ELECTRONIC SUPPLEMENTARY INFORMATION

for

Can Kohn-Sham Density Functional Theory Predict Accurate Charge Distributions for Both Single-Reference and Multi-Reference Molecules?

Pragya Verma and Donald G. Truhlar*

Department of Chemistry, Nanoporous Materials Genome Center, Chemical Theory Center, and Minnesota Supercomputing Institute, 207 Pleasant Street SE, University of Minnesota, Minneapolis, MN 55455-0431

*E-mail: truhlar@umn.edu

Date and time of finalization of Supporting Information: March 10, 2017, 7:00 pm.

Table of Contents

Table S1. Comparison of def2-TZVP and def2-QZVP basis sets for dipole moments (in D) of 21 molecules calculated with 13 density functionals.

molecule	BLYP	GAM	HCTH/407	HLE16	HSE06	M06-L	M11-L	MN15-L	PBE	PBE0	PBEsol	TPSS	HLE17	Expt.
def2-TZVP														
CrO	3.79	3.71	3.94	4.52	4.23	4.12	4.40	4.40	3.68	4.26	3.59	3.85	4.50	3.88
CuF	4.67	4.92	4.97	5.76	5.33	4.90	4.98	5.04	4.69	5.37	4.62	4.81	5.57	5.77
CuO	4.19	4.25	4.42	5.07	4.75	4.50	4.55	4.51	4.26	4.79	4.25	4.40	4.98	4.45
H_2CO	2.21	2.15	2.15	2.27	2.32	2.08	1.96	2.16	2.16	2.31	2.16	2.23	2.41	2.33
H_2O	2.03	2.01	2.01	2.00	2.07	2.03	2.01	2.03	2.04	2.07	2.07	2.04	2.01	1.85
H_2S	1.07	1.15	1.13	1.13	1.16	1.13	1.07	1.18	1.13	1.16	1.17	1.13	1.07	0.98
HCN	2.95	2.92	2.92	2.95	3.04	2.94	2.92	3.01	2.93	3.03	2.96	2.96	2.98	2.99
HF	1.90	1.88	1.89	1.87	1.93	1.89	1.85	1.90	1.90	1.93	1.92	1.90	1.89	1.83
HfO_2	7.44	7.40	7.45	7.61	8.09	8.01	7.90	8.06	7.44	8.10	7.42	7.71	8.01	7.92
HfO	3.39	3.24	3.49	4.15	3.46	3.16	3.29	3.55	3.24	3.43	3.20	3.47	4.49	3.43
LaO	4.33	3.78	3.70	5.32	4.10	3.87	4.39	3.96	3.99	4.00	3.95	3.94	5.32	3.21
N_2O	0.09	0.22	0.18	0.19	0.02	0.17	0.18	0.06	0.16	0.02	0.20	0.10	0.02	0.16
NH_3	1.67	1.66	1.67	1.57	1.69	1.70	1.72	1.71	1.70	1.69	1.71	1.70	1.58	1.47
PbO	4.41	4.44	4.39	4.79	4.67	4.55	4.22	4.49	4.32	4.66	4.24	4.40	4.95	4.64
PbS	3.88	3.99	4.01	4.42	4.11	4.25	3.82	4.27	3.89	4.15	3.75	4.04	4.51	3.59
PH_3	0.57	0.70	0.67	0.75	0.69	0.65	0.55	0.66	0.65	0.70	0.70	0.68	0.69	0.57
SO_2	1.69	1.54	1.57	1.50	1.70	1.56	1.49	1.53	1.60	1.69	1.58	1.60	1.64	1.63
TiO	3.71	3.43	3.39	4.52	3.86	3.80	3.80	3.76	3.54	3.81	3.47	3.67	3.88	2.96
YO	4.72	4.35	4.10	4.08	4.65	4.64	4.00	4.59	4.41	4.55	4.39	4.44	4.34	4.52
ZrO_2	7.49	7.41	7.38	7.25	7.93	7.94	7.77	8.01	7.45	7.92	7.42	7.68	7.72	7.8
ZrO	3.19	2.90	3.17	3.98	3.37	3.19	3.14	3.12	3.12	3.39	3.04	3.40	4.54	2.55
def2-QZVP														
CrO	3.66	3.66	3.93	4.56	4.09	3.99	4.08	4.25	3.54	4.13	3.45	3.73	4.48	3.88
CuF	4.55	4.84	4.83	5.59	5.21	4.81	4.75	4.94	4.56	5.25	4.49	4.66	5.41	5.77
CuO	4.16	4.23	4.35	4.99	4.69	4.47	4.42	4.47	4.22	4.74	4.21	4.35	4.90	4.45
H_2CO	2.25	2.19	2.20	2.29	2.35	2.11	2.00	2.22	2.21	2.34	2.20	2.27	2.42	2.33
H_2O	1.87	1.84	1.87	1.88	1.91	1.85	1.85	1.87	1.87	1.91	1.89	1.87	1.87	1.85
H_2S	0.98	1.07	1.04	1.05	1.05	1.03	0.99	1.10	1.02	1.06	1.05	1.02	0.98	0.98
HCN	2.96	2.94	2.95	2.96	3.04	2.92	2.93	3.03	2.95	3.04	2.97	2.96	2.98	2.99

HF	1.81	1.78	1.80	1.80	1.84	1.79	1.76	1.82	1.80	1.83	1.82	1.81	1.81	1.83
HfO_2	7.45	7.42	7.47	7.56	8.06	7.92	7.79	8.10	7.44	8.07	7.41	7.68	7.95	7.92
HfO	3.38	3.21	3.45	4.03	3.42	3.13	3.20	3.45	3.24	3.39	3.17	3.47	4.41	3.43
LaO	4.25	3.77	3.59	4.81	3.94	3.79	4.19	3.79	3.88	3.84	3.82	3.81	5.03	3.21
N_2O	0.07	0.20	0.16	0.18	0.03	0.16	0.17	0.03	0.14	0.03	0.18	0.09	0.01	0.16
NH_3	1.52	1.51	1.53	1.48	1.55	1.54	1.55	1.56	1.54	1.55	1.55	1.53	1.47	1.47
PbO	4.51	4.56	4.50	4.83	4.73	4.64	4.26	4.62	4.40	4.73	4.30	4.45	4.97	4.64
PbS	3.92	4.08	4.06	4.38	4.11	4.25	3.79	4.35	3.90	4.15	3.75	4.02	4.45	3.59
PH_3	0.53	0.67	0.63	0.72	0.65	0.63	0.56	0.65	0.60	0.66	0.64	0.63	0.65	0.57
SO_2	1.66	1.50	1.55	1.49	1.65	1.49	1.44	1.50	1.57	1.65	1.55	1.57	1.62	1.63
TiO	3.48	3.15	3.15	4.37	3.52	3.39	3.15	3.39	3.26	3.45	3.19	3.37	3.71	2.96
YO	4.71	4.25	4.04	4.02	4.58	4.43	3.82	4.58	4.38	4.48	4.34	4.36	4.23	4.52
ZrO_2	7.45	7.37	7.34	7.15	7.85	7.83	7.64	8.00	7.39	7.85	7.36	7.60	7.61	7.8
ZrO	3.15	2.83	3.10	3.74	3.27	2.90	2.87	3.05	3.07	3.30	2.97	3.33	4.36	2.55
MUE [a,b]	0.30	0.27	0.26	0.49	0.28	0.27	0.31	0.28	0.29	0.27	0.30	0.26	0.46	0.00
MUE [a,c]	0.27	0.24	0.22	0.44	0.21	0.20	0.25	0.22	0.26	0.21	0.27	0.23	0.42	0.00
	BLYP	**GAM**	**HCTH/407**	**HLE16**	**HSE06**	**M06-L**	**M11-L**	**MN15-L**	**PBE**	**PBE0**	**PBEsol**	**TPSS**	**HLE17**	**Expt.**

[a] MUE = mean unsigned error

[b] def2-TZVP

[c] def2-QZVP

Table S2. Spin-splitting energies (ΔE in kcal/mol),[a] $\langle S^2 \rangle$ values, and dipole moments (in D) using M06-L/def2-QZVP.

molecule	spin state	ΔE	$\langle S^2 \rangle$	dipole moment
CrN	quartet	0.0	4.07	3.06
	doublet	12.9	1.93	2.38
CrO	quintet	0.0	6.16	3.99
	triplet	14.8	2.77	2.29
CuF	singlet	0.0	-[b]	4.81
	triplet	42.5	2.00	1.95
CuO	doublet	0.0	0.77	4.47
	quartet	35.4	3.77	0.11
HfO_2	singlet	0.0	-[b]	7.92
	triplet	34.0	2.03	4.45
HfO	singlet	0.0	-[b]	3.13
	triplet	27.8	2.00	4.71
LaO	doublet	0.0	0.75	3.79
	quartet	77.9	3.76	3.23
TiO	triplet	0.0	2.02	3.39
	singlet	-0.8	0.94	2.84
YO	doublet	0.0	0.75	4.43
	quartet	79.7	3.76	3.14
ZrO_2	singlet	0.0	-[b]	7.83
	triplet	49.0	2.03	4.15
ZrO	singlet	0.0	0.80	2.90
	triplet	9.0	2.00	3.77
FeO	quintet	0.0	6.11	4.31
	triplet	24.5	3.03	4.21
NiH	doublet	0.0	0.77	2.48
	quartet	33.8	3.75	0.41
ScF	singlet	0.0	0.74	2.29
	triplet	11.9	2.00	2.71
TiH	quartet	0.0	3.76	3.64
	doublet	4.4	1.59	2.33
VN	triplet	0.0	2.07	4.12
	singlet	5.8	1.03	2.82
VO	quartet	0.0	3.81	3.32
	doublet	10.6	1.75	2.42

[a]For each molecule, ΔE is calculated with respect to the energy of the experimental ground spin state.

[b]These singlet calculations were restricted Kohn-Sham calculations.

Table S3. Dipole moments (in D) of CuF, CuO, MgO, PbO and PbS calculated with 47 density functionals and the def2-QZVP basis set.

Functional	CuF	CuO	MgO	PbO	PbS
BLYP	4.55	4.16	6.95	4.51	3.92
PBE	4.56	4.22	7.04	4.40	3.90
HCTH/407	4.83	4.35	7.23	4.50	4.06
OLYP	4.77	4.34	7.14	4.47	4.09
PBEsol	4.49	4.21	7.10	4.30	3.75
OreLYP	4.72	4.30	7.10	4.44	4.05
SOGGA11	4.71	4.59	7.76	4.43	4.38
HLE16	5.59	4.99	8.16	4.83	4.38
N12	4.79	4.22	7.12	4.55	3.98
GAM	4.84	4.23	7.02	4.56	4.08
τ-HCTH	4.92	4.48	7.38	4.44	3.95
TPSS	4.66	4.35	7.21	4.45	4.02
M06-L	4.81	4.47	7.09	4.64	4.25
M11-L	4.75	4.42	7.20	4.26	3.79
MGGA_MS2	4.50	4.21	6.88	4.24	3.85
HLE17	5.41	4.90	7.91	4.97	4.45
MN12-L	4.74	4.44	7.08	4.25	3.88
MN15-L	4.94	4.47	7.27	4.62	4.35
BHandHLYP	5.78	5.28	8.11	5.13	4.40
B3LYP	5.12	4.59	7.45	4.78	4.12
B1LYP	5.24	4.68	7.52	4.85	4.18
mPW1PW	5.26	4.76	7.71	4.74	4.15
B97-1	5.20	4.70	7.53	4.75	4.21
PBE0	5.25	4.74	7.67	4.73	4.15
MPW1K	5.66	5.18	8.19	4.95	4.31
B3LYP*	4.97	4.48	7.34	4.70	4.05
CAM-B3LYP	5.31	4.87	7.93	4.92	4.24
MPW3LYP	5.14	4.61	7.48	4.79	4.12
B97-3	5.38	4.85	7.57	4.89	4.36
LC-ωPBE	5.41	5.14	8.63	4.93	4.42
HSE06	5.21	4.69	7.64	4.73	4.11
SOGGA11-X	5.49	4.95	7.95	4.98	4.33
N12-SX	5.20	4.75	7.79	4.82	4.21
τ-HCTHhyb	5.05	4.58	7.53	4.63	4.04
TPSSh	4.94	4.54	7.45	4.58	4.11
MPWB1K	5.64	5.14	8.04	4.96	4.26
M05	5.37	4.77	7.82	5.01	4.45
M05-2X	5.82	5.37	8.32	5.21	4.38
PW6B95	5.31	4.77	7.61	4.82	4.15
M06-HF	6.33	6.03	9.09	5.35	4.20
M06	5.15	4.58	7.62	4.93	4.24
M06-2X	5.80	5.33	7.94	5.26	4.59
M08-HX	5.98	5.53	8.41	5.36	4.71

M08-SO	5.94	5.40	7.92	5.15	4.24
M11	6.04	5.67	9.17	5.10	4.31
MN12-SX	5.39	4.91	7.60	4.65	3.97
MN15	5.45	5.00	7.67	4.82	4.13
Expt.	5.77	4.45	6.2	4.64	3.59