974	0.964
CuMe	0.750	0.758	0.863	0.921	0.975	0.959	0.982	0.981	**0.982**
dithiotane	0.662	0.731	0.932	0.979	**0.982**	0.928	0.977	0.975	0.979
PhSH	0.572	0.680	0.911	0.982	**0.983**	0.861	0.915	0.915	0.917
furan	0.521	0.642	0.895	0.977	0.979	0.958	0.981	0.981	**0.983**
silole	0.583	0.676	0.906	0.980	**0.983**	0.877	0.949	0.948	0.954
thiophene	0.601	0.691	0.916	0.982	**0.983**	0.888	0.962	0.961	0.965

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
bh3	0.514	0.694	0.828	0.963	0.965	0.942	0.983	0.983	**0.983**
Zn(CH3)2	0.686	0.697	0.884	0.949	0.980	0.958	**0.984**	0.983	0.983
c2clh5	0.594	0.702	0.932	0.981	**0.984**	0.848	0.971	0.970	0.975
ED02	0.616	0.659	0.887	0.955	0.966	0.940	0.982	**0.984**	0.984
n2h4	0.450	0.625	0.882	0.969	0.976	0.954	0.983	0.983	**0.984**
ocs	0.647	0.756	0.929	0.983	**0.984**	0.927	0.977	0.975	0.979
c2clh3	0.621	0.714	0.932	0.984	**0.985**	0.866	0.952	0.950	0.958
ch2nh	0.480	0.621	0.873	0.970	0.973	0.958	0.984	0.984	**0.985**
PR06	0.585	0.640	0.891	0.965	0.978	0.887	0.981	0.984	**0.985**
PR01	0.575	0.640	0.891	0.966	0.978	0.902	0.982	**0.985**	0.984
VOCl3	0.734	0.776	0.946	0.979	**0.985**	0.900	0.971	0.975	0.983
c2h3f	0.520	0.654	0.908	0.977	0.979	0.945	0.984	0.984	**0.985**
dioxetane	0.518	0.638	0.899	0.967	0.972	0.956	0.984	0.983	**0.985**
acetic	0.508	0.651	0.902	0.971	0.974	0.941	0.984	0.983	**0.985**
PhSeH	0.671	0.729	0.928	0.984	**0.985**	0.892	0.933	0.933	0.934
cclh3	0.654	0.736	0.943	0.983	0.985	0.941	0.985	0.984	**0.986**
Ni(PH3)2	0.740	0.765	0.908	0.961	0.972	0.970	0.986	**0.986**	0.986
c2h2	0.518	0.596	0.868	0.978	0.974	0.968	0.986	0.985	**0.986**
ch3f	0.535	0.665	0.915	0.973	0.976	0.954	0.985	0.985	**0.986**
Cr(CO)6	0.576	0.647	0.891	0.966	0.978	0.906	0.983	**0.986**	0.986
ED40b	0.640	0.703	0.932	0.982	**0.986**	0.871	0.981	0.981	0.982
TiCl3Me	0.720	0.771	0.948	0.984	**0.986**	0.821	0.964	0.968	0.977
ketene	0.511	0.654	0.892	0.973	0.976	0.952	0.986	0.985	**0.987**
c2clh	0.642	0.746	0.934	**0.987**	0.984	0.887	0.975	0.974	0.978
ccl2o	0.684	0.773	0.955	0.987	0.987	0.954	0.985	0.984	**0.988**
cis-c2f2cl2	0.678	0.758	0.956	**0.988**	0.987	0.899	0.978	0.978	0.983
formamide	0.497	0.650	0.898	0.973	0.976	0.946	0.987	0.986	**0.988**

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
trans-c2f2cl2	0.678	0.756	0.956	**0.988**	0.987	0.910	0.978	0.978	0.983
clcof	0.631	0.750	0.948	0.985	0.985	0.936	0.985	0.984	**0.988**
cs2	0.741	0.784	0.942	0.985	0.986	0.974	0.988	0.987	**0.989**
Ni(CO)4	0.626	0.684	0.889	0.968	0.973	0.969	0.988	**0.989**	0.988
PR03	0.626	0.684	0.889	0.968	0.973	0.969	0.988	**0.989**	0.988
c2cl6	0.724	0.780	0.968	0.988	**0.989**	0.945	0.981	0.981	0.986
clcn	0.651	0.758	0.933	0.985	0.983	0.949	0.988	0.987	**0.989**
oxirene	0.507	0.682	0.882	0.966	0.966	0.972	0.989	0.989	**0.990**
ch2clf	0.639	0.741	0.949	0.984	0.985	0.917	0.988	0.987	**0.990**
h2o	0.492	0.691	0.895	0.967	0.971	0.969	**0.990**	0.990	0.990
c2cl4	0.733	0.787	0.965	**0.990**	0.990	0.955	0.981	0.981	0.984
oxadiazole	0.539	0.653	0.891	0.976	0.979	0.964	0.989	0.989	**0.990**
c2cl2	0.694	0.784	0.954	**0.990**	0.988	0.945	0.980	0.979	0.982
h2co	0.520	0.649	0.886	0.972	0.975	0.969	0.990	0.990	**0.990**
nh2oh	0.478	0.650	0.888	0.968	0.974	0.968	0.990	0.990	**0.990**
ccl2h2	0.700	0.771	0.959	0.987	0.988	0.957	0.989	0.988	**0.990**
nh2cl	0.642	0.745	0.938	0.982	0.987	0.960	0.990	0.990	**0.991**
ED01	0.588	0.649	0.888	0.960	0.977	0.924	0.989	**0.991**	0.991
c-hcoh	0.539	0.656	0.867	0.971	0.977	0.970	0.991	0.991	**0.991**
glyoxal	0.541	0.688	0.892	0.975	0.977	0.966	0.990	0.990	**0.991**
dioxetan2one	0.519	0.655	0.908	0.972	0.974	0.931	0.989	0.989	**0.991**
hnc	0.531	0.648	0.857	0.980	0.978	0.962	**0.991**	0.991	0.991
sio	0.708	0.779	0.896	0.986	**0.991**	0.965	0.985	0.984	0.985
dioxirane	0.518	0.672	0.892	0.966	0.972	0.967	0.991	0.991	**0.992**
ch2-sing	0.509	0.526	0.792	0.732	0.968	0.972	**0.992**	0.991	0.991
hccf	0.534	0.696	0.908	0.982	0.980	0.979	0.992	0.991	**0.992**
Cr(NO)4	0.599	0.638	0.895	0.971	0.985	0.919	0.988	0.991	**0.992**

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
t-hcoh	0.538	0.659	0.867	0.970	0.972	0.967	0.991	0.991	**0.992**
formic-anhydride	0.563	0.652	0.904	0.975	0.976	0.945	0.990	0.990	**0.992**
hnnn	0.516	0.621	0.883	0.974	0.974	0.955	0.991	0.990	**0.992**
ED03	0.651	0.699	0.884	0.943	0.972	0.976	0.991	**0.992**	0.991
CrO2(NO3)2	0.588	0.648	0.903	0.964	0.978	0.908	0.991	0.992	**0.992**
c-n2h2	0.509	0.577	0.867	0.973	0.977	0.978	0.992	0.992	**0.992**
s2o	0.705	0.769	0.942	0.983	0.986	0.967	0.991	0.991	**0.992**
honc	0.525	0.687	0.879	0.975	0.976	0.889	0.992	0.991	**0.992**
ccl3h	0.724	0.803	0.966	0.988	0.989	0.968	0.991	0.990	**0.993**
clno	0.668	0.736	0.929	0.982	0.986	0.922	0.987	0.986	**0.993**
nccn	0.553	0.693	0.872	0.981	0.978	0.976	0.992	0.992	**0.993**
t-n2h2	0.511	0.581	0.867	0.973	0.969	0.977	0.993	0.992	**0.993**
si2h6	0.681	0.720	0.942	0.985	0.988	0.972	0.991	0.992	**0.993**
formic	0.534	0.698	0.903	0.974	0.976	0.971	0.993	0.992	**0.993**
cs	0.702	0.761	0.910	0.987	0.991	0.982	0.993	0.993	**0.993**
CrO2Cl2	0.713	0.750	0.930	0.969	0.988	0.891	0.985	0.986	**0.993**
ch2f2	0.539	0.694	0.932	0.978	0.979	0.975	0.993	0.992	**0.993**
cf2cl2	0.676	0.748	0.963	0.987	0.987	0.948	0.991	0.990	**0.993**
hcn	0.537	0.644	0.864	0.977	0.975	0.978	**0.994**	0.993	0.994
nh2f	0.510	0.677	0.908	0.973	0.978	0.973	0.994	0.994	**0.994**
ccl4	0.746	0.786	0.969	0.989	0.989	0.977	0.992	0.991	**0.994**
TiCl4	0.749	0.787	0.960	0.988	0.989	0.920	0.987	0.990	**0.994**
sih4	0.664	0.709	0.936	0.981	0.985	0.971	0.993	0.993	**0.994**
alf	0.712	0.800	0.908	0.987	0.993	0.979	0.994	0.993	**0.994**
hocl	0.653	0.761	0.943	0.982	0.988	0.973	0.994	0.994	**0.994**
hcno	0.529	0.678	0.895	0.975	0.976	0.980	0.994	0.994	**0.994**
hnco	0.532	0.682	0.897	0.978	0.979	0.979	0.994	0.994	**0.994**

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
hocn	0.527	0.700	0.889	0.975	0.975	0.968	0.994	0.994	**0.995**
hoclo	0.630	0.741	0.935	0.972	0.979	0.977	**0.995**	0.995	0.995
fccf	0.560	0.723	0.926	0.984	0.982	0.988	0.995	0.995	**0.995**
so2	0.638	0.741	0.928	0.978	0.981	0.981	**0.995**	0.995	0.995
hooh	0.497	0.666	0.895	0.969	0.976	0.981	0.995	0.995	**0.995**
ccl2	0.722	0.795	0.952	0.987	0.992	0.985	0.994	0.994	**0.995**
sih3f	0.645	0.728	0.940	0.981	0.984	0.982	0.994	0.994	**0.995**
hcof	0.552	0.718	0.918	0.979	0.979	0.985	0.996	0.995	**0.996**
c2f4	0.582	0.757	0.941	0.984	0.983	0.985	0.995	0.995	**0.996**
c2f6	0.558	0.684	0.948	0.984	0.982	0.980	0.995	0.995	**0.996**
ph3	0.672	0.736	0.935	0.979	0.982	0.983	0.996	0.996	**0.996**
t-hono	0.527	0.622	0.894	0.974	0.978	0.973	0.996	0.996	**0.996**
hno	0.527	0.661	0.878	0.975	0.977	0.987	0.996	0.996	**0.996**
hoclo2	0.617	0.728	0.933	0.970	0.976	0.979	**0.997**	0.996	0.996
chf3	0.562	0.738	0.944	0.982	0.981	0.985	0.996	0.996	**0.997**
bhf2	0.565	0.725	0.930	0.984	0.983	0.988	0.996	0.996	**0.997**
c-hono	0.524	0.619	0.895	0.975	0.979	0.980	**0.997**	0.997	0.997
hf	0.538	0.739	0.937	0.983	0.982	0.991	**0.997**	0.997	0.997
n2o4	0.520	0.638	0.907	0.974	0.977	0.980	0.996	0.996	**0.997**
co	0.564	0.678	0.863	0.982	0.987	0.983	**0.997**	0.997	0.997
Ni(PF3)4	0.620	0.715	0.946	0.978	0.982	0.982	0.997	**0.997**	0.996
n2o	0.522	0.688	0.895	0.977	0.978	0.980	0.997	0.997	**0.997**
hof	0.519	0.701	0.915	0.974	0.983	0.985	0.998	0.998	**0.998**
alcl	0.776	0.825	0.939	0.992	0.995	0.988	0.997	0.997	**0.998**
h2s	0.698	0.769	0.949	0.983	0.985	0.989	0.998	0.998	**0.998**
p4	0.783	0.803	0.940	0.983	0.988	0.989	0.997	0.997	**0.998**
f2co	0.550	0.721	0.936	0.983	0.982	0.991	0.998	0.998	**0.998**

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
co2	0.554	0.751	0.907	0.981	0.982	0.990	0.998	0.998	**0.998**
hclo4	0.615	0.721	0.933	0.970	0.976	0.984	**0.998**	0.998	0.998
CrF6	0.628	0.724	0.928	0.971	0.981	0.986	**0.998**	0.998	0.995
cf4	0.598	0.681	0.952	0.985	0.983	0.991	0.998	0.998	**0.998**
so3	0.618	0.706	0.933	0.978	0.982	0.991	**0.998**	0.998	0.998
bf	0.589	0.718	0.871	0.982	0.989	0.987	**0.998**	0.998	0.998
clf	0.671	0.779	0.957	0.984	0.993	0.990	0.998	0.998	**0.998**
pf3	0.614	0.733	0.948	0.983	0.987	0.987	**0.998**	0.998	0.998
alh3	0.708	0.680	0.911	0.986	0.987	0.987	0.998	0.998	**0.998**
alf3	0.656	0.799	0.944	0.990	0.988	0.992	**0.999**	0.998	0.998
bh	0.615	0.550	0.709	0.944	0.975	0.981	**0.999**	0.998	0.998
bf3	0.583	0.760	0.944	0.988	0.986	0.993	0.999	0.999	**0.999**
n2	0.592	0.624	0.862	0.983	0.987	0.992	**0.999**	0.999	0.999
ScF3	0.626	0.703	0.939	0.989	0.987	0.995	**0.999**	0.999	0.998
alh	0.785	0.736	0.875	0.855	0.993	0.974	0.999	0.999	**0.999**
MnO3F	0.650	0.699	0.897	0.953	0.985	0.956	0.998	0.998	**0.999**
CrO2F2	0.646	0.739	0.910	0.964	0.984	0.991	0.999	**0.999**	0.997
cf2	0.568	0.729	0.921	0.982	0.986	0.993	**0.999**	0.999	0.999
hcl	0.721	0.799	0.971	0.991	0.990	0.995	**0.999**	0.999	0.999
VOF3	0.629	0.731	0.923	0.975	0.981	0.970	0.999	0.999	**0.999**
fno	0.569	0.679	0.909	0.979	0.983	0.994	**0.999**	0.999	0.999
sif4	0.617	0.714	0.955	0.988	0.987	0.995	**0.999**	0.999	0.999
p2	0.772	0.789	0.928	0.993	0.995	0.994	0.999	0.999	**0.999**
VF5	0.622	0.731	0.935	0.979	0.983	0.966	0.999	0.999	**1.000**
pf5	0.594	0.729	0.960	0.987	0.987	0.994	0.999	0.999	**1.000**
sf6	0.609	0.745	0.961	0.985	0.986	0.993	0.999	0.999	**1.000**
TiF4	0.620	0.714	0.935	0.984	0.985	0.987	1.000	**1.000**	0.999

Table S7– *Continued on next page*

Table S7– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
alcl3	0.763	0.830	0.973	0.995	0.994	0.996	1.000	1.000	**1.000**
cl2	0.739	0.805	0.971	0.990	0.995	0.997	1.000	1.000	**1.000**
f2	0.547	0.714	0.936	0.978	0.991	0.997	1.000	1.000	**1.000**
h2	0.557	0.976	0.851	0.945	0.945	0.976	**1.000**	1.000	1.000
Best	0	0	0	20	45	1	28	18	**110**

Table S8: Non-neutral and/or non-singlet molecules, revTPSSh/pcseg-0: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ch	0.508	0.555	0.737	0.711	**0.888**	0.847	0.877	0.885	0.857
bn3pi	0.571	0.646	0.789	0.901	0.902	**0.972**	0.929	0.909	0.909
cyclopropyl	0.517	0.579	0.879	0.970	**0.972**	0.931	0.970	0.969	0.972
Cu(acac)2	0.577	0.641	0.896	0.953	**0.973**	0.928	0.941	0.926	0.955
Ti(BH4)3	0.611	0.619	0.894	0.969	0.919	0.815	0.968	0.971	**0.974**
allyl	0.477	0.601	0.876	0.974	**0.977**	0.939	0.973	0.972	0.975
ch2ch	0.494	0.610	0.859	0.969	0.969	0.943	0.978	0.977	**0.979**
ch3nh	0.476	0.607	0.866	0.958	0.965	0.936	0.978	0.977	**0.979**
V(NMe2)4	0.513	0.575	0.891	0.971	**0.979**	0.841	0.960	0.970	0.952
ch2nh2	0.478	0.625	0.876	0.971	0.976	0.947	0.980	0.979	**0.981**
ch3	0.461	0.665	0.847	0.968	0.973	0.943	**0.981**	0.980	0.981
cch	0.512	0.696	0.840	0.979	0.965	0.946	0.982	0.981	**0.982**
h2ccn	0.528	0.619	0.868	0.970	0.971	0.904	0.985	0.984	**0.986**
h2cn	0.497	0.621	0.856	0.965	0.968	0.951	0.986	0.985	**0.986**
clo	0.677	0.777	0.939	0.977	0.973	0.966	0.976	**0.988**	0.984
hcnh	0.511	0.635	0.861	0.974	0.971	0.968	0.989	0.988	**0.989**
so	0.682	0.763	0.921	0.986	**0.991**	0.972	0.990	0.989	0.990
sif	0.703	0.783	0.909	0.974	**0.992**	0.970	0.965	0.970	0.964

Table S8– *Continued on next page*

Table S8– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
nh2	0.493	0.613	0.834	0.858	0.969	0.973	**0.992**	0.991	0.992
cn	0.548	0.675	0.837	0.983	0.980	0.976	0.991	0.991	**0.992**
ch2-trip	0.514	0.694	0.802	0.972	0.975	0.969	**0.992**	0.991	0.991
h2no	0.493	0.659	0.889	0.970	0.976	0.968	0.993	0.992	**0.993**
t-hooo	0.523	0.660	0.892	0.969	0.978	0.951	0.993	0.993	**0.994**
hco	0.542	0.662	0.873	0.976	0.976	0.981	0.994	0.994	**0.994**
n2h	0.530	0.601	0.861	0.975	0.973	0.977	0.994	0.994	**0.995**
c-hooo	0.524	0.659	0.894	0.969	0.978	0.965	**0.996**	0.996	0.996
oh	0.531	0.662	0.857	0.926	0.978	0.988	0.996	**0.997**	0.890
hoo	0.515	0.659	0.888	0.971	0.978	0.982	0.997	0.997	**0.997**
hs	0.734	0.775	0.929	0.941	0.987	0.987	0.942	**0.998**	0.995
nh	0.552	0.656	0.788	0.966	0.977	0.991	**0.998**	0.998	0.998
no	0.553	0.673	0.872	0.917	0.923	0.971	0.954	0.933	**0.999**
sih	0.747	0.729	0.879	0.966	0.924	0.971	**0.999**	0.998	0.985
no2	0.550	0.650	0.900	0.977	0.980	0.992	0.999	0.999	**0.999**
ssh	0.730	0.783	0.947	0.986	0.989	0.988	0.999	0.999	**0.999**
cf	0.583	0.682	0.873	0.982	0.981	0.941	**0.999**	0.935	0.966
o2	0.560	0.685	0.887	0.982	0.990	0.994	**1.000**	1.000	1.000
s2	0.746	0.801	0.944	0.992	0.995	0.996	1.000	1.000	**1.000**
Best	0	0	0	0	7	1	8	3	**18**

Table S9: Neutral singlet molecules, HF/pcseg-1: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Mn(NO)3CO	0.564	0.619	0.892	0.950	0.948	0.914	0.951	**0.953**	0.951
Ni(C5H5)NO	0.613	0.617	0.893	**0.957**	0.956	0.867	0.956	0.955	0.956
Fe(CO)2(NO)2	0.580	0.611	0.891	0.953	0.949	0.929	0.958	**0.959**	0.958
Mn(CO)5CN	0.568	0.547	0.889	0.950	0.958	0.900	0.956	**0.960**	0.958

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
b2h6	0.494	0.560	0.865	0.942	0.946	0.897	0.958	0.957	**0.960**
Mn(C5H5)(CO)3	0.573	0.578	0.893	**0.961**	0.958	0.790	0.934	0.941	0.943
ch4	0.466	0.633	0.872	0.953	0.960	0.904	0.961	0.960	**0.961**
MnCp(CO)3	0.574	0.564	0.893	**0.961**	0.958	0.790	0.931	0.938	0.940
ED14	0.571	0.587	0.897	0.951	**0.961**	0.830	0.924	0.927	0.926
Fe(C4H4)(CO)3	0.583	0.579	0.893	**0.962**	0.955	0.817	0.936	0.942	0.948
Fe(CO)4(C2H4)	0.573	0.555	0.892	0.961	0.957	0.842	0.957	0.961	**0.962**
Fe(C4H6)(CO)3	0.570	0.560	0.891	**0.962**	0.956	0.806	0.943	0.950	0.952
PR05	0.563	0.551	0.892	0.952	0.960	0.877	0.958	**0.962**	0.961
Fe(CO)3(tmm)	0.573	0.565	0.892	**0.963**	0.956	0.806	0.932	0.940	0.944
PR04	0.585	0.568	0.893	**0.963**	0.957	0.871	0.933	0.934	0.939
Co(C3H5)(CO)3	0.582	0.571	0.892	0.960	0.958	0.838	0.958	0.962	**0.964**
tetrahedrane	0.512	0.614	0.880	0.962	**0.964**	0.934	0.961	0.959	0.963
Fe(C2H4)(CO)4	0.573	0.556	0.892	0.961	0.957	0.846	0.960	0.963	**0.964**
Cr(C6H6)(CO)3	0.563	0.578	0.893	0.961	**0.965**	0.795	0.937	0.945	0.950
ED04	0.600	0.587	0.892	**0.966**	0.954	0.868	0.945	0.947	0.954
c2h6	0.464	0.595	0.877	0.959	**0.966**	0.901	0.955	0.954	0.957
ED15	0.604	0.592	0.890	0.954	0.956	0.925	0.964	0.965	**0.966**
Ni(C3H5)2	0.604	0.592	0.890	0.953	0.955	0.926	0.965	0.965	**0.967**
cyclopropene	0.503	0.592	0.875	0.964	**0.967**	0.934	0.965	0.964	0.967
Mn(CO)4NO	0.570	0.574	0.892	0.953	0.957	0.913	0.965	**0.968**	0.967
propene	0.498	0.592	0.877	0.962	**0.968**	0.913	0.959	0.958	0.962
cyclopropane	0.486	0.563	0.881	0.962	**0.968**	0.911	0.955	0.954	0.958
cyclobutene	0.502	0.590	0.879	0.962	**0.968**	0.918	0.957	0.955	0.960
ED05	0.576	0.574	0.892	0.954	0.959	0.892	0.966	0.968	**0.968**
c2h4	0.492	0.638	0.870	0.964	**0.968**	0.932	0.967	0.966	0.968
oxetane	0.527	0.623	0.887	0.961	**0.969**	0.924	0.965	0.964	0.968

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
PR14	0.543	0.548	0.897	0.961	**0.969**	0.792	0.946	0.953	0.921
propyne	0.505	0.604	0.876	0.963	0.965	0.925	0.967	0.966	**0.969**
propane	0.485	0.585	0.880	0.962	**0.969**	0.895	0.952	0.951	0.955
ch3nh2	0.502	0.621	0.877	0.959	0.967	0.923	0.967	0.966	**0.969**
Cr(NO)4	0.554	0.591	0.893	0.953	0.957	0.909	0.967	0.969	**0.969**
ethanol	0.548	0.635	0.888	0.963	**0.969**	0.921	0.967	0.966	0.969
VCp(CO)4	0.553	0.550	0.895	0.959	**0.970**	0.779	0.924	0.936	0.933
allene	0.523	0.594	0.875	0.962	0.965	0.942	0.968	0.967	**0.970**
n-butane	0.492	0.588	0.882	0.964	**0.970**	0.884	0.951	0.950	0.954
cyclobutane	0.492	0.565	0.882	0.964	**0.971**	0.900	0.950	0.948	0.954
n-pentane	0.507	0.591	0.883	0.965	**0.971**	0.847	0.951	0.951	0.954
cyclopentadiene	0.511	0.613	0.882	0.967	**0.971**	0.926	0.960	0.959	0.963
PR15	0.598	0.610	0.892	0.957	0.958	0.912	0.971	**0.971**	0.971
FeCp2	0.596	0.585	0.895	**0.972**	0.952	0.890	0.948	0.950	0.953
beta-lactim	0.540	0.646	0.889	0.964	0.969	0.922	0.968	0.967	**0.972**
ch2c	0.525	0.656	0.835	0.954	0.956	0.927	0.972	0.970	**0.972**
t-butadiene	0.519	0.597	0.877	0.968	**0.972**	0.920	0.961	0.961	0.964
cyclobutadiene	0.519	0.619	0.872	0.968	**0.972**	0.941	0.967	0.966	0.969
PR40	0.617	0.603	0.913	0.972	**0.972**	0.881	0.954	0.957	0.965
Co(CO)3(NO)	0.589	0.596	0.892	0.961	0.956	0.947	0.971	**0.973**	0.971
borole	0.543	0.605	0.871	0.913	**0.973**	0.886	0.965	0.964	0.967
Fe(C5Me5)(P5)	0.637	0.661	0.916	**0.973**	0.964	0.816	0.894	0.897	0.894
c2h5f	0.570	0.656	0.904	0.967	0.972	0.906	0.971	0.970	**0.973**
ED40a	0.558	0.524	0.885	0.961	0.957	0.936	**0.973**	0.971	0.970
Ni(acac)2	0.570	0.592	0.895	0.956	0.961	0.908	**0.973**	0.957	0.969
PMe3	0.565	0.566	0.901	0.968	**0.973**	0.893	0.966	0.966	0.968
PR02	0.582	0.562	0.893	0.959	0.960	0.922	0.971	**0.973**	0.973

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
PR12	0.554	0.533	0.891	0.957	0.964	0.822	0.970	**0.974**	0.972
Fe(CO)5	0.582	0.562	0.893	0.959	0.960	0.922	0.972	**0.974**	0.973
furan	0.546	0.648	0.890	0.971	**0.974**	0.947	0.972	0.971	0.974
silole	0.599	0.668	0.900	0.970	**0.974**	0.868	0.938	0.936	0.942
ED28	0.596	0.592	0.904	0.970	**0.974**	0.878	0.962	0.963	0.962
oxirane	0.537	0.648	0.886	0.961	0.966	0.937	0.973	0.972	**0.974**
acetaldehyde	0.544	0.633	0.887	0.960	0.967	0.911	0.972	0.971	**0.974**
ED27	0.591	0.576	0.906	0.970	**0.975**	0.898	0.966	0.966	0.967
pyrrole	0.516	0.637	0.887	0.972	**0.975**	0.937	0.967	0.965	0.969
ch3ph2	0.670	0.681	0.914	0.968	0.973	0.914	0.974	0.973	**0.976**
Cr(C6H6)2	0.581	0.569	0.895	**0.976**	0.964	0.873	0.957	0.960	0.962
PCy3	0.500	0.502	0.894	0.971	**0.976**	0.739	0.949	0.950	0.947
ED31	0.531	0.539	0.896	0.974	**0.976**	0.781	0.955	0.953	0.934
CoH(CO)4	0.593	0.582	0.894	0.963	0.959	0.932	0.975	**0.976**	0.976
MnO3F	0.564	0.620	0.895	0.947	0.941	0.941	0.976	0.976	**0.976**
benzene	0.518	0.630	0.885	0.973	**0.976**	0.935	0.965	0.964	0.967
Sc(acac)3	0.545	0.571	0.902	0.972	**0.976**	0.826	0.969	0.973	0.958
ED30	0.566	0.570	0.898	0.974	**0.977**	0.790	0.964	0.967	0.957
methanol	0.536	0.649	0.888	0.961	0.967	0.939	0.976	0.975	**0.977**
c2h2	0.515	0.612	0.866	0.972	0.970	0.958	**0.978**	0.977	0.978
dithiotane	0.721	0.739	0.927	0.973	**0.978**	0.915	0.969	0.967	0.972
nh3	0.459	0.667	0.872	0.958	0.967	0.938	**0.978**	0.977	0.978
thiophene	0.654	0.680	0.910	0.976	**0.978**	0.881	0.953	0.952	0.956
PhSH	0.623	0.684	0.906	0.976	**0.979**	0.853	0.907	0.907	0.910
acetic	0.559	0.671	0.899	0.966	0.971	0.933	0.977	0.976	**0.979**
CuCN	0.733	0.711	0.860	0.931	0.953	**0.979**	0.951	0.944	0.953
AcCl	0.669	0.739	0.927	0.975	**0.979**	0.854	0.946	0.944	0.953

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
c2h3f	0.577	0.666	0.904	0.972	0.975	0.937	0.978	0.977	**0.979**
c2clh5	0.678	0.658	0.927	0.975	**0.979**	0.838	0.963	0.961	0.968
ch2nh	0.545	0.635	0.869	0.965	0.968	0.950	0.979	0.978	**0.979**
bh3	0.508	0.715	0.818	0.950	0.953	0.943	0.980	0.979	**0.980**
ketene	0.562	0.667	0.890	0.968	0.971	0.945	0.979	0.978	**0.980**
dioxetane	0.577	0.650	0.893	0.962	0.968	0.948	0.978	0.977	**0.980**
n2h4	0.497	0.638	0.877	0.962	0.970	0.944	0.979	0.978	**0.980**
ED40b	0.677	0.657	0.929	0.976	**0.980**	0.858	0.976	0.976	0.977
ED02	0.588	0.605	0.887	0.947	0.955	0.938	0.979	**0.980**	0.980
c2clh3	0.689	0.685	0.928	0.979	**0.981**	0.859	0.944	0.941	0.949
cclh3	0.710	0.691	0.939	0.978	**0.981**	0.924	0.979	0.978	0.981
PR06	0.561	0.600	0.892	0.954	0.964	0.885	0.978	0.980	**0.982**
oxadiazole	0.584	0.658	0.886	0.972	0.976	0.952	0.981	0.979	**0.982**
Zn(CH3)2	0.653	0.651	0.887	0.947	0.965	0.956	**0.982**	0.981	0.981
PR01	0.566	0.543	0.891	0.955	0.966	0.900	0.979	**0.982**	0.981
formamide	0.545	0.670	0.894	0.968	0.973	0.937	0.981	0.980	**0.982**
TiCl2Me2	0.626	0.653	0.936	0.979	**0.982**	0.828	0.913	0.928	0.945
ocs	0.705	0.797	0.929	0.982	**0.982**	0.918	0.966	0.965	0.969
oxirene	0.562	0.692	0.879	0.962	0.964	0.962	0.982	0.981	**0.983**
clcn	0.706	0.770	0.932	**0.983**	0.980	0.938	0.979	0.978	0.981
PhSeH	0.677	0.671	0.924	0.979	**0.983**	0.886	0.927	0.926	0.928
ch3f	0.574	0.677	0.910	0.968	0.972	0.949	0.982	0.982	**0.983**
CuMe	0.734	0.733	0.863	0.944	0.959	0.962	0.983	0.982	**0.983**
Cr(CO)6	0.567	0.543	0.891	0.955	0.965	0.904	0.981	**0.983**	0.983
c2clh	0.702	0.742	0.932	**0.983**	0.981	0.880	0.965	0.963	0.968
cs2	0.776	0.828	0.941	0.983	**0.984**	0.963	0.979	0.978	0.980
clcof	0.685	0.762	0.946	**0.985**	0.984	0.926	0.977	0.976	0.981

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ch2clf	0.707	0.774	0.946	0.981	0.983	0.908	0.982	0.981	**0.985**
dioxetan2one	0.582	0.665	0.904	0.969	0.972	0.923	0.982	0.982	**0.985**
hccf	0.585	0.712	0.907	0.980	0.977	0.971	0.985	0.985	**0.986**
glyoxal	0.581	0.714	0.890	0.908	0.974	0.957	0.984	0.983	**0.986**
ccl2h2	0.777	0.807	0.956	0.984	**0.986**	0.943	0.983	0.982	0.985
ccl2o	0.750	0.792	0.954	0.986	**0.986**	0.945	0.977	0.976	0.980
clno	0.707	0.777	0.929	0.983	**0.986**	0.912	0.974	0.972	0.981
trans-c2f2cl2	0.693	0.774	0.954	**0.986**	0.986	0.903	0.969	0.969	0.975
cis-c2f2cl2	0.705	0.785	0.954	**0.986**	0.986	0.907	0.970	0.969	0.975
cs	0.759	0.794	0.910	**0.986**	0.986	0.971	0.984	0.983	0.984
formic-anhydride	0.555	0.672	0.901	0.972	0.974	0.936	0.985	0.984	**0.987**
h2co	0.583	0.666	0.882	0.968	0.971	0.962	0.986	0.986	**0.987**
dioxirane	0.585	0.694	0.887	0.963	0.970	0.957	0.986	0.985	**0.987**
ED01	0.564	0.608	0.889	0.950	0.963	0.922	0.985	**0.987**	0.986
CrO2(NO3)2	0.560	0.617	0.903	0.964	0.976	0.906	0.986	0.986	**0.987**
Ni(PH3)2	0.708	0.705	0.906	0.952	0.959	0.971	0.987	**0.987**	0.987
nccn	0.534	0.741	0.872	0.978	0.976	0.969	0.986	0.986	**0.987**
c2cl2	0.768	0.819	0.952	**0.988**	0.986	0.935	0.970	0.969	0.973
hnnn	0.517	0.649	0.881	0.969	0.970	0.950	0.987	0.986	**0.988**
nh2oh	0.543	0.672	0.885	0.965	0.971	0.959	0.987	0.987	**0.988**
hnc	0.536	0.664	0.855	0.974	0.972	0.959	**0.988**	0.987	0.987
TiCl3Me	0.670	0.689	0.952	0.985	**0.988**	0.814	0.954	0.958	0.968
CrO2Cl2	0.648	0.677	0.933	0.973	0.987	0.885	0.977	0.978	**0.988**
ccl3h	0.807	0.821	0.963	0.986	**0.988**	0.956	0.984	0.983	0.987
Ni(CO)4	0.597	0.587	0.892	0.964	0.964	0.966	0.987	**0.988**	0.987
PR03	0.598	0.587	0.892	0.964	0.964	0.966	0.987	**0.988**	0.987
cf2cl2	0.707	0.782	0.961	0.986	0.987	0.938	0.985	0.984	**0.988**

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
p4	0.829	0.811	0.936	0.981	0.986	0.977	0.986	0.985	**0.988**
nh2cl	0.720	0.780	0.936	0.980	0.985	0.950	0.987	0.986	**0.988**
c2cl4	0.755	0.798	0.963	0.988	**0.988**	0.943	0.973	0.972	0.976
hcno	0.557	0.699	0.893	0.973	0.974	0.969	0.988	0.987	**0.988**
formic	0.563	0.720	0.900	0.972	0.974	0.962	0.987	0.987	**0.988**
c2cl6	0.753	0.790	0.966	0.987	**0.988**	0.937	0.972	0.972	0.978
honc	0.564	0.710	0.877	0.970	0.969	0.883	0.987	0.986	**0.988**
hcn	0.555	0.662	0.863	0.974	0.972	0.970	**0.988**	0.988	0.988
hnco	0.572	0.679	0.897	0.976	0.977	0.970	0.988	0.987	**0.988**
ccl4	0.788	0.817	0.967	0.987	**0.988**	0.967	0.985	0.984	0.988
t-hcoh	0.569	0.676	0.864	0.966	0.966	0.961	0.988	0.988	**0.988**
c-hcoh	0.569	0.674	0.864	0.966	0.971	0.965	0.988	0.988	**0.989**
t-n2h2	0.526	0.594	0.865	0.969	0.967	0.967	0.988	0.988	**0.989**
c-n2h2	0.522	0.591	0.865	0.970	0.974	0.969	0.989	0.988	**0.989**
si2h6	0.736	0.727	0.931	0.970	0.973	0.972	0.987	0.987	**0.989**
s2o	0.757	0.797	0.939	0.982	0.985	0.960	0.988	0.987	**0.989**
h2o	0.535	0.717	0.893	0.967	0.972	0.962	**0.989**	0.989	0.989
fccf	0.614	0.745	0.925	0.984	0.981	0.981	0.989	0.989	**0.990**
hocn	0.562	0.738	0.889	0.972	0.972	0.959	0.989	0.988	**0.990**
sio	0.741	0.807	0.896	0.985	**0.990**	0.967	0.987	0.987	0.987
ccl2	0.796	0.835	0.951	0.988	**0.990**	0.975	0.987	0.987	0.989
ch2-sing	0.514	0.543	0.788	0.918	0.965	0.731	**0.990**	0.989	0.990
ch2f2	0.630	0.717	0.929	0.976	0.977	0.968	0.989	0.989	**0.990**
sih4	0.713	0.762	0.924	0.964	0.967	0.973	0.989	0.989	**0.991**
c2f4	0.637	0.785	0.939	0.983	0.983	0.977	0.989	0.989	**0.991**
ED03	0.617	0.608	0.885	0.941	0.963	0.974	0.990	**0.991**	0.990
VOCl3	0.673	0.698	0.950	0.983	**0.991**	0.894	0.963	0.967	0.975

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
n2o4	0.539	0.672	0.906	0.974	0.977	0.967	0.990	0.989	**0.991**
hcof	0.590	0.731	0.916	0.978	0.977	0.977	0.991	0.991	**0.992**
c2f6	0.599	0.704	0.947	0.983	0.983	0.971	0.990	0.989	**0.992**
TiCl4	0.700	0.716	0.965	0.991	**0.992**	0.916	0.980	0.983	0.988
nh2f	0.579	0.701	0.906	0.971	0.977	0.965	0.992	0.991	**0.992**
t-hono	0.568	0.644	0.892	0.973	0.976	0.963	0.992	0.991	**0.992**
hoclo	0.671	0.773	0.932	0.974	0.981	0.970	0.993	0.992	**0.993**
hocl	0.722	0.802	0.941	0.981	0.988	0.966	0.993	0.992	**0.993**
n2o	0.548	0.710	0.895	0.976	0.976	0.974	0.993	0.992	**0.993**
c-hono	0.561	0.642	0.893	0.974	0.978	0.970	0.993	0.992	**0.993**
co2	0.551	0.756	0.907	0.981	0.980	0.983	0.993	0.993	**0.993**
ph3	0.744	0.778	0.929	0.970	0.974	0.974	0.993	0.993	**0.993**
chf3	0.627	0.770	0.941	0.981	0.981	0.978	0.993	0.992	**0.993**
hoclo2	0.601	0.693	0.929	0.971	0.977	0.970	0.993	0.993	**0.994**
hooh	0.540	0.692	0.892	0.968	0.976	0.974	0.994	0.993	**0.994**
f2co	0.587	0.713	0.935	0.983	0.982	0.984	0.993	0.993	**0.994**
sih3f	0.706	0.750	0.935	0.973	0.976	0.983	0.993	0.993	**0.994**
hno	0.578	0.684	0.876	0.974	0.976	0.979	**0.994**	0.994	0.994
alf	0.770	0.828	0.909	0.986	0.990	0.978	0.994	0.993	**0.994**
bhf2	0.640	0.754	0.929	0.984	0.981	0.984	0.994	0.994	**0.994**
hclo4	0.562	0.636	0.930	0.970	0.976	0.974	0.994	0.993	**0.994**
so2	0.693	0.762	0.925	0.976	0.980	0.980	**0.995**	0.994	0.994
cf4	0.641	0.708	0.950	0.985	0.984	0.984	0.994	0.994	**0.995**
co	0.597	0.698	0.863	0.979	0.982	0.980	**0.995**	0.994	0.995
CrF6	0.549	0.645	0.932	0.977	0.985	0.972	0.995	**0.995**	0.994
p2	0.824	0.814	0.928	0.990	0.993	0.990	0.995	0.994	**0.995**
n2	0.566	0.638	0.862	0.981	0.985	0.985	**0.995**	0.995	0.995

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Ni(PF3)4	0.562	0.612	0.947	0.980	0.983	0.976	0.995	**0.995**	0.993
fno	0.588	0.707	0.908	0.979	0.983	0.986	0.996	0.995	**0.996**
alh3	0.757	0.767	0.903	0.975	0.974	0.986	0.996	0.996	**0.996**
bf3	0.657	0.798	0.944	0.989	0.986	0.989	0.996	0.996	**0.996**
h2s	0.782	0.815	0.946	0.980	0.981	0.981	**0.996**	0.996	0.996
so3	0.620	0.722	0.931	0.977	0.981	0.987	0.996	0.996	**0.996**
hof	0.579	0.733	0.914	0.974	0.983	0.978	**0.996**	0.996	0.996
alcl	0.846	0.846	0.938	0.990	0.991	0.986	0.996	0.996	**0.996**
cf2	0.637	0.759	0.919	0.982	0.984	0.989	0.996	0.996	**0.997**
pf3	0.710	0.758	0.946	0.983	0.988	0.983	0.996	0.996	**0.997**
alcl3	0.847	0.866	0.972	0.994	0.993	0.992	0.996	0.996	**0.997**
VOF3	0.530	0.583	0.927	0.980	0.988	0.959	0.995	0.996	**0.997**
sf6	0.590	0.688	0.958	0.985	0.987	0.986	0.996	0.996	**0.997**
bf	0.646	0.731	0.872	0.980	0.982	0.985	**0.997**	0.996	0.997
CrO2F2	0.545	0.595	0.913	0.969	0.983	0.982	0.997	**0.997**	0.996
bh	0.609	0.568	0.706	0.951	0.971	0.978	**0.997**	0.997	0.997
pf5	0.625	0.741	0.958	0.987	0.989	0.989	0.997	0.997	**0.997**
hf	0.609	0.770	0.937	0.985	0.984	0.987	**0.997**	0.997	0.997
VF5	0.528	0.611	0.939	0.985	0.988	0.954	0.996	0.997	**0.998**
sif4	0.691	0.737	0.954	0.989	0.989	0.992	0.998	0.998	**0.998**
alh	0.830	0.851	0.872	0.972	0.987	0.973	0.998	0.998	**0.998**
clf	0.740	0.820	0.956	0.984	0.993	0.988	0.998	0.998	**0.998**
ScF3	0.643	0.671	0.945	0.995	0.992	0.991	**0.998**	0.998	0.998
TiF4	0.527	0.570	0.942	0.991	0.990	0.977	0.997	0.998	**0.998**
alf3	0.710	0.835	0.945	0.993	0.989	0.992	**0.998**	0.998	0.998
cl2	0.811	0.848	0.969	0.990	0.994	0.994	0.999	0.999	**0.999**
hcl	0.813	0.852	0.969	0.990	0.990	0.990	**0.999**	0.999	0.999

Table S9– *Continued on next page*

Table S9– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
f2	0.606	0.783	0.935	0.978	0.991	0.995	**0.999**	0.999	0.999
h2	-0.000	0.969	0.840	0.929	0.929	0.969	**0.999**	0.999	0.999
Best	0	0	0	18	57	1	23	22	**101**

Table S10: Non-neutral and/or non-singlet molecules, HF/pcseg-1: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
cch	0.517	0.681	0.832	0.957	0.944	0.930	**0.963**	0.962	0.963
cyclopropyl	0.498	0.582	0.871	0.960	**0.964**	0.920	0.960	0.958	0.962
ch2ch	0.530	0.637	0.851	0.951	0.953	0.930	0.964	0.963	**0.965**
bn3pi	0.601	0.661	0.790	0.898	0.899	0.893	0.935	0.912	**0.965**
Ti(BH4)3	0.560	0.518	0.898	**0.965**	0.942	0.807	0.955	0.959	0.964
ch	0.507	0.724	0.735	0.827	0.927	0.833	**0.966**	0.861	0.861
allyl	0.517	0.607	0.868	0.963	**0.967**	0.927	0.962	0.961	0.964
Cu(acac)2	0.573	0.597	0.895	0.949	**0.968**	0.919	0.937	0.922	0.950
V(NMe2)4	0.510	0.526	0.888	0.967	**0.972**	0.836	0.953	0.965	0.945
ch3nh	0.532	0.619	0.860	0.948	0.956	0.929	0.972	0.971	**0.973**
h2cn	0.562	0.634	0.849	0.950	0.954	0.938	0.973	0.972	**0.974**
cn	0.544	0.693	0.830	0.956	0.946	0.960	**0.974**	0.973	0.973
ch2nh2	0.529	0.638	0.869	0.960	0.966	0.938	0.973	0.972	**0.974**
t-hooo	0.563	0.688	0.886	0.955	0.962	0.937	0.975	0.975	**0.976**
ch3	0.472	0.680	0.839	0.957	0.964	0.937	**0.977**	0.976	0.977
h2ccn	0.565	0.634	0.863	0.961	0.963	0.895	0.976	0.975	**0.977**
oh	0.595	0.691	0.856	0.899	0.870	0.881	**0.977**	0.946	0.891
clo	0.746	0.796	0.936	0.963	0.973	0.949	0.967	0.973	**0.979**
hs	0.804	0.815	0.927	0.949	**0.980**	0.933	0.940	0.980	0.942
hcnh	0.540	0.652	0.857	0.964	0.960	0.957	0.980	0.979	**0.980**
c-hooo	0.564	0.686	0.888	0.959	0.968	0.948	**0.983**	0.983	0.983

Table S10– *Continued on next page*

Table S10– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
n2h	0.540	0.624	0.856	0.964	0.962	0.966	**0.986**	0.985	0.986
sif	0.761	0.808	0.908	0.974	**0.988**	0.941	0.952	0.955	0.953
ch2-trip	0.547	0.726	0.796	0.964	0.968	0.962	**0.989**	0.988	0.988
h2no	0.555	0.678	0.884	0.963	0.970	0.961	0.989	0.988	**0.989**
so	0.745	0.802	0.919	0.983	0.989	0.971	0.990	0.989	**0.990**
nh2	0.528	0.635	0.832	0.963	0.969	0.967	**0.991**	0.990	0.990
hco	0.586	0.682	0.871	0.974	0.972	0.975	**0.991**	0.990	0.991
no	0.580	0.704	0.871	0.934	0.925	0.981	0.971	**0.991**	0.978
hoo	0.578	0.687	0.884	0.964	0.971	0.976	**0.993**	0.993	0.993
no2	0.584	0.678	0.899	0.976	0.979	0.983	0.994	0.994	**0.995**
ssh	0.800	0.830	0.943	0.981	0.984	0.981	0.995	0.995	**0.995**
cf	0.633	0.726	0.872	0.939	0.917	0.927	0.996	0.954	**0.997**
s2	0.819	0.855	0.942	0.989	0.992	0.991	0.997	0.997	**0.997**
o2	0.591	0.706	0.885	0.981	0.988	0.988	**0.997**	0.997	0.997
nh	0.600	0.768	0.787	0.855	0.978	0.987	**0.997**	0.997	0.997
sih	0.799	0.832	0.876	0.866	0.938	0.922	**0.998**	0.995	0.934
Best	0	0	0	1	6	0	14	1	**15**

Table S11: Neutral singlet molecules, revTPSSh/pcseg-1: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ED14	0.571	0.588	0.896	0.950	**0.960**	0.833	0.929	0.931	0.931
ch4	0.471	0.637	0.871	0.952	0.959	0.906	0.962	0.961	**0.962**
Mn(CO)5CN	0.569	0.547	0.891	0.961	0.963	0.902	0.959	**0.963**	0.962
b2h6	0.495	0.564	0.864	0.941	0.945	0.901	0.961	0.960	**0.963**
Ni(C5H5)NO	0.613	0.617	0.893	**0.964**	0.962	0.870	0.962	0.962	0.963
tetrahedrane	0.513	0.616	0.879	0.961	0.963	0.937	0.963	0.961	**0.965**
c2h6	0.467	0.598	0.877	0.959	**0.966**	0.903	0.957	0.955	0.959

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
PR04	0.586	0.569	0.893	**0.967**	0.961	0.870	0.934	0.935	0.942
ED04	0.599	0.588	0.891	**0.967**	0.956	0.869	0.947	0.949	0.958
Co(C3H5)(CO)3	0.582	0.569	0.893	0.965	0.960	0.840	0.961	0.965	**0.967**
cyclopropane	0.487	0.566	0.880	0.961	**0.967**	0.914	0.957	0.955	0.960
Cr(C6H6)(CO)3	0.563	0.577	0.894	0.966	**0.968**	0.795	0.942	0.950	0.955
propene	0.499	0.595	0.877	0.963	**0.968**	0.916	0.962	0.960	0.964
PR05	0.563	0.551	0.894	0.963	0.964	0.880	0.965	**0.968**	0.968
Fe(CO)4(C2H4)	0.573	0.555	0.894	**0.968**	0.959	0.846	0.962	0.966	0.967
Fe(C2H4)(CO)4	0.573	0.556	0.894	0.968	0.959	0.850	0.964	0.968	**0.968**
propane	0.487	0.588	0.880	0.962	**0.969**	0.897	0.954	0.952	0.957
cyclobutene	0.503	0.593	0.879	0.963	**0.969**	0.921	0.959	0.957	0.962
cyclopropene	0.504	0.596	0.874	0.963	0.966	0.937	0.967	0.966	**0.969**
Mn(C5H5)(CO)3	0.574	0.577	0.894	**0.969**	0.962	0.788	0.937	0.945	0.947
MnCp(CO)3	0.575	0.565	0.894	**0.969**	0.962	0.788	0.934	0.941	0.944
oxetane	0.527	0.625	0.886	0.960	0.968	0.926	0.966	0.965	**0.969**
Fe(C4H6)(CO)3	0.571	0.561	0.893	**0.970**	0.960	0.806	0.947	0.955	0.957
ch3nh2	0.503	0.624	0.877	0.959	0.966	0.924	0.968	0.967	**0.970**
Fe(C4H4)(CO)3	0.584	0.578	0.894	**0.970**	0.958	0.818	0.939	0.945	0.951
PR14	0.543	0.549	0.897	0.961	**0.970**	0.793	0.948	0.955	0.923
ethanol	0.549	0.637	0.888	0.962	0.968	0.923	0.968	0.967	**0.970**
Fe(CO)3(tmm)	0.574	0.563	0.893	**0.970**	0.959	0.807	0.935	0.943	0.949
n-butane	0.494	0.591	0.882	0.964	**0.970**	0.887	0.953	0.952	0.956
Mn(NO)3CO	0.567	0.619	0.895	0.970	0.966	0.922	0.967	**0.970**	0.969
c2h4	0.493	0.643	0.870	0.964	0.968	0.935	0.969	0.968	**0.970**
cyclobutane	0.494	0.567	0.882	0.964	**0.970**	0.902	0.951	0.950	0.956
FeCp2	0.595	0.586	0.895	**0.971**	0.956	0.893	0.954	0.956	0.959
propyne	0.506	0.607	0.875	0.963	0.965	0.928	0.969	0.968	**0.971**

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
n-pentane	0.509	0.593	0.883	0.965	**0.971**	0.849	0.953	0.952	0.955
PR40	0.620	0.605	0.912	0.970	**0.971**	0.884	0.957	0.960	0.967
ED15	0.603	0.594	0.890	0.956	0.958	0.928	0.969	0.970	**0.971**
Ni(C3H5)2	0.604	0.594	0.889	0.955	0.958	0.930	0.970	0.970	**0.972**
cyclobutadiene	0.519	0.623	0.872	0.968	**0.972**	0.944	0.969	0.968	0.971
cyclopentadiene	0.511	0.616	0.883	0.968	**0.972**	0.929	0.963	0.962	0.966
t-butadiene	0.520	0.599	0.877	0.968	**0.972**	0.923	0.964	0.963	0.966
Fe(CO)2(NO)2	0.582	0.609	0.894	**0.973**	0.962	0.935	0.970	0.972	0.971
borole	0.543	0.607	0.871	0.913	**0.973**	0.889	0.967	0.966	0.969
allene	0.527	0.598	0.874	0.962	0.966	0.946	0.971	0.970	**0.973**
PMe3	0.567	0.567	0.902	0.968	**0.973**	0.895	0.968	0.967	0.969
ED05	0.575	0.573	0.894	0.965	0.963	0.895	0.971	0.973	**0.974**
VCp(CO)4	0.553	0.553	0.895	0.963	**0.974**	0.779	0.929	0.941	0.938
beta-lactim	0.543	0.648	0.889	0.963	0.969	0.927	0.971	0.970	**0.974**
Mn(CO)4NO	0.571	0.573	0.894	0.965	0.964	0.917	0.972	**0.974**	0.973
c2h5f	0.570	0.658	0.903	0.966	0.972	0.910	0.972	0.971	**0.974**
ED28	0.598	0.593	0.904	0.970	**0.975**	0.880	0.964	0.965	0.963
ED27	0.593	0.577	0.906	0.970	**0.975**	0.900	0.967	0.968	0.968
Fe(C5Me5)(P5)	0.638	0.660	0.916	**0.975**	0.966	0.817	0.895	0.898	0.895
ch2c	0.526	0.661	0.836	0.957	0.959	0.930	0.975	0.974	**0.975**
Cr(C6H6)2	0.581	0.569	0.895	**0.976**	0.965	0.876	0.960	0.963	0.965
pyrrole	0.517	0.639	0.888	0.972	**0.976**	0.940	0.969	0.968	0.971
ED40a	0.562	0.529	0.884	0.957	0.956	0.939	**0.976**	0.974	0.972
Sc(acac)3	0.545	0.571	0.901	0.970	**0.976**	0.828	0.972	0.975	0.961
silole	0.600	0.670	0.900	0.971	**0.976**	0.871	0.941	0.939	0.945
oxirane	0.538	0.650	0.885	0.959	0.965	0.940	0.974	0.973	**0.976**
furan	0.546	0.649	0.890	0.970	0.974	0.950	0.974	0.973	**0.976**

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
benzene	0.519	0.633	0.885	0.973	**0.976**	0.939	0.968	0.967	0.970
Ni(acac)2	0.571	0.593	0.894	0.956	0.961	0.910	**0.976**	0.961	0.972
PR15	0.598	0.611	0.891	0.956	0.960	0.912	0.976	0.976	**0.976**
acetaldehyde	0.545	0.636	0.886	0.959	0.967	0.916	0.975	0.974	**0.977**
PCy3	0.500	0.503	0.895	0.971	**0.977**	0.740	0.951	0.952	0.949
ED30	0.567	0.571	0.899	0.974	**0.977**	0.791	0.966	0.969	0.959
PR12	0.553	0.535	0.892	0.964	0.967	0.828	0.974	**0.977**	0.976
PR02	0.581	0.561	0.895	0.968	0.962	0.925	0.975	**0.977**	0.977
ED31	0.531	0.540	0.897	0.975	**0.977**	0.782	0.957	0.955	0.936
ch3ph2	0.672	0.684	0.914	0.968	0.973	0.916	0.975	0.974	**0.977**
methanol	0.537	0.652	0.887	0.960	0.966	0.940	0.977	0.976	**0.977**
dithiotane	0.723	0.740	0.926	0.973	**0.978**	0.917	0.971	0.969	0.973
Fe(CO)5	0.582	0.561	0.894	0.968	0.962	0.925	0.976	**0.978**	0.977
nh3	0.462	0.669	0.871	0.957	0.966	0.938	**0.978**	0.977	0.978
CuCN	0.730	0.707	0.859	0.933	0.956	**0.978**	0.954	0.947	0.956
AcCl	0.671	0.741	0.927	0.974	**0.978**	0.857	0.950	0.948	0.956
thiophene	0.655	0.681	0.910	0.976	**0.979**	0.884	0.956	0.955	0.959
c2clh5	0.679	0.659	0.927	0.975	**0.979**	0.840	0.965	0.963	0.969
PhSH	0.625	0.685	0.906	0.976	**0.979**	0.856	0.910	0.910	0.912
Co(CO)3(NO)	0.590	0.594	0.894	0.972	0.962	0.950	0.978	**0.979**	0.978
c2h2	0.516	0.617	0.865	0.971	0.969	0.962	**0.980**	0.979	0.980
n2h4	0.501	0.640	0.876	0.961	0.969	0.945	0.979	0.978	**0.980**
CoH(CO)4	0.593	0.579	0.896	0.969	0.962	0.934	0.979	**0.980**	0.980
c2clh3	0.690	0.687	0.928	0.978	**0.981**	0.862	0.947	0.945	0.953
ED40b	0.678	0.657	0.929	0.976	**0.981**	0.860	0.978	0.978	0.978
ch2nh	0.548	0.637	0.868	0.963	0.967	0.952	0.980	0.979	**0.981**
CuMe	0.730	0.729	0.861	0.941	0.959	0.958	0.980	0.979	**0.981**

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
TiCl2Me2	0.629	0.656	0.934	0.976	**0.981**	0.833	0.919	0.934	0.951
dioxetane	0.577	0.651	0.892	0.961	0.966	0.950	0.979	0.978	**0.981**
acetic	0.560	0.673	0.898	0.966	0.970	0.937	0.979	0.979	**0.981**
bh3	0.511	0.719	0.816	0.948	0.951	0.945	0.981	0.981	**0.981**
Zn(CH3)2	0.652	0.650	0.887	0.947	0.964	0.955	**0.982**	0.981	0.981
c2h3f	0.577	0.668	0.904	0.971	0.975	0.943	0.981	0.980	**0.982**
cclh3	0.711	0.692	0.938	0.978	0.981	0.927	0.981	0.980	**0.982**
ocs	0.706	0.795	0.928	0.981	**0.982**	0.924	0.971	0.969	0.973
c2clh	0.702	0.743	0.932	**0.983**	0.981	0.885	0.969	0.967	0.972
PhSeH	0.678	0.672	0.925	0.980	**0.983**	0.887	0.928	0.928	0.930
ketene	0.562	0.672	0.889	0.967	0.971	0.950	0.982	0.982	**0.983**
ED02	0.588	0.603	0.889	0.953	0.957	0.940	0.982	**0.983**	0.983
clcof	0.687	0.762	0.946	**0.984**	0.984	0.929	0.979	0.978	0.983
clcn	0.707	0.772	0.931	0.982	0.981	0.943	0.982	0.981	**0.984**
formamide	0.546	0.671	0.894	0.968	0.972	0.941	0.983	0.982	**0.984**
ch3f	0.574	0.679	0.910	0.967	0.971	0.951	0.983	0.983	**0.984**
cs2	0.778	0.828	0.940	0.982	**0.984**	0.968	0.983	0.982	0.984
oxirene	0.563	0.695	0.877	0.960	0.962	0.965	0.984	0.983	**0.985**
oxadiazole	0.583	0.660	0.886	0.970	0.975	0.956	0.984	0.983	**0.985**
PR01	0.567	0.543	0.893	0.963	0.969	0.905	0.983	**0.985**	0.985
PR06	0.561	0.600	0.893	0.962	0.968	0.889	0.982	0.984	**0.985**
ccl2o	0.752	0.793	0.953	0.985	**0.986**	0.948	0.980	0.979	0.983
trans-c2f2cl2	0.694	0.774	0.954	0.986	**0.986**	0.905	0.972	0.972	0.978
cis-c2f2cl2	0.707	0.785	0.954	0.986	**0.986**	0.909	0.973	0.972	0.977
ch2clf	0.708	0.775	0.945	0.980	0.982	0.910	0.984	0.983	**0.986**
Cr(CO)6	0.567	0.544	0.893	0.963	0.969	0.908	0.984	**0.986**	0.986
TiCl3Me	0.674	0.693	0.950	0.982	**0.986**	0.821	0.961	0.965	0.975

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ccl2h2	0.779	0.808	0.955	0.984	0.985	0.945	0.984	0.984	**0.986**
c2cl2	0.770	0.818	0.952	**0.987**	0.986	0.940	0.974	0.973	0.976
clno	0.708	0.779	0.928	0.980	0.984	0.916	0.980	0.979	**0.987**
Ni(PH3)2	0.706	0.703	0.906	0.951	0.958	0.970	0.987	**0.987**	0.987
cs	0.761	0.794	0.909	0.984	0.987	0.976	**0.987**	0.986	0.987
dioxetan2one	0.582	0.668	0.903	0.967	0.970	0.928	0.985	0.984	**0.987**
h2co	0.585	0.666	0.881	0.966	0.970	0.965	0.987	0.987	**0.987**
c2cl6	0.755	0.791	0.965	0.986	**0.988**	0.940	0.974	0.974	0.980
nh2oh	0.544	0.674	0.884	0.963	0.970	0.960	0.987	0.987	**0.988**
glyoxal	0.581	0.713	0.889	0.907	0.974	0.961	0.987	0.986	**0.988**
c2cl4	0.757	0.801	0.962	0.987	**0.988**	0.946	0.975	0.974	0.979
hccf	0.584	0.714	0.906	0.979	0.977	0.975	0.988	0.988	**0.988**
Ni(CO)4	0.595	0.583	0.894	0.965	0.964	0.967	0.987	**0.988**	0.987
PR03	0.597	0.583	0.894	0.965	0.964	0.967	0.987	**0.988**	0.987
nh2cl	0.723	0.783	0.935	0.978	0.984	0.951	0.987	0.987	**0.988**
hnc	0.538	0.666	0.855	0.974	0.973	0.959	**0.988**	0.987	0.988
ccl3h	0.810	0.822	0.963	0.986	0.987	0.958	0.986	0.985	**0.988**
dioxirane	0.585	0.695	0.886	0.960	0.968	0.961	0.988	0.987	**0.988**
h2o	0.537	0.718	0.893	0.966	0.971	0.962	**0.989**	0.988	0.988
c-hcoh	0.570	0.674	0.863	0.965	0.972	0.964	0.989	0.988	**0.989**
t-hcoh	0.569	0.675	0.864	0.965	0.966	0.961	0.989	0.988	**0.989**
formic-anhydride	0.556	0.671	0.900	0.971	0.973	0.942	0.987	0.987	**0.989**
c-n2h2	0.524	0.596	0.864	0.968	0.972	0.970	0.989	0.988	**0.989**
cf2cl2	0.708	0.784	0.961	0.986	0.986	0.940	0.986	0.985	**0.989**
t-n2h2	0.528	0.598	0.864	0.967	0.964	0.969	0.989	0.988	**0.989**
ccl4	0.789	0.819	0.966	0.987	0.988	0.969	0.987	0.986	**0.990**
p4	0.833	0.811	0.935	0.979	0.985	0.980	0.988	0.987	**0.990**

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
formic	0.563	0.720	0.900	0.971	0.973	0.965	0.989	0.989	**0.990**
honc	0.566	0.710	0.876	0.970	0.971	0.884	0.989	0.987	**0.990**
nccn	0.534	0.746	0.871	0.976	0.975	0.973	0.989	0.988	**0.990**
hnnn	0.521	0.657	0.880	0.969	0.971	0.953	0.989	0.988	**0.990**
sio	0.743	0.807	0.896	0.984	**0.990**	0.965	0.985	0.984	0.985
hcn	0.555	0.665	0.862	0.972	0.971	0.973	**0.990**	0.989	0.990
ch2-sing	0.518	0.546	0.787	0.951	0.963	0.732	**0.990**	0.990	0.990
ED01	0.563	0.607	0.890	0.955	0.967	0.926	0.989	0.990	**0.990**
s2o	0.761	0.800	0.939	0.980	0.983	0.963	0.989	0.989	**0.990**
VOCl3	0.677	0.703	0.948	0.980	**0.990**	0.898	0.968	0.972	0.980
hcno	0.563	0.701	0.892	0.971	0.973	0.974	0.990	0.990	**0.991**
si2h6	0.738	0.730	0.931	0.971	0.975	0.975	0.989	0.989	**0.991**
hnco	0.573	0.680	0.896	0.975	0.976	0.974	0.991	0.990	**0.991**
CrO2Cl2	0.652	0.682	0.931	0.970	0.989	0.889	0.982	0.983	**0.991**
ED03	0.615	0.604	0.886	0.941	0.963	0.973	0.991	**0.991**	0.990
CrO2(NO3)2	0.563	0.616	0.902	0.963	0.978	0.911	0.990	0.991	**0.991**
hocn	0.562	0.742	0.888	0.972	0.972	0.963	0.991	0.990	**0.991**
ch2f2	0.630	0.718	0.928	0.975	0.976	0.971	0.991	0.990	**0.992**
Cr(NO)4	0.558	0.594	0.895	0.971	0.977	0.920	0.988	0.991	**0.992**
TiCl4	0.704	0.720	0.963	0.988	0.990	0.919	0.985	0.988	**0.992**
ccl2	0.797	0.835	0.950	0.986	0.990	0.979	0.991	0.990	**0.992**
fccf	0.615	0.743	0.924	0.982	0.980	0.984	0.992	0.992	**0.992**
nh2f	0.579	0.702	0.905	0.969	0.975	0.967	0.992	0.992	**0.992**
sih4	0.716	0.766	0.925	0.965	0.968	0.975	0.991	0.991	**0.992**
hocl	0.725	0.804	0.941	0.980	0.987	0.967	0.992	0.992	**0.993**
c2f4	0.639	0.784	0.939	0.982	0.982	0.980	0.992	0.992	**0.993**
hcof	0.591	0.730	0.916	0.977	0.976	0.980	0.993	0.993	**0.994**

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
hooh	0.542	0.693	0.891	0.966	0.974	0.974	0.994	0.993	**0.994**
hoclo	0.673	0.775	0.931	0.970	0.977	0.972	**0.994**	0.994	0.994
c2f6	0.604	0.707	0.946	0.982	0.982	0.975	0.992	0.992	**0.994**
alf	0.769	0.827	0.908	0.985	0.991	0.978	0.994	0.993	**0.994**
ph3	0.748	0.781	0.929	0.970	0.974	0.976	0.994	0.994	**0.994**
t-hono	0.568	0.648	0.891	0.970	0.974	0.967	0.994	0.994	**0.994**
hno	0.580	0.685	0.875	0.972	0.974	0.981	0.995	0.994	**0.995**
so2	0.699	0.768	0.925	0.974	0.977	0.979	**0.995**	0.994	0.994
sih3f	0.707	0.752	0.934	0.973	0.976	0.984	0.994	0.994	**0.995**
chf3	0.628	0.769	0.941	0.980	0.980	0.981	0.994	0.994	**0.995**
c-hono	0.565	0.646	0.892	0.971	0.976	0.973	0.995	0.994	**0.995**
n2o4	0.545	0.678	0.904	0.971	0.974	0.973	0.994	0.993	**0.995**
n2o	0.554	0.713	0.893	0.974	0.976	0.977	0.995	0.995	**0.995**
hoclo2	0.605	0.696	0.928	0.967	0.972	0.973	**0.995**	0.995	0.995
bhf2	0.639	0.752	0.928	0.983	0.981	0.985	0.995	0.995	**0.995**
co	0.598	0.698	0.862	0.978	0.982	0.980	**0.996**	0.995	0.995
co2	0.548	0.754	0.906	0.979	0.979	0.985	**0.996**	0.995	0.995
f2co	0.588	0.714	0.934	0.982	0.981	0.987	0.996	0.995	**0.996**
p2	0.826	0.816	0.927	0.989	0.992	0.992	0.996	0.995	**0.996**
hclo4	0.567	0.642	0.928	0.967	0.973	0.978	0.996	0.996	**0.996**
Ni(PF3)4	0.566	0.613	0.947	0.979	0.981	0.978	0.996	**0.996**	0.994
cf4	0.644	0.709	0.949	0.984	0.983	0.986	0.996	0.996	**0.997**
n2	0.566	0.644	0.861	0.979	0.983	0.988	**0.997**	0.996	0.996
h2s	0.785	0.818	0.945	0.979	0.981	0.983	**0.997**	0.996	0.997
hof	0.580	0.735	0.913	0.972	0.981	0.980	0.997	0.997	**0.997**
hf	0.609	0.769	0.937	0.984	0.983	0.987	**0.997**	0.997	0.997
alcl	0.847	0.846	0.938	0.989	0.991	0.987	0.997	0.996	**0.997**

Table S11– *Continued on next page*

Table S11– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
alh3	0.759	0.768	0.903	0.975	0.975	0.987	0.997	0.997	**0.997**
so3	0.627	0.731	0.930	0.976	0.980	0.988	**0.997**	0.997	0.997
bf3	0.658	0.795	0.944	0.989	0.986	0.990	0.997	0.997	**0.997**
bf	0.644	0.730	0.871	0.978	0.984	0.985	**0.997**	0.997	0.997
pf3	0.714	0.759	0.946	0.982	0.986	0.984	0.997	0.997	**0.998**
alcl3	0.850	0.866	0.972	0.994	0.993	0.993	0.997	0.997	**0.998**
CrF6	0.561	0.656	0.929	0.972	0.986	0.985	**0.998**	0.997	0.994
clf	0.742	0.822	0.956	0.984	0.992	0.988	0.998	0.998	**0.998**
bh	0.613	0.571	0.704	0.646	0.968	0.981	**0.998**	0.998	0.998
sf6	0.598	0.691	0.958	0.984	0.985	0.988	0.997	0.997	**0.998**
cf2	0.636	0.757	0.919	0.980	0.984	0.990	0.998	0.998	**0.998**
alf3	0.712	0.832	0.945	0.992	0.989	0.991	**0.998**	0.998	0.998
fno	0.589	0.710	0.907	0.976	0.981	0.990	**0.998**	0.998	0.998
ScF3	0.649	0.675	0.942	0.990	0.989	0.992	**0.998**	0.998	0.998
pf5	0.632	0.743	0.958	0.986	0.987	0.991	0.998	0.998	**0.998**
sif4	0.695	0.737	0.954	0.988	0.988	0.992	0.998	0.998	**0.999**
MnO3F	0.567	0.614	0.898	0.954	0.957	0.954	0.997	0.998	**0.999**
alh	0.832	0.853	0.872	0.982	0.986	0.974	**0.999**	0.998	0.999
VOF3	0.537	0.590	0.924	0.975	0.986	0.968	0.998	0.999	**0.999**
CrO2F2	0.551	0.602	0.911	0.965	0.983	0.988	0.999	**0.999**	0.997
hcl	0.815	0.854	0.969	0.990	0.989	0.990	**0.999**	0.999	0.999
VF5	0.536	0.618	0.935	0.980	0.986	0.964	0.999	0.999	**0.999**
cl2	0.813	0.850	0.969	0.989	0.994	0.994	0.999	0.999	**0.999**
TiF4	0.535	0.577	0.938	0.986	0.987	0.984	**0.999**	0.999	0.999
h2	0.000	0.971	0.836	0.924	0.924	0.971	**1.000**	0.999	0.999
f2	0.607	0.786	0.934	0.976	0.990	0.995	**1.000**	1.000	1.000
Best	0	0	0	16	46	1	30	18	**111**

Table S12: Non-neutral and/or non-singlet molecules, revTPSSh/pcseg-1: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ch	0.512	0.736	0.734	0.739	0.890	0.851	0.879	0.856	**0.941**
bn3pi	0.605	0.664	0.790	0.898	0.900	0.910	0.910	**0.952**	0.921
cyclopropyl	0.499	0.585	0.871	0.960	**0.965**	0.923	0.962	0.960	0.964
no	0.584	0.683	0.870	**0.967**	0.946	0.922	0.937	0.940	0.933
Cu(acac)2	0.574	0.597	0.895	0.949	**0.967**	0.921	0.938	0.922	0.951
Ti(BH4)3	0.565	0.522	0.897	0.963	0.941	0.812	0.963	0.967	**0.970**
allyl	0.519	0.611	0.869	0.966	**0.971**	0.933	0.967	0.966	0.969
ch2ch	0.532	0.643	0.854	0.959	0.962	0.937	0.973	0.972	**0.973**
V(NMe2)4	0.512	0.527	0.888	0.965	**0.974**	0.838	0.956	0.966	0.948
ch3nh	0.533	0.622	0.860	0.950	0.958	0.931	0.974	0.973	**0.975**
ch2nh2	0.530	0.639	0.870	0.962	0.968	0.939	0.975	0.974	**0.976**
cch	0.519	0.693	0.838	0.972	0.962	0.943	0.978	0.977	**0.978**
ch3	0.474	0.683	0.838	0.957	0.963	0.938	**0.978**	0.977	0.978
clo	0.744	0.799	0.937	0.977	0.951	0.966	0.969	0.960	**0.980**
h2cn	0.567	0.639	0.852	0.958	0.962	0.947	0.982	0.981	**0.983**
h2ccn	0.568	0.637	0.865	0.964	0.967	0.901	0.982	0.981	**0.983**
cf	0.631	0.725	0.872	0.922	**0.984**	0.941	0.979	0.957	0.983
hcnh	0.545	0.652	0.858	0.968	0.965	0.961	0.985	0.984	**0.985**
cn	0.554	0.695	0.838	0.979	0.978	0.971	0.988	0.987	**0.988**
ch2-trip	0.551	0.728	0.795	0.963	0.968	0.963	**0.990**	0.989	0.990
so	0.746	0.804	0.919	0.983	0.989	0.971	0.990	0.989	**0.990**
h2no	0.559	0.683	0.885	0.966	0.972	0.960	0.990	0.989	**0.990**
nh2	0.531	0.637	0.831	0.961	0.968	0.967	**0.991**	0.990	0.990
hco	0.587	0.681	0.870	0.972	0.972	0.976	**0.991**	0.991	0.991
n2h	0.541	0.628	0.858	0.969	0.968	0.972	0.992	0.991	**0.992**

Table S12– *Continued on next page*

Table S12– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
t-hooo	0.559	0.690	0.889	0.966	0.974	0.948	0.992	0.992	**0.993**
c-hooo	0.562	0.690	0.890	0.966	0.975	0.959	**0.995**	0.994	0.995
sif	0.761	0.808	0.908	0.944	0.975	0.942	**0.995**	0.953	0.982
hoo	0.576	0.690	0.885	0.968	0.976	0.976	**0.996**	0.996	0.996
oh	0.596	0.691	0.855	0.971	0.920	0.983	0.963	**0.997**	0.896
no2	0.590	0.683	0.897	0.974	0.977	0.986	0.997	0.997	**0.997**
ssh	0.803	0.830	0.943	0.982	0.985	0.983	0.997	0.997	**0.997**
s2	0.821	0.857	0.941	0.989	0.992	0.993	0.998	0.998	**0.998**
nh	0.602	0.769	0.786	0.854	0.977	0.988	**0.998**	0.998	0.998
sih	0.802	0.834	0.876	0.862	0.919	0.925	0.935	0.991	**0.998**
hs	0.800	0.857	0.927	0.936	0.979	0.942	**0.999**	0.948	0.999
o2	0.592	0.710	0.885	0.979	0.987	0.990	**0.999**	0.999	0.999
Best	0	0	0	1	5	0	10	2	**19**

Table S13: Neutral singlet molecules, HF/aug-pcseg-2: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Mn(NO)3CO	0.470	0.494	0.888	0.945	0.943	0.912	0.950	**0.952**	0.951
Ni(C5H5)NO	0.414	0.509	0.890	**0.956**	0.954	0.865	0.954	0.952	0.954
Mn(C5H5)(CO)3	0.337	0.458	0.889	**0.958**	0.955	0.787	0.931	0.939	0.941
b2h6	0.284	0.504	0.854	0.932	0.936	0.889	0.956	0.955	**0.958**
Fe(C4H4)(CO)3	0.340	0.467	0.889	**0.959**	0.954	0.813	0.935	0.941	0.947
ED14	0.317	0.479	0.894	0.951	**0.959**	0.821	0.922	0.925	0.923
Fe(CO)2(NO)2	0.456	0.488	0.888	0.949	0.946	0.928	0.957	**0.959**	0.957
MnCp(CO)3	0.329	0.459	0.889	**0.959**	0.956	0.787	0.929	0.935	0.938
Fe(CO)3(tmm)	0.331	0.463	0.889	**0.959**	0.955	0.803	0.930	0.938	0.944
Mn(CO)5CN	0.299	0.453	0.886	0.947	0.955	0.898	0.955	**0.959**	0.958
Fe(C4H6)(CO)3	0.333	0.464	0.888	**0.959**	0.954	0.803	0.941	0.948	0.950

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Cr(C6H6)(CO)3	0.326	0.445	0.888	0.958	**0.960**	0.793	0.927	0.944	0.948
c2h6	0.385	0.556	0.869	0.951	**0.960**	0.899	0.954	0.952	0.956
ch4	0.370	0.590	0.862	0.942	0.951	0.902	0.960	0.959	**0.960**
PR04	0.336	0.461	0.889	**0.960**	0.957	0.867	0.931	0.932	0.937
Fe(CO)4(C2H4)	0.322	0.466	0.889	0.958	0.956	0.837	0.956	0.960	**0.961**
tetrahedrane	0.184	0.582	0.873	0.956	0.961	0.933	0.960	0.958	**0.962**
PR05	0.307	0.445	0.888	0.949	0.957	0.873	0.958	**0.962**	0.961
propene	0.336	0.555	0.870	0.956	**0.963**	0.912	0.958	0.957	0.961
Co(C3H5)(CO)3	0.349	0.481	0.890	0.957	0.956	0.828	0.957	0.961	**0.963**
cyclopropane	0.320	0.531	0.873	0.956	**0.963**	0.909	0.954	0.952	0.957
ED04	0.354	0.485	0.888	**0.963**	0.954	0.864	0.945	0.946	0.953
Fe(C2H4)(CO)4	0.323	0.465	0.889	0.957	0.955	0.841	0.959	0.963	**0.963**
propane	0.321	0.547	0.873	0.956	**0.964**	0.893	0.950	0.949	0.954
cyclobutene	0.350	0.560	0.872	0.957	**0.964**	0.916	0.955	0.953	0.958
ED15	0.393	0.511	0.887	0.955	0.954	0.922	0.963	0.963	**0.965**
Ni(C3H5)2	0.386	0.510	0.887	0.954	0.954	0.923	0.963	0.964	**0.965**
n-butane	0.283	0.553	0.875	0.958	**0.966**	0.882	0.949	0.949	0.953
cyclopropene	0.311	0.560	0.868	0.957	0.962	0.933	0.964	0.962	**0.966**
VCp(CO)4	0.279	0.435	0.889	0.956	**0.966**	0.775	0.922	0.935	0.932
oxetane	0.304	0.593	0.879	0.956	0.965	0.921	0.963	0.962	**0.966**
cyclobutane	0.269	0.535	0.874	0.958	**0.967**	0.897	0.948	0.946	0.952
n-pentane	0.264	0.556	0.876	0.959	**0.967**	0.846	0.949	0.949	0.952
c2h4	0.381	0.523	0.864	0.958	0.964	0.930	0.966	0.964	**0.967**
ch3nh2	0.323	0.581	0.870	0.952	0.961	0.920	0.965	0.964	**0.967**
Mn(CO)4NO	0.371	0.468	0.888	0.949	0.953	0.912	0.965	**0.967**	0.966
ethanol	0.374	0.597	0.882	0.957	0.965	0.919	0.965	0.964	**0.967**
cyclopentadiene	0.348	0.585	0.876	0.962	**0.967**	0.924	0.958	0.956	0.961

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Cr(NO)4	0.450	0.491	0.888	0.948	0.948	0.908	0.965	**0.968**	0.968
propyne	0.419	0.567	0.869	0.957	0.960	0.923	0.966	0.965	**0.968**
PR14	0.257	0.458	0.894	0.963	**0.968**	0.782	0.944	0.950	0.919
ED05	0.326	0.467	0.888	0.951	0.956	0.889	0.965	0.968	**0.968**
t-butadiene	0.334	0.565	0.871	0.963	**0.968**	0.919	0.960	0.959	0.963
cyclobutadiene	0.312	0.588	0.866	0.963	**0.968**	0.940	0.965	0.964	0.967
FeCp2	0.348	0.459	0.890	**0.968**	0.951	0.885	0.946	0.947	0.951
Fe(C5Me5)(P5)	0.343	0.559	0.914	**0.968**	0.963	0.814	0.893	0.896	0.892
allene	0.455	0.560	0.869	0.956	0.960	0.941	0.967	0.966	**0.968**
borole	0.316	0.577	0.865	0.964	**0.969**	0.885	0.963	0.962	0.965
PMe3	0.400	0.521	0.896	0.963	**0.969**	0.891	0.964	0.963	0.966
beta-lactim	0.332	0.616	0.883	0.959	0.966	0.921	0.966	0.965	**0.970**
PR15	0.384	0.464	0.889	0.955	0.956	0.911	0.970	**0.970**	0.970
silole	0.361	0.564	0.895	0.965	**0.971**	0.867	0.935	0.934	0.939
PR40	0.384	0.542	0.908	0.969	**0.971**	0.879	0.955	0.958	0.964
ch2c	0.431	0.618	0.830	0.947	0.950	0.925	0.971	0.969	**0.971**
Ni(acac)2	0.325	0.473	0.891	0.953	0.958	0.907	**0.971**	0.955	0.968
ED28	0.276	0.518	0.899	0.966	**0.972**	0.874	0.960	0.961	0.959
c2h5f	0.357	0.618	0.897	0.961	0.968	0.907	0.969	0.968	**0.972**
ED27	0.280	0.515	0.901	0.966	**0.972**	0.896	0.964	0.964	0.964
furan	0.380	0.619	0.885	0.966	0.971	0.946	0.970	0.969	**0.972**
Co(CO)3(NO)	0.446	0.498	0.889	0.957	0.954	0.946	0.971	**0.972**	0.971
pyrrole	0.324	0.606	0.882	0.967	**0.972**	0.936	0.964	0.963	0.967
Sc(acac)3	0.253	0.501	0.897	0.967	**0.972**	0.819	0.968	0.971	0.956
ED40a	0.385	0.489	0.879	0.957	0.949	0.935	**0.972**	0.971	0.969
PR12	0.272	0.439	0.886	0.953	0.958	0.818	0.969	**0.973**	0.972
oxirane	0.386	0.613	0.879	0.954	0.962	0.935	0.971	0.970	**0.973**

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
PR02	0.355	0.477	0.890	0.957	0.958	0.920	0.971	**0.973**	0.973
Cr(C6H6)2	0.305	0.443	0.890	**0.973**	0.959	0.867	0.954	0.957	0.960
acetaldehyde	0.383	0.599	0.881	0.954	0.962	0.910	0.971	0.970	**0.973**
benzene	0.399	0.603	0.880	0.969	**0.973**	0.934	0.963	0.962	0.966
Fe(CO)5	0.371	0.476	0.890	0.957	0.958	0.921	0.971	**0.974**	0.973
PCy3	0.222	0.460	0.889	0.968	**0.974**	0.726	0.947	0.948	0.940
ch3ph2	0.507	0.507	0.908	0.963	0.969	0.912	0.972	0.970	**0.974**
ED31	0.239	0.484	0.892	0.972	**0.975**	0.772	0.953	0.952	0.930
ED30	0.246	0.526	0.894	0.971	**0.975**	0.772	0.962	0.965	0.953
methanol	0.368	0.609	0.882	0.955	0.962	0.937	0.974	0.974	**0.975**
thiophene	0.433	0.587	0.906	0.972	**0.976**	0.880	0.951	0.950	0.954
dithiotane	0.524	0.556	0.923	0.970	**0.976**	0.912	0.965	0.963	0.969
CoH(CO)4	0.424	0.504	0.892	0.959	0.958	0.930	0.974	**0.976**	0.976
c2clh5	0.514	0.540	0.922	0.971	**0.976**	0.833	0.960	0.958	0.965
PhSH	0.424	0.587	0.902	0.973	**0.976**	0.852	0.906	0.906	0.908
nh3	0.359	0.627	0.866	0.952	0.962	0.935	**0.976**	0.975	0.976
AcCl	0.507	0.577	0.924	0.971	**0.976**	0.853	0.945	0.943	0.951
c2h2	0.467	0.581	0.862	0.966	0.965	0.957	**0.977**	0.975	0.976
ED40b	0.438	0.573	0.925	0.972	**0.977**	0.854	0.975	0.975	0.976
CuCN	0.626	0.655	0.862	0.935	0.945	**0.977**	0.948	0.942	0.950
acetic	0.377	0.632	0.894	0.962	0.968	0.932	0.975	0.974	**0.978**
ch2nh	0.394	0.598	0.864	0.959	0.964	0.948	0.977	0.976	**0.978**
c2clh3	0.531	0.543	0.925	0.975	**0.978**	0.859	0.942	0.940	0.948
n2h4	0.371	0.600	0.871	0.956	0.966	0.942	0.977	0.976	**0.978**
c2h3f	0.385	0.631	0.900	0.967	0.971	0.937	0.977	0.976	**0.978**
dioxetane	0.418	0.620	0.887	0.957	0.964	0.946	0.976	0.975	**0.978**
cclh3	0.543	0.554	0.935	0.974	0.978	0.918	0.977	0.976	**0.979**

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ketene	0.414	0.632	0.885	0.963	0.967	0.944	0.978	0.977	**0.979**
bh3	0.405	0.652	0.807	0.938	0.942	0.939	0.979	0.979	**0.980**
TiCl2Me2	0.549	0.588	0.931	0.977	**0.980**	0.825	0.920	0.927	0.944
ED02	0.426	0.496	0.884	0.944	0.952	0.937	0.978	**0.980**	0.980
c2clh	0.559	0.559	0.929	**0.980**	0.978	0.879	0.962	0.960	0.966
oxadiazole	0.400	0.634	0.881	0.968	0.973	0.950	0.979	0.977	**0.980**
formamide	0.405	0.628	0.890	0.964	0.970	0.936	0.979	0.978	**0.981**
clcn	0.599	0.559	0.930	**0.981**	0.979	0.936	0.977	0.975	0.979
PhSeH	0.504	0.615	0.921	0.977	**0.981**	0.884	0.926	0.925	0.927
PR06	0.335	0.455	0.887	0.949	0.958	0.883	0.977	0.980	**0.981**
oxirene	0.397	0.655	0.873	0.956	0.960	0.960	0.981	0.980	**0.981**
ocs	0.605	0.540	0.927	0.980	**0.981**	0.918	0.965	0.963	0.967
Zn(CH3)2	0.596	0.595	0.886	0.946	0.957	0.956	**0.981**	0.981	0.981
CuMe	0.673	0.671	0.864	0.939	0.947	0.960	0.981	0.980	**0.981**
PR01	0.271	0.448	0.887	0.950	0.960	0.899	0.979	**0.982**	0.981
ch3f	0.377	0.638	0.904	0.962	0.967	0.947	0.981	0.981	**0.982**
ch2clf	0.537	0.551	0.943	0.978	0.980	0.905	0.980	0.979	**0.982**
Cr(CO)6	0.272	0.448	0.887	0.949	0.959	0.902	0.980	**0.983**	0.982
dioxetan2one	0.419	0.631	0.900	0.966	0.970	0.920	0.981	0.980	**0.983**
clcof	0.534	0.585	0.945	**0.983**	0.983	0.925	0.974	0.973	0.978
cs2	0.654	0.648	0.940	0.982	**0.984**	0.961	0.977	0.976	0.978
cs	0.648	0.601	0.908	**0.984**	0.984	0.969	0.982	0.981	0.982
ccl2h2	0.605	0.615	0.953	0.982	**0.984**	0.937	0.980	0.979	0.983
cis-c2f2cl2	0.549	0.569	0.952	0.984	**0.984**	0.906	0.967	0.966	0.972
trans-c2f2cl2	0.544	0.568	0.952	0.984	**0.984**	0.901	0.967	0.966	0.972
glyoxal	0.418	0.676	0.886	0.905	0.972	0.956	0.983	0.982	**0.985**
clno	0.563	0.543	0.927	0.981	**0.985**	0.911	0.971	0.969	0.979

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
p4	0.713	0.717	0.934	0.979	**0.985**	0.974	0.983	0.981	0.985
hccf	0.432	0.673	0.903	0.975	0.974	0.971	0.985	0.984	**0.985**
c2cl2	0.590	0.606	0.950	**0.985**	0.984	0.933	0.968	0.967	0.971
ccl2o	0.610	0.580	0.952	0.984	**0.985**	0.942	0.974	0.973	0.978
formic-anhydride	0.407	0.637	0.898	0.970	0.972	0.935	0.983	0.983	**0.985**
dioxirane	0.415	0.658	0.882	0.958	0.967	0.955	0.985	0.984	**0.985**
h2co	0.434	0.628	0.878	0.964	0.968	0.961	0.985	0.985	**0.986**
nh2oh	0.363	0.630	0.880	0.959	0.967	0.957	0.985	0.985	**0.986**
cf2cl2	0.550	0.582	0.960	0.985	**0.986**	0.935	0.981	0.980	0.985
ED01	0.359	0.462	0.884	0.944	0.955	0.921	0.985	**0.986**	0.986
nh2cl	0.559	0.552	0.933	0.977	0.982	0.945	0.985	0.984	**0.986**
ccl3h	0.633	0.650	0.962	0.985	**0.987**	0.951	0.981	0.980	0.984
hnc	0.466	0.630	0.853	0.970	0.969	0.957	**0.987**	0.985	0.986
hnnn	0.460	0.612	0.877	0.964	0.966	0.949	0.986	0.985	**0.987**
TiCl3Me	0.621	0.631	0.948	0.984	**0.987**	0.810	0.951	0.956	0.967
CrO2Cl2	0.626	0.614	0.930	0.975	0.986	0.883	0.975	0.977	**0.987**
formic	0.409	0.686	0.897	0.969	0.972	0.961	0.986	0.985	**0.987**
nccn	0.496	0.674	0.869	0.973	0.972	0.969	0.986	0.985	**0.987**
c2cl4	0.622	0.644	0.961	0.986	**0.987**	0.939	0.969	0.968	0.973
t-hcoh	0.393	0.640	0.860	0.961	0.961	0.959	0.987	0.986	**0.987**
sio	0.618	0.702	0.896	0.982	**0.987**	0.965	0.986	0.985	0.986
s2o	0.643	0.611	0.937	0.980	0.983	0.958	0.986	0.985	**0.987**
t-n2h2	0.383	0.558	0.860	0.963	0.962	0.965	0.987	0.986	**0.987**
honc	0.451	0.672	0.873	0.966	0.966	0.882	0.986	0.985	**0.987**
c-hcoh	0.401	0.638	0.860	0.962	0.967	0.850	0.987	0.986	**0.987**
hcno	0.452	0.662	0.889	0.968	0.970	0.968	0.987	0.986	**0.987**
hnco	0.437	0.655	0.893	0.972	0.974	0.969	0.987	0.986	**0.987**

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
Ni(CO)4	0.466	0.515	0.891	0.962	0.963	0.966	0.986	**0.987**	0.986
PR03	0.466	0.515	0.891	0.962	0.963	0.966	0.986	**0.987**	0.986
c-n2h2	0.392	0.555	0.861	0.965	0.970	0.967	0.987	0.986	**0.988**
c2cl6	0.627	0.683	0.965	0.986	**0.988**	0.931	0.967	0.966	0.974
CrO2(NO3)2	0.449	0.488	0.900	0.965	0.974	0.900	0.986	0.987	**0.988**
hcn	0.466	0.629	0.860	0.970	0.969	0.969	**0.988**	0.987	0.988
ccl4	0.646	0.672	0.966	0.986	**0.988**	0.963	0.982	0.981	0.985
Ni(PH3)2	0.608	0.662	0.904	0.949	0.952	0.970	0.988	**0.988**	0.987
h2o	0.340	0.674	0.890	0.964	0.970	0.959	**0.988**	0.987	0.987
ccl2	0.636	0.647	0.949	0.986	**0.988**	0.973	0.985	0.984	0.987
si2h6	0.646	0.594	0.926	0.965	0.970	0.967	0.987	0.987	**0.988**
hocn	0.468	0.678	0.886	0.969	0.969	0.958	0.988	0.988	**0.989**
fccf	0.430	0.710	0.922	0.980	0.978	0.981	0.989	0.989	**0.989**
ch2-sing	0.438	0.502	0.782	0.708	0.959	0.731	**0.989**	0.989	0.989
ch2f2	0.402	0.679	0.925	0.973	0.974	0.967	0.989	0.988	**0.989**
MnO3F	0.551	0.521	0.895	0.956	0.970	0.944	0.988	0.989	**0.990**
c2f4	0.419	0.744	0.936	0.981	0.981	0.976	0.989	0.988	**0.990**
ED03	0.507	0.542	0.884	0.940	0.959	0.974	0.990	**0.990**	0.989
c2f6	0.399	0.669	0.944	0.982	0.982	0.969	0.988	0.988	**0.990**
sih4	0.632	0.576	0.919	0.957	0.962	0.967	0.989	0.989	**0.991**
n2o4	0.436	0.633	0.902	0.971	0.975	0.966	0.989	0.988	**0.991**
hcof	0.429	0.706	0.914	0.976	0.976	0.976	0.990	0.990	**0.991**
nh2f	0.388	0.659	0.901	0.967	0.974	0.963	0.991	0.990	**0.991**
VOCl3	0.654	0.640	0.947	0.984	**0.991**	0.889	0.960	0.964	0.973
t-hono	0.422	0.602	0.889	0.969	0.973	0.962	0.991	0.990	**0.991**
hoclo	0.526	0.538	0.929	0.971	0.979	0.967	0.992	0.991	**0.992**
hocl	0.563	0.550	0.940	0.979	0.986	0.963	0.991	0.991	**0.992**

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
TiCl4	0.672	0.664	0.962	0.991	**0.992**	0.924	0.977	0.980	0.985
c-hono	0.410	0.601	0.890	0.971	0.976	0.969	0.992	0.991	**0.992**
ph3	0.635	0.587	0.925	0.966	0.970	0.969	0.992	0.991	**0.992**
hooh	0.358	0.651	0.889	0.965	0.974	0.972	0.992	0.992	**0.992**
hoclo2	0.510	0.568	0.926	0.969	0.974	0.969	0.992	0.992	**0.992**
chf3	0.381	0.727	0.939	0.979	0.980	0.977	0.992	0.991	**0.993**
n2o	0.464	0.670	0.891	0.972	0.974	0.973	0.992	0.992	**0.993**
co2	0.474	0.723	0.905	0.979	0.978	0.982	0.993	0.992	**0.993**
hclo4	0.504	0.588	0.928	0.968	0.974	0.972	0.992	0.992	**0.993**
f2co	0.427	0.705	0.933	0.982	0.981	0.983	0.993	0.992	**0.993**
sih3f	0.548	0.666	0.931	0.969	0.973	0.979	0.992	0.992	**0.993**
hno	0.398	0.646	0.873	0.971	0.973	0.978	**0.993**	0.993	0.993
so2	0.564	0.533	0.923	0.973	0.977	0.978	**0.994**	0.993	0.993
bhf2	0.379	0.715	0.926	0.982	0.978	0.983	0.993	0.993	**0.994**
alf	0.646	0.778	0.908	0.984	0.987	0.977	0.993	0.993	**0.994**
p2	0.710	0.702	0.927	0.989	0.991	0.988	0.994	0.993	**0.994**
cf4	0.408	0.662	0.948	0.984	0.984	0.983	0.993	0.993	**0.994**
co	0.479	0.665	0.861	0.976	0.979	0.979	**0.995**	0.994	0.994
Ni(PF3)4	0.509	0.488	0.946	0.980	0.982	0.974	0.994	**0.995**	0.992
n2	0.446	0.600	0.859	0.976	0.980	0.985	**0.995**	0.995	0.995
fno	0.432	0.664	0.905	0.977	0.981	0.985	0.995	0.995	**0.995**
alcl3	0.662	0.706	0.971	0.994	0.992	0.991	0.995	0.995	**0.995**
sf6	0.461	0.636	0.957	0.984	0.986	0.984	0.994	0.994	**0.995**
bf3	0.377	0.753	0.943	0.988	0.985	0.988	0.995	0.995	**0.996**
so3	0.537	0.547	0.929	0.975	0.979	0.986	0.995	0.995	**0.996**
h2s	0.626	0.603	0.943	0.977	0.979	0.978	0.996	0.995	**0.996**
pf3	0.501	0.582	0.945	0.982	0.987	0.982	0.995	0.995	**0.996**

Table S13– *Continued on next page*

Table S13– *Continued from previous page*

Molecule	**GWH**	**CORE**	**SAD**	**SADNO**	**HUCKEL**	**GSZ**	**LDA-X**	**CAP-X**	**CHA-X**
hof	0.410	0.683	0.910	0.971	0.981	0.977	0.996	0.995	**0.996**
alcl	0.685	0.714	0.937	0.989	0.990	0.985	0.995	0.995	**0.996**
CrF6	0.496	0.528	0.928	0.977	0.986	0.972	0.996	**0.996**	0.995
alh3	0.658	0.628	0.900	0.969	0.968	0.983	0.995	0.995	**0.996**
cf2	0.448	0.719	0.917	0.980	0.982	0.988	0.996	0.996	**0.996**
VOF3	0.519	0.538	0.923	0.981	0.986	0.958	0.994	0.995	**0.996**
bf	0.485	0.701	0.870	0.977	0.978	0.984	**0.996**	0.996	0.996
CrO2F2	0.538	0.527	0.909	0.970	0.979	0.981	0.996	**0.996**	0.996
pf5	0.469	0.608	0.957	0.987	0.988	0.988	0.996	0.995	**0.996**
VF5	0.500	0.537	0.935	0.986	0.988	0.952	0.994	0.996	**0.997**
bh	0.558	0.518	0.700	0.701	0.961	0.977	**0.997**	0.997	0.997
sif4	0.469	0.579	0.953	0.988	0.988	0.991	0.997	0.997	**0.997**
hf	0.391	0.724	0.935	0.984	0.983	0.985	**0.997**	0.997	0.997
clf	0.565	0.551	0.954	0.983	0.991	0.986	0.997	0.997	**0.997**
TiF4	0.504	0.528	0.938	0.991	0.987	0.977	0.996	0.997	**0.997**
ScF3	0.541	0.475	0.942	0.994	0.988	0.990	**0.998**	0.998	0.997
alh	0.745	0.683	0.870	0.848	0.983	0.971	0.998	0.997	**0.998**
alf3	0.464	0.690	0.945	0.991	0.987	0.990	**0.998**	0.998	0.998
cl2	0.648	0.680	0.968	0.989	0.994	0.993	0.998	0.998	**0.998**
hcl	0.610	0.708	0.968	0.990	0.989	0.988	**0.999**	0.998	0.999
f2	0.426	0.702	0.932	0.975	0.990	0.994	0.999	0.999	**0.999**
h2	0.000	0.969	0.827	0.910	0.910	0.969	**0.999**	0.999	0.999
Best	0	0	0	16	54	1	20	23	**108**

Table S14: Non-neutral and/or non-singlet molecules, HF/aug-pcseg-2: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
cf	0.479	0.679	0.870	0.910	0.914	**0.957**	0.942	0.951	0.948
cyclopropyl	0.318	0.547	0.863	0.953	0.959	0.918	0.958	0.956	**0.961**
Ti(BH4)3	0.340	0.484	0.886	0.955	0.939	0.802	0.953	0.958	**0.962**
cch	0.456	0.633	0.828	0.949	0.938	0.929	**0.962**	0.961	0.962
allyl	0.377	0.571	0.862	0.957	**0.963**	0.926	0.960	0.959	0.962
ch	0.473	0.541	0.730	0.715	0.847	0.833	0.849	0.931	**0.963**
ch2ch	0.404	0.551	0.845	0.944	0.947	0.928	0.963	0.961	**0.963**
V(NMe2)4	0.285	0.417	0.883	**0.964**	0.954	0.829	0.955	0.963	0.943
Cu(acac)2	0.326	0.475	0.891	0.946	**0.965**	0.917	0.935	0.920	0.948
sih	0.707	0.644	0.874	0.854	0.935	0.964	**0.971**	0.939	0.954
ch3nh	0.383	0.580	0.853	0.940	0.950	0.926	0.971	0.969	**0.972**
ch2nh2	0.367	0.599	0.863	0.954	0.960	0.936	0.971	0.970	**0.972**
h2cn	0.432	0.600	0.844	0.944	0.949	0.937	0.972	0.971	**0.972**
cn	0.458	0.662	0.827	0.949	0.940	0.959	**0.973**	0.972	0.972
t-hooo	0.408	0.643	0.882	0.952	0.960	0.935	0.974	0.974	**0.975**
clo	0.573	0.566	0.935	0.946	0.953	0.960	0.957	**0.975**	0.961
ch3	0.396	0.637	0.831	0.949	0.957	0.935	**0.976**	0.975	0.976
h2ccn	0.424	0.598	0.859	0.955	0.959	0.894	0.975	0.974	**0.976**
hcnh	0.406	0.616	0.852	0.958	0.955	0.955	0.978	0.977	**0.978**
bn3pi	0.495	0.631	0.788	0.894	0.895	0.914	0.976	**0.982**	0.974
c-hooo	0.408	0.642	0.885	0.956	0.966	0.947	**0.982**	0.981	0.982
n2h	0.434	0.580	0.852	0.958	0.958	0.964	**0.984**	0.983	0.984
oh	0.384	0.641	0.854	0.977	0.978	0.946	0.891	**0.985**	0.898
no	0.450	0.669	0.868	0.976	0.980	0.940	**0.988**	0.984	0.978
h2no	0.412	0.636	0.880	0.959	0.967	0.959	0.988	0.987	**0.988**
ch2-trip	0.411	0.658	0.789	0.957	0.962	0.960	**0.988**	0.987	0.987

Table S14– *Continued on next page*

Table S14– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
so	0.583	0.569	0.917	0.980	0.987	0.969	0.989	0.988	**0.989**
hco	0.429	0.647	0.868	0.970	0.969	0.974	**0.990**	0.989	0.990
nh2	0.391	0.593	0.828	0.958	0.966	0.965	**0.990**	0.989	0.990
sif	0.614	0.752	0.907	0.951	0.974	0.955	0.955	**0.992**	0.955
hoo	0.376	0.639	0.881	0.961	0.969	0.974	**0.992**	0.992	0.992
ssh	0.652	0.656	0.942	0.980	0.983	0.978	0.993	0.993	**0.994**
no2	0.430	0.632	0.896	0.974	0.977	0.982	0.994	0.993	**0.994**
s2	0.669	0.682	0.940	0.988	0.991	0.990	0.996	0.995	**0.996**
o2	0.452	0.662	0.883	0.978	0.985	0.987	**0.997**	0.996	0.997
hs	0.628	0.600	0.925	0.930	0.928	0.929	0.958	0.975	**0.997**
nh	0.430	0.637	0.783	0.968	0.975	0.986	**0.997**	0.997	0.997
Best	0	0	0	1	2	1	13	4	**16**

Table S15: Neutral singlet molecules, revTPSSh/aug-pcseg-2: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ED14	0.316	0.479	0.893	0.950	**0.958**	0.824	0.927	0.929	0.929
c2h6	0.386	0.560	0.869	0.952	**0.961**	0.901	0.955	0.954	0.958
b2h6	0.284	0.509	0.854	0.932	0.937	0.893	0.959	0.958	**0.961**
ch4	0.370	0.594	0.862	0.943	0.952	0.904	0.961	0.960	**0.962**
Mn(CO)5CN	0.302	0.452	0.888	0.959	0.959	0.900	0.959	**0.963**	0.961
tetrahedrane	0.184	0.585	0.872	0.956	0.961	0.935	0.962	0.959	**0.963**
Cr(C6H6)(CO)3	0.327	0.445	0.890	**0.964**	0.962	0.792	0.932	0.948	0.953
cyclopropane	0.321	0.534	0.873	0.956	**0.964**	0.912	0.956	0.954	0.958
propene	0.336	0.559	0.871	0.957	**0.964**	0.914	0.960	0.959	0.963
Ni(C5H5)NO	0.415	0.510	0.890	**0.964**	0.961	0.868	0.960	0.959	0.960
propane	0.321	0.551	0.873	0.957	**0.964**	0.895	0.952	0.951	0.955
ED04	0.354	0.485	0.888	**0.965**	0.956	0.864	0.947	0.948	0.957

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
PR04	0.336	0.463	0.890	**0.965**	0.961	0.867	0.932	0.933	0.940
cyclobutene	0.350	0.564	0.872	0.958	**0.965**	0.919	0.957	0.955	0.960
Fe(CO)4(C2H4)	0.324	0.465	0.890	0.964	0.958	0.841	0.961	0.965	**0.966**
Co(C3H5)(CO)3	0.352	0.480	0.891	0.962	0.959	0.829	0.960	0.964	**0.966**
Fe(CO)3(tmm)	0.333	0.464	0.890	**0.966**	0.959	0.804	0.933	0.942	0.948
n-butane	0.284	0.556	0.875	0.959	**0.967**	0.885	0.951	0.950	0.954
Fe(C4H4)(CO)3	0.341	0.468	0.890	**0.967**	0.958	0.814	0.937	0.943	0.950
Fe(C4H6)(CO)3	0.335	0.463	0.889	**0.967**	0.958	0.803	0.945	0.953	0.955
Mn(C5H5)(CO)3	0.338	0.458	0.890	**0.967**	0.959	0.784	0.934	0.942	0.945
MnCp(CO)3	0.331	0.458	0.890	**0.967**	0.960	0.785	0.931	0.939	0.942
cyclopropene	0.311	0.563	0.867	0.957	0.962	0.935	0.966	0.964	**0.967**
cyclobutane	0.270	0.538	0.874	0.959	**0.967**	0.899	0.949	0.947	0.954
oxetane	0.305	0.596	0.879	0.956	0.964	0.923	0.964	0.963	**0.967**
Fe(C2H4)(CO)4	0.326	0.464	0.890	0.964	0.958	0.844	0.963	0.967	**0.967**
ch3nh2	0.323	0.584	0.870	0.952	0.961	0.922	0.966	0.965	**0.968**
PR05	0.309	0.444	0.890	0.960	0.961	0.876	0.964	**0.968**	0.967
n-pentane	0.265	0.559	0.877	0.960	**0.968**	0.848	0.951	0.951	0.954
ethanol	0.375	0.600	0.882	0.957	0.964	0.920	0.966	0.965	**0.968**
c2h4	0.382	0.527	0.864	0.958	0.964	0.933	0.968	0.966	**0.969**
FeCp2	0.347	0.461	0.890	**0.969**	0.956	0.887	0.952	0.953	0.957
t-butadiene	0.333	0.568	0.872	0.964	**0.969**	0.922	0.962	0.962	0.965
cyclopentadiene	0.348	0.588	0.877	0.963	**0.969**	0.927	0.960	0.959	0.963
cyclobutadiene	0.312	0.591	0.865	0.963	0.969	0.942	0.967	0.966	**0.969**
borole	0.316	0.579	0.865	0.965	**0.969**	0.887	0.965	0.964	0.967
PR14	0.258	0.458	0.894	0.965	**0.969**	0.783	0.946	0.952	0.921
VCp(CO)4	0.280	0.435	0.890	0.960	**0.970**	0.775	0.926	0.939	0.936
ED15	0.395	0.512	0.887	0.957	0.957	0.926	0.968	0.968	**0.970**

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
propyne	0.418	0.571	0.869	0.958	0.961	0.926	0.968	0.967	**0.970**
Mn(NO)3CO	0.472	0.496	0.891	0.966	0.961	0.920	0.967	**0.970**	0.969
Ni(C3H5)2	0.389	0.511	0.886	0.956	0.957	0.927	0.969	0.969	**0.970**
PMe3	0.401	0.521	0.897	0.964	**0.970**	0.892	0.966	0.965	0.967
allene	0.454	0.564	0.869	0.957	0.961	0.944	0.970	0.969	**0.971**
Fe(C5Me5)(P5)	0.343	0.560	0.914	**0.971**	0.965	0.815	0.894	0.897	0.893
Fe(CO)2(NO)2	0.460	0.490	0.890	0.969	0.960	0.933	0.970	**0.972**	0.970
beta-lactim	0.333	0.618	0.883	0.959	0.966	0.925	0.968	0.967	**0.972**
silole	0.362	0.565	0.896	0.967	**0.972**	0.869	0.938	0.936	0.942
ED28	0.277	0.520	0.900	0.967	**0.972**	0.876	0.961	0.962	0.961
ED27	0.281	0.516	0.902	0.967	**0.972**	0.898	0.965	0.966	0.966
pyrrole	0.323	0.609	0.882	0.968	**0.973**	0.938	0.966	0.965	0.969
PR40	0.384	0.543	0.908	0.968	**0.973**	0.883	0.957	0.960	0.966
ED05	0.328	0.466	0.890	0.961	0.960	0.892	0.970	0.972	**0.973**
Cr(C6H6)2	0.304	0.444	0.890	**0.973**	0.962	0.870	0.957	0.960	0.962
c2h5f	0.358	0.620	0.898	0.961	0.968	0.910	0.971	0.970	**0.973**
Sc(acac)3	0.253	0.501	0.896	0.966	0.972	0.821	0.970	**0.973**	0.959
benzene	0.398	0.607	0.880	0.969	**0.973**	0.937	0.965	0.965	0.968
Mn(CO)4NO	0.374	0.468	0.890	0.961	0.960	0.915	0.971	**0.973**	0.973
furan	0.380	0.621	0.885	0.966	0.971	0.948	0.972	0.971	**0.974**
oxirane	0.387	0.616	0.878	0.953	0.961	0.937	0.972	0.971	**0.974**
ED40a	0.382	0.493	0.878	0.954	0.950	0.938	**0.974**	0.972	0.971
ch2c	0.431	0.622	0.831	0.950	0.954	0.928	0.974	0.972	**0.974**
Ni(acac)2	0.325	0.473	0.891	0.953	0.959	0.908	**0.975**	0.959	0.971
PCy3	0.223	0.461	0.890	0.969	**0.975**	0.727	0.948	0.950	0.942
PR15	0.385	0.466	0.888	0.956	0.958	0.910	0.975	0.975	**0.975**
acetaldehyde	0.384	0.602	0.881	0.954	0.963	0.915	0.973	0.972	**0.975**

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
dithiotane	0.524	0.557	0.923	0.970	**0.975**	0.914	0.967	0.965	0.970
ch3ph2	0.506	0.508	0.909	0.964	0.970	0.915	0.973	0.972	**0.976**
nh3	0.360	0.629	0.866	0.952	0.962	0.935	**0.976**	0.975	0.975
methanol	0.369	0.612	0.881	0.954	0.961	0.937	0.975	0.974	**0.976**
ED30	0.246	0.527	0.895	0.972	**0.976**	0.773	0.964	0.967	0.955
ED31	0.238	0.485	0.893	0.973	**0.976**	0.773	0.955	0.953	0.933
CuCN	0.626	0.652	0.861	0.938	0.947	**0.976**	0.952	0.945	0.954
PR12	0.274	0.438	0.888	0.960	0.961	0.823	0.973	**0.976**	0.975
thiophene	0.432	0.587	0.906	0.972	**0.976**	0.883	0.954	0.953	0.957
c2clh5	0.514	0.541	0.922	0.971	**0.976**	0.835	0.962	0.960	0.967
AcCl	0.507	0.578	0.924	0.971	**0.976**	0.855	0.948	0.946	0.954
PhSH	0.423	0.588	0.902	0.973	**0.976**	0.854	0.908	0.908	0.911
PR02	0.357	0.475	0.892	0.966	0.961	0.923	0.974	**0.976**	0.976
Fe(CO)5	0.373	0.475	0.892	0.966	0.961	0.924	0.975	**0.977**	0.977
n2h4	0.372	0.603	0.871	0.955	0.965	0.942	0.977	0.975	**0.978**
ED40b	0.439	0.573	0.925	0.973	**0.978**	0.856	0.976	0.976	0.977
c2clh3	0.531	0.544	0.925	0.975	**0.978**	0.862	0.946	0.943	0.951
Co(CO)3(NO)	0.449	0.497	0.892	0.969	0.961	0.949	0.977	**0.978**	0.977
c2h2	0.465	0.586	0.861	0.965	0.965	0.960	**0.978**	0.977	0.978
dioxetane	0.419	0.621	0.887	0.956	0.963	0.947	0.977	0.976	**0.979**
ch2nh	0.396	0.600	0.863	0.958	0.963	0.950	0.978	0.977	**0.979**
acetic	0.379	0.634	0.894	0.962	0.968	0.935	0.978	0.977	**0.979**
CoH(CO)4	0.428	0.503	0.894	0.965	0.961	0.932	0.978	**0.980**	0.980
c2clh	0.557	0.559	0.929	**0.980**	0.979	0.884	0.966	0.964	0.969
CuMe	0.672	0.668	0.863	0.939	0.948	0.956	0.979	0.978	**0.980**
cclh3	0.543	0.555	0.935	0.974	0.978	0.920	0.978	0.977	**0.980**
c2h3f	0.386	0.633	0.899	0.967	0.971	0.942	0.979	0.978	**0.980**

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
PhSeH	0.502	0.616	0.921	0.977	**0.981**	0.886	0.927	0.927	0.929
bh3	0.405	0.656	0.807	0.937	0.942	0.941	0.981	0.980	**0.981**
TiCl2Me2	0.548	0.591	0.930	0.975	**0.981**	0.830	0.927	0.933	0.950
Zn(CH3)2	0.595	0.593	0.885	0.946	0.958	0.954	**0.981**	0.980	0.980
clcn	0.599	0.559	0.929	0.980	0.980	0.941	0.980	0.978	**0.981**
ocs	0.605	0.541	0.926	0.980	**0.982**	0.923	0.969	0.967	0.971
formamide	0.406	0.631	0.890	0.964	0.970	0.939	0.981	0.980	**0.982**
ketene	0.414	0.636	0.885	0.963	0.968	0.949	0.981	0.980	**0.982**
oxirene	0.397	0.658	0.872	0.954	0.958	0.962	0.982	0.981	**0.983**
ED02	0.431	0.495	0.886	0.950	0.954	0.938	0.981	**0.983**	0.983
clcof	0.536	0.585	0.944	0.983	**0.983**	0.927	0.977	0.976	0.981
ch3f	0.377	0.640	0.904	0.962	0.966	0.948	0.982	0.982	**0.983**
oxadiazole	0.401	0.636	0.881	0.967	0.972	0.954	0.982	0.981	**0.983**
cs2	0.654	0.649	0.939	0.981	**0.984**	0.965	0.980	0.979	0.981
ch2clf	0.539	0.552	0.942	0.978	0.980	0.907	0.981	0.980	**0.984**
ccl2h2	0.605	0.616	0.953	0.982	0.984	0.939	0.982	0.980	**0.984**
cis-c2f2cl2	0.550	0.569	0.952	0.984	**0.984**	0.907	0.969	0.968	0.974
trans-c2f2cl2	0.545	0.569	0.952	0.984	**0.984**	0.903	0.969	0.969	0.975
PR01	0.272	0.447	0.889	0.957	0.963	0.903	0.982	**0.984**	0.984
PR06	0.337	0.454	0.889	0.957	0.961	0.887	0.981	0.983	**0.984**
clno	0.564	0.544	0.926	0.978	0.983	0.915	0.978	0.976	**0.984**
c2cl2	0.592	0.606	0.950	**0.985**	0.984	0.938	0.971	0.970	0.974
ccl2o	0.611	0.580	0.952	0.984	**0.985**	0.945	0.977	0.976	0.980
cs	0.648	0.602	0.907	0.982	0.984	0.973	**0.985**	0.984	0.985
nh2oh	0.364	0.632	0.879	0.958	0.966	0.956	0.985	0.984	**0.985**
Cr(CO)6	0.273	0.446	0.889	0.957	0.963	0.906	0.983	**0.985**	0.985
dioxetan2one	0.421	0.635	0.899	0.965	0.969	0.924	0.983	0.982	**0.985**

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
p4	0.712	0.717	0.933	0.977	0.983	0.976	0.985	0.983	**0.986**
h2co	0.436	0.630	0.877	0.962	0.967	0.963	0.986	0.985	**0.986**
ccl3h	0.632	0.650	0.961	0.985	**0.986**	0.953	0.983	0.982	0.986
h2o	0.341	0.675	0.889	0.962	0.969	0.957	**0.986**	0.986	0.986
glyoxal	0.420	0.676	0.885	0.904	0.971	0.960	0.985	0.984	**0.987**
cf2cl2	0.551	0.583	0.959	0.985	0.985	0.937	0.983	0.982	**0.987**
nh2cl	0.559	0.553	0.933	0.976	0.982	0.946	0.986	0.985	**0.987**
dioxirane	0.417	0.660	0.880	0.956	0.965	0.958	0.986	0.985	**0.987**
c2cl4	0.622	0.644	0.961	0.986	**0.987**	0.942	0.972	0.971	0.976
t-hcoh	0.394	0.640	0.860	0.961	0.962	0.958	0.987	0.986	**0.987**
hnc	0.466	0.631	0.852	0.970	0.970	0.957	**0.987**	0.986	0.987
c-hcoh	0.403	0.638	0.860	0.961	0.968	0.851	0.987	0.986	**0.987**
hccf	0.431	0.676	0.903	0.975	0.974	0.973	0.987	0.986	**0.987**
c2cl6	0.627	0.684	0.964	0.986	**0.987**	0.934	0.969	0.968	0.976
TiCl3Me	0.620	0.633	0.947	0.982	**0.987**	0.816	0.959	0.963	0.973
formic-anhydride	0.409	0.637	0.897	0.969	0.971	0.940	0.986	0.985	**0.987**
Ni(PH3)2	0.608	0.661	0.904	0.948	0.951	0.968	0.987	**0.987**	0.987
ccl4	0.646	0.673	0.966	0.986	**0.987**	0.965	0.983	0.982	0.987
Ni(CO)4	0.469	0.512	0.893	0.964	0.964	0.966	0.987	**0.987**	0.987
PR03	0.469	0.512	0.893	0.964	0.964	0.966	0.987	**0.987**	0.987
t-n2h2	0.385	0.562	0.859	0.962	0.960	0.966	0.987	0.986	**0.988**
c-n2h2	0.394	0.560	0.860	0.963	0.969	0.968	0.987	0.987	**0.988**
sio	0.618	0.701	0.896	0.982	**0.988**	0.963	0.984	0.983	0.984
formic	0.411	0.686	0.897	0.969	0.971	0.963	0.988	0.987	**0.988**
honc	0.450	0.673	0.873	0.967	0.968	0.882	0.988	0.986	**0.988**
s2o	0.644	0.614	0.937	0.978	0.981	0.961	0.987	0.987	**0.988**
hnnn	0.459	0.620	0.876	0.965	0.968	0.952	0.988	0.987	**0.989**

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
hcn	0.465	0.632	0.859	0.969	0.969	0.972	**0.989**	0.988	0.989
nccn	0.497	0.678	0.868	0.972	0.972	0.972	0.988	0.988	**0.989**
ch2-sing	0.439	0.505	0.781	0.708	0.957	0.732	**0.989**	0.989	0.989
ED01	0.361	0.462	0.886	0.950	0.959	0.925	0.988	0.989	**0.989**
hnco	0.439	0.661	0.892	0.972	0.974	0.972	0.989	0.989	**0.990**
hcno	0.450	0.664	0.888	0.966	0.970	0.973	0.989	0.988	**0.990**
CrO2Cl2	0.628	0.617	0.928	0.971	0.988	0.888	0.980	0.981	**0.990**
ccl2	0.637	0.647	0.948	0.984	0.988	0.977	0.988	0.988	**0.990**
hocn	0.469	0.682	0.885	0.969	0.970	0.961	0.990	0.989	**0.990**
CrO2(NO3)2	0.447	0.491	0.898	0.962	0.976	0.906	0.989	0.990	**0.990**
ED03	0.509	0.539	0.886	0.940	0.960	0.972	0.990	**0.990**	0.990
ch2f2	0.405	0.679	0.924	0.972	0.973	0.968	0.990	0.989	**0.990**
si2h6	0.645	0.594	0.927	0.967	0.971	0.970	0.989	0.989	**0.991**
nh2f	0.389	0.660	0.900	0.965	0.972	0.964	0.991	0.990	**0.991**
Cr(NO)4	0.451	0.492	0.890	0.967	0.968	0.920	0.988	0.991	**0.991**
fccf	0.432	0.708	0.921	0.979	0.978	0.983	0.991	0.991	**0.992**
hocl	0.564	0.551	0.939	0.978	0.985	0.963	0.991	0.990	**0.992**
hooh	0.359	0.652	0.888	0.962	0.972	0.971	0.992	0.991	**0.992**
VOCl3	0.654	0.643	0.945	0.980	**0.992**	0.894	0.966	0.970	0.978
TiCl4	0.671	0.667	0.960	0.988	**0.992**	0.931	0.983	0.985	0.990
sih4	0.630	0.576	0.919	0.959	0.963	0.970	0.991	0.991	**0.992**
hcof	0.432	0.706	0.913	0.975	0.975	0.978	0.992	0.992	**0.992**
hoclo	0.527	0.542	0.928	0.968	0.975	0.969	0.992	0.992	**0.992**
c2f4	0.422	0.743	0.936	0.980	0.980	0.979	0.991	0.991	**0.993**
c2f6	0.402	0.670	0.944	0.981	0.981	0.972	0.991	0.990	**0.993**
t-hono	0.424	0.606	0.888	0.967	0.972	0.965	0.993	0.992	**0.993**
hno	0.400	0.647	0.872	0.968	0.971	0.978	0.993	0.993	**0.993**

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
ph3	0.633	0.587	0.925	0.967	0.971	0.971	0.993	0.993	**0.993**
so2	0.567	0.536	0.923	0.971	0.975	0.978	**0.994**	0.993	0.993
alf	0.647	0.777	0.908	0.982	0.988	0.976	0.993	0.993	**0.994**
c-hono	0.413	0.605	0.889	0.969	0.974	0.971	0.994	0.993	**0.994**
chf3	0.384	0.727	0.938	0.978	0.978	0.978	0.993	0.992	**0.994**
n2o4	0.436	0.639	0.901	0.969	0.973	0.972	0.993	0.992	**0.994**
hoclo2	0.511	0.574	0.925	0.965	0.970	0.971	0.994	0.994	**0.994**
sih3f	0.548	0.665	0.931	0.969	0.973	0.980	0.993	0.993	**0.994**
p2	0.709	0.702	0.927	0.988	0.991	0.989	0.994	0.994	**0.994**
bhf2	0.383	0.714	0.926	0.981	0.979	0.983	0.994	0.994	**0.994**
n2o	0.463	0.674	0.890	0.971	0.974	0.976	0.994	0.994	**0.995**
co2	0.477	0.722	0.904	0.978	0.978	0.984	**0.995**	0.994	0.995
co	0.481	0.665	0.860	0.975	0.979	0.978	**0.995**	0.994	0.994
hclo4	0.504	0.592	0.926	0.965	0.971	0.975	0.994	0.994	**0.995**
f2co	0.430	0.707	0.932	0.981	0.980	0.985	0.995	0.994	**0.995**
cf4	0.411	0.664	0.948	0.983	0.982	0.984	0.995	0.994	**0.996**
Ni(PF3)4	0.512	0.487	0.946	0.979	0.981	0.976	0.995	**0.996**	0.993
hof	0.410	0.685	0.909	0.969	0.980	0.977	0.996	0.996	**0.996**
h2s	0.626	0.603	0.943	0.978	0.979	0.979	**0.996**	0.996	0.996
alcl3	0.663	0.706	0.971	0.994	0.992	0.991	0.996	0.996	**0.996**
n2	0.448	0.606	0.858	0.974	0.978	0.986	**0.996**	0.996	0.996
bf3	0.382	0.751	0.942	0.988	0.985	0.988	0.996	0.996	**0.996**
so3	0.539	0.552	0.929	0.974	0.978	0.987	**0.996**	0.996	0.996
hf	0.392	0.723	0.935	0.982	0.982	0.983	**0.996**	0.996	0.996
alcl	0.685	0.713	0.937	0.988	0.990	0.986	0.996	0.996	**0.997**
pf3	0.504	0.587	0.945	0.980	0.985	0.982	0.996	0.996	**0.997**
sf6	0.464	0.636	0.956	0.983	0.985	0.986	0.996	0.996	**0.997**

Table S15– *Continued on next page*

Table S15– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
bf	0.487	0.699	0.869	0.975	0.980	0.984	**0.997**	0.996	0.997
alh3	0.658	0.628	0.899	0.969	0.969	0.983	0.996	0.996	**0.997**
pf5	0.472	0.609	0.956	0.985	0.986	0.989	0.997	0.997	**0.997**
cf2	0.451	0.718	0.916	0.978	0.982	0.988	0.997	0.997	**0.997**
clf	0.566	0.552	0.954	0.982	0.991	0.986	0.997	0.997	**0.997**
CrF6	0.500	0.536	0.925	0.972	0.988	0.983	**0.997**	0.997	0.994
alf3	0.467	0.689	0.944	0.991	0.987	0.988	**0.997**	0.997	0.997
fno	0.434	0.667	0.904	0.974	0.979	0.988	0.998	0.997	**0.998**
sif4	0.472	0.582	0.953	0.987	0.987	0.990	0.998	0.997	**0.998**
ScF3	0.544	0.479	0.938	0.990	0.987	0.991	**0.998**	0.997	0.997
MnO3F	0.554	0.524	0.894	0.955	0.978	0.952	0.996	0.997	**0.998**
VOF3	0.523	0.541	0.920	0.976	0.987	0.968	0.997	0.998	**0.998**
bh	0.557	0.521	0.698	0.641	0.959	0.979	**0.998**	0.997	0.998
CrO2F2	0.542	0.531	0.906	0.966	0.980	0.987	0.998	**0.998**	0.996
alh	0.744	0.681	0.870	0.973	0.982	0.972	**0.998**	0.998	0.998
VF5	0.504	0.542	0.931	0.980	0.987	0.963	0.998	0.998	**0.998**
TiF4	0.509	0.531	0.934	0.985	0.987	0.984	**0.998**	0.998	0.998
cl2	0.648	0.682	0.968	0.988	0.993	0.993	0.998	0.998	**0.998**
hcl	0.610	0.709	0.968	0.989	0.989	0.988	**0.999**	0.999	0.999
f2	0.426	0.702	0.931	0.974	0.989	0.994	0.999	0.999	**1.000**
h2	0.000	0.971	0.824	0.907	0.907	0.971	**1.000**	0.999	0.999
Best	0	0	0	14	47	1	26	20	**114**

Table S16: Non-neutral and/or non-singlet molecules, revTPSSh/aug-pcseg-2: fraction f of electron density covered.

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
cyclopropyl	0.319	0.550	0.864	0.954	0.961	0.920	0.960	0.958	**0.962**

Table S16– *Continued on next page*

Table S16– *Continued from previous page*

Molecule	GWH	CORE	SAD	SADNO	HUCKEL	GSZ	LDA-X	CAP-X	CHA-X
V(NMe2)4	0.285	0.419	0.883	0.962	0.959	0.831	0.958	**0.964**	0.947
Cu(acac)2	0.326	0.476	0.891	0.946	**0.965**	0.919	0.936	0.921	0.949
allyl	0.378	0.574	0.864	0.961	0.967	0.931	0.965	0.964	**0.967**
Ti(BH4)3	0.339	0.486	0.886	0.955	0.942	0.807	0.961	0.965	**0.968**
bn3pi	0.503	0.634	0.789	0.894	0.896	0.959	0.909	**0.968**	0.910
ch2ch	0.406	0.550	0.849	0.952	0.956	0.935	0.971	0.970	**0.972**
ch2nh2	0.368	0.600	0.864	0.956	0.963	0.936	0.973	0.971	**0.974**
ch3nh	0.383	0.584	0.854	0.943	0.953	0.928	0.973	0.971	**0.974**
cch	0.461	0.635	0.835	0.965	0.957	0.941	**0.976**	0.975	0.976
ch3	0.396	0.641	0.831	0.949	0.957	0.936	**0.977**	0.976	0.977
h2cn	0.433	0.604	0.848	0.953	0.958	0.945	0.981	0.980	**0.981**
h2ccn	0.425	0.601	0.861	0.959	0.963	0.900	0.981	0.980	**0.982**
hcnh	0.408	0.617	0.854	0.962	0.961	0.959	0.983	0.982	**0.983**
sif	0.614	0.752	0.907	0.968	0.956	0.940	**0.985**	0.974	0.957
cn	0.468	0.663	0.837	0.974	0.973	0.969	0.987	0.986	**0.987**
clo	0.573	0.567	0.935	0.946	0.952	0.952	**0.988**	0.986	0.964
h2no	0.413	0.641	0.881	0.962	0.969	0.957	0.988	0.987	**0.988**
ch	0.480	0.533	0.730	0.698	0.823	0.917	0.941	**0.989**	0.973
ch2-trip	0.413	0.658	0.789	0.957	0.963	0.961	**0.989**	0.988	0.989
no	0.452	0.644	0.868	0.910	0.915	0.925	0.954	0.945	**0.989**
so	0.584	0.570	0.918	0.980	0.987	0.969	0.989	0.989	**0.989**
nh2	0.393	0.595	0.827	0.886	0.965	0.964	**0.990**	0.989	0.989
hco	0.432	0.647	0.867	0.968	0.969	0.974	**0.990**	0.990	0.990
n2h	0.435	0.583	0.855	0.964	0.964	0.970	0.991	0.990	**0.991**
hs	0.628	0.599	0.925	0.984	0.987	0.976	**0.991**	0.975	0.949
t-hooo	0.409	0.646	0.886	0.963	0.973	0.946	0.991	0.990	**0.991**
c-hooo	0.409	0.646	0.887	0.963	0.973	0.957	0.993	0.993	**0.993**

Table S16– *Continued on next page*

Table S16– *Continued from previous page*

Molecule	**GWH**	**CORE**	**SAD**	**SADNO**	**HUCKEL**	**GSZ**	**LDA-X**	**CAP-X**	**CHA-X**
hoo	0.377	0.641	0.882	0.966	0.974	0.973	**0.995**	0.994	0.995
cf	0.481	0.679	0.870	0.910	0.916	0.937	**0.996**	0.932	0.942
ssh	0.652	0.657	0.942	0.981	0.984	0.979	0.996	0.995	**0.996**
no2	0.431	0.637	0.894	0.971	0.975	0.985	0.996	0.996	**0.996**
oh	0.386	0.641	0.853	0.978	0.978	0.874	0.890	0.978	**0.996**
s2	0.668	0.682	0.940	0.988	0.991	0.991	0.997	0.996	**0.997**
nh	0.432	0.637	0.783	0.971	0.975	0.986	**0.998**	0.998	0.998
sih	0.706	0.642	0.874	0.855	0.934	0.962	0.956	0.954	**0.998**
o2	0.454	0.666	0.883	0.977	0.985	0.988	**0.998**	0.998	0.998
Best	0	0	0	0	1	0	12	3	**21**