Supporting Information for:

Density Functionals for Inorganometallic and Organometallic Chemistry

Nathan E. Schultz, Yan Zhao, and Donald G. Truhlar

To be published in *J. Phys. Chem. A*

Date of preparation of this supplement: July 16, 2005
Total number number of pages: 11

Contents

S.1 Zero-Point Energies

In a previous paper,[1] we have determined a zero-point energy scaling factor for the B3LYP DFT method with the DZQ basis set for transition elements and the 6-31G(2d,p) basis set for main group elements. The scale factor is 0.983. We have a limited amount of diatomic data available that we can use to compute experimental zero-point energies and assess the accuracy of our scaling factor. The experimental zero-point energies and scaled zero-point energies are given in Table S-1. The experimental values were computed from ω_e and $\chi_e\omega_e$ for AgH,[2] BeO,[2] CoH,[3,4] FeH,[5] FeO,[6,7] LiCl,[2] LiO,[8] RhC,[2,9] and VO.[7,10] The scaled values approximate the experimental values quite well, and the mean unsigned error (MUE) is 0.05 kcal/mol.

S.2 Bond Lengths

We have constructed a small database of accurate bond lengths for all of the transition element–ligand diatomics in the TMBDE14/05 database; however, the experimental bond lengths for CoO^+, and FeS, and VS are r_0 values and not r_e values, where r_0 is the 0 K bond length and r_e is the equilibrium bond length. The calculated DFT bond lengths are r_0 values and not r_e values, therefore one can not make a direct comparison between experiment and theory unless the r_0 valuess are converted to r_e values, which can be done using the Pekeris relationship[11]

$$\alpha_e = \frac{6\sqrt{x_e\omega_e B_e^{\,3}}}{\omega_e} - \frac{6B_e^{\,2}}{\omega_e}, \qquad \text{(S-1)}$$

where α_e and B_e are the rotational-vibration interaction constant and equilibrium rotational rotational constant, respectively, and the following relationship

$$B_0 = B_e - \alpha_e \frac{1}{2} \qquad \text{(S-2)}$$

where B_0 is the rotational constant in the first vibrational level. Therefore, B_e can be calculated numerically if B_0, ω_e, and $x_e\omega_e$ are known, and the r_e can subsequently be extracted from B_e. For CoO^+, FeS, and VS only B_0 is known, and we can estimate ω_e, and $x_e\omega_e$ by a procedure that we will describe in the next paragraph.

It has been shown that calculated harmonic frequencies can be scaled to reproduce true harmonic frequencies, fundamental frequencies, or zero-point energies.[12] We begin by calculating the harmonic frequencies for AgH, CoH, FeH, FeO, RhC, and VO with all of the DFT methods using the DZQ basis set for the transition elements and the 6-31G(2d,p) basis set for the main group elements, and then we determine the optimum scale factor for each method so that the calculated harmonic frequencies reproduce, as best as possible, the experimental harmonic frequencies. Table S-2 gives the scale factor, *f*, unscaled harmonic frequencies, mean unsigned error between the unscaled harmonic and the experimental frequencies, and the mean unsigned error (MUE) between the scaled and experimental frequencies for each method. As shown in Table S-2, XLYP has the lowest error when the frequencies are scaled, and G96LYP has the lowest error when the frequencies are not scaled. The mean unsigned error in either case is small (18 cm^{-1} for scaled XLYP and 26 cm^{-1} for G96LYP), so we elect to use scaled XLYP frequencies to calculate the harmonic frequencies CoO^+, FeS, and VS. We also note that the unscaled XLYP frequencies are marginally less accurate than the unscaled G96LYP frequencies, where the MUEs for the unscaled XLYP and G96LYP are 27 and 26 cm^{-1}, respectively. Once we have accurate ω_e values, the anharmonicity constant (x_e) can be calculated by using the following relationship[13]

$$x_e = \frac{h\omega_e}{4D_e} \qquad \text{(S-3)}$$

where h is Planck's constant, and D_e is the experimental dissociation energy. The r_e values for CoO^+, and FeS, and VS along with the r_e values for the other dimers are given in Table 1.

Table S-1. Experimental and scaled B3LYP[a] zero-point energies (given in kcal/mol) and the mean unsigned error (MUE) for the scaled B3LYP values.

	experiment	scaled
AgH	2.49	2.45
BeO	2.12	2.17
CoH	2.72	2.61
FeH	2.59	2.49
FeO	1.26	1.29
LiCl	0.92	0.89
RhC	1.50	1.53
VO	1.44	1.45
MUE		0.05

[a] The DZQ basis set was used for the transition elements and the 6-31G(2d,p) basis set was used for the main group elements.

Table S-2. The computed and experimental harmonic frequencies, MUEs for the unscaled frequencies and scaled frequencies (in cm^{-1}), and scale factors (*f*) for each method

	AgH	BeO	CoH	FeH	FeO	LiCl	LiO	MgO	RhC	VO	MUE		*f*
	ω_e										unscaled	scaled	
experiment	**1760**	**1487**	**1927**	**1827**	**880**	**643**	**813**	**785**	**1050**	**1013**			
						LSDA							
SPWL	1860	1520	1945	1848	969	641	881	641	1119	1055	59	46	0.973
SVWN3	1869	1528	1957	1863	984	644	887	644	1122	1061	66	46	0.967
						GGA							
BLYP	1740	1466	1855	1796	906	626	856	626	1046	994	41	33	1.020
BP86	1777	1469	1859	1810	928	620	845	620	1067	1010	41	40	1.011
BPBE	1772	1469	1864	1799	926	619	844	619	1070	1006	41	39	1.013
BPW91	1770	1470	1865	1801	925	619	845	619	1068	1005	41	38	1.013
G96LYP	1750	1469	1860	1797	916	620	838	620	1051	1000	39	35	1.018
HCTH	1713	1475	1785	1730	897	628	829	628	1072	949	59	50	1.041
mPWLYP	1746	1470	1852	1800	906	630	861	630	1048	995	39	34	1.018
mPWPBE	1776	1472	1870	1804	927	623	849	623	1072	1008	40	39	1.010
mPWPW91	1774	1473	1872	1805	926	623	850	623	1070	1007	39	38	1.010
OLYP	1716	1463	1788	1741	888	624	837	624	1071	992	55	46	1.038
PBEPBE	1770	1470	1852	1800	925	628	854	628	1074	1008	41	40	1.013
XLYP	1743	1468	1858	1798	906	628	858	628	1049	995	40	33	1.019
						Hybrid GGA							
B3LYP	1746	1544	1857	1790	914	636	884	636	1088	1029	49	49	1.005
B3P86	1783	1555	1886	1811	936	633	880	633	1107	1044	52	50	0.992
B3PW91	1767	1547	1863	1790	925	630	874	630	1103	1034	52	52	1.001
B97-1	1745	1547	1851	1801	938	624	888	624	1083	1034	54	54	1.003
B97-2	1744	1541	1853	1781	909	628	862	628	1096	1035	51	50	1.008
B98	1744	1554	1852	1800	943	623	888	623	1084	1035	56	56	1.002
BHandHLYP	1727	1643	1666	1674	708	648	913	648	1116	961	113	108	1.038
MPW1K	1759	1625	1786	1716	821	640	898	640	1129	954	82	81	1.016
mPW1PW91	1769	1564	1856	1785	916	634	882	634	1111	1040	55	55	0.999
MPW3LYP	1750	1551	1858	1790	913	641	891	641	1093	1032	50	50	1.002
O3LYP	1722	1510	1814	1750	915	630	858	630	1091	1012	54	51	1.022
PBE1PBE	1763	1560	1851	1779	917	637	884	637	1116	1042	56	56	1.000
X3LYP	1747	1550	1856	1788	913	630	864	639	1114	1032	51	51	1.004
						Meta GGA							
BB95	1751	1460	1821	1785	915	622	838	622	1066	1004	45	41	1.023
mPWB95	1756	1463	1824	1790	917	626	841	626	1067	1004	43	41	1.021
MPWKCIS	1752	1471	1845	1800	916	623	849	623	1058	1000	41	38	1.018
PBEKCIS	1744	1469	1841	1797	913	628	854	628	1060	1000	42	37	1.019
TPSSKCIS	1783	1480	1873	1810	925	630	855	630	1064	1002	38	37	1.007
TPSSTPSS	1792	1485	1869	1811	928	629	857	629	1066	1000	40	39	1.006
VSXC	1747	1479	1858	1789	898	619	855	619	1063	998	41	37	1.018
						Hybrid Meta GGA							
B1B95	1747	1552	1852	1775	921	634	871	634	1116	1042	56	55	1.004
BB1K	1742	1608	1847	1738	883	640	885	404	1130	954	90	89	1.012
MPW1B95	1750	1561	1854	1774	919	639	878	639	1120	1047	57	56	1.001
MPW1KCIS	1749	1525	1856	1792	920	630	869	630	1088	1023	47	46	1.007
MPWKCIS1K	1735	1617	1810	1742	836	639	895	639	1119	957	76	70	1.014
PBE1KCIS	1738	1548	1847	1783	913	636	881	636	1101	1033	53	53	1.006
TPSS1KCIS	1773	1524	1864	1798	926	635	871	635	1088	1021	45	43	0.992

TPSSh	1784	1520	1859	1800	928	633	869	633	1086	1014	45	45	0.986

Table S-3. Errors in Bond Dissociation Energies: The mean signed-, mean unsigned-, root mean squared-, and average mean unsigned errors (MSE, MUE, and AMUE, respectively), in kcal/mol, for the complexes in TMAE4/05.

method	MSE	MUE	RMSE	MSE	MUE	RMSE	AMUE
	DZQ			TZQ			
			LSDA				
SPWL	30.3	30.3	30.8	30.3	30.3	30.5	30.3
SVWN3	32.5	32.5	32.8	32.5	32.5	32.7	32.5
			GGA				
BLYP	9.2	9.2	11.4	10.0	10.0	11.1	9.6
BP86	11.9	11.9	13.0	12.6	12.6	13.0	12.3
BPBE	8.1	8.4	9.6	9.1	9.1	9.8	8.7
BPW91	8.0	8.4	9.6	8.9	8.9	9.6	8.6
G96LYP	7.0	8.1	9.7	7.2	7.2	8.4	7.7
HCTH	6.2	6.2	7.8	7.8	7.8	9.2	7.0
mPWLYP	11.1	11.1	12.9	11.7	11.7	12.5	11.4
mPWPBE	10.0	10.0	11.2	11.0	11.0	11.5	10.5
mPWPW91	9.9	9.9	11.1	10.8	10.8	11.4	10.4
OLYP	3.6	4.1	5.5	4.8	4.8	5.7	4.5
PBEPBE	12.1	12.1	12.8	12.9	12.9	13.4	12.5
XLYP	10.1	10.1	12.1	10.7	10.7	11.7	10.4
			GGA				
B3LYP	-1.3	6.4	7.6	-1.4	5.3	6.1	5.9
B3P86	1.2	5.1	6.3	1.3	5.1	5.6	5.1
B3PW91	-2.5	5.5	7.1	-2.4	5.9	6.6	5.7
B97-1	0.7	8.4	10.6	1.7	4.5	6.5	6.4
B97-2	-0.6	5.5	6.2	0.2	4.5	5.5	5.0
B98	-0.7	8.0	10.2	0.3	5.0	6.1	6.5
BHandHLYP	-17.7	17.8	21.8	-17.8	17.8	20.6	17.8
MPW1K	-13.1	13.1	15.6	-13.4	13.4	15.8	13.2
mPW1PW91	-4.7	7.0	8.6	-4.6	6.6	8.2	6.8
MPW3LYP	-1.2	7.0	8.4	-1.0	5.4	6.2	6.2
MPWLYP1M	7.7	8.2	10.4	8.2	8.2	9.2	8.2
O3LYP	-1.7	5.1	5.6	-1.0	4.2	4.8	4.7
PBE1PBE	-3.3	6.3	7.8	-3.2	6.4	7.4	6.4
X3LYP	-1.7	6.9	8.3	-1.6	5.7	6.3	6.3
			Meta GGA				
BB95	12.1	12.1	13.1	13.9	13.9	14.4	13.0
mPWB95	14.5	14.5	15.2	15.9	15.9	16.1	15.2
MPWKCIS	8.8	8.8	10.2	9.5	9.5	10.1	9.1
PBEKCIS	10.3	10.3	11.5	11.4	11.4	12.1	10.8
TPSSKCIS	8.0	8.0	9.1	9.6	9.6	10.1	8.8
TPSSTPSS	7.0	7.0	8.2	8.7	8.7	9.3	7.8
VSXC	7.8	7.8	9.2	5.5	5.5	6.0	6.7
			Hybrid Meta GGA				
B1B95	-4.4	7.2	8.1	-3.5	6.6	7.2	6.9
BB1K	-11.0	11.7	13.6	-10.2	11.2	12.8	11.4

MPW1B95	-4.6	7.6	8.4	-3.6	7.0	7.5	7.3
MPWK1CIS	0.0	5.0	6.4	-0.1	4.7	5.4	4.9
MPWKCIS1K	-13.6	13.6	16.1	-13.9	13.9	16.2	13.8
PBE1KCIS	-3.2	6.6	7.7	-3.0	6.1	6.8	6.4
TPSSTPSSh	1.4	4.6	5.4	2.6	4.8	5.5	4.7
TPSS1KCIS	0.8	4.4	5.5	1.6	4.6	5.2	4.5
			GGE				
BPWL	2.8	6.2	6.9	3.1	4.3	5.5	5.2
BVWN5	2.5	6.3	6.9	3.0	4.3	5.4	5.3
G96PWL	0.3	6.1	6.4	0.5	3.8	4.2	5.0
G96VWN5	0.1	6.1	6.4	0.4	3.8	4.2	4.9
mPWPWL	4.7	6.1	7.7	5.1	5.1	6.8	5.6
mPWVWN5	4.4	6.2	7.7	4.9	4.9	6.6	5.5
OPWL	-2.7	4.8	4.9	-1.8	3.9	3.9	4.3
OVWN5	-3.1	5.0	5.2	-1.7	3.7	3.7	4.4
PBEPWL	6.3	6.6	8.9	6.7	6.7	8.2	6.7
PBEVWN5	6.1	6.6	8.8	6.6	6.6	8.1	6.6
TPSSPWL	3.8	6.0	7.3	2.8	3.4	4.9	4.7
TPSSVWN5	3.7	6.0	7.2	2.7	3.4	4.9	4.7
			GGSC				
G96HLYP	3.9	6.3	7.5	4.1	4.9	5.8	5.6
MOHLYP	3.9	4.8	6.4	4.6	4.6	6.1	4.7

Table S-4: The root-mean-square errors (RMSEs) for the MLBE21/05 and TMAE9/05 databases of energies, the MLBL13/05 and TMBL8/05 databases of bond lengths, and the IP7/05 database of ionization potentials. The units are kcal/mol and Angstroms.

	Bond Energies				Bond Lengths				Ionization Pots.	
	MLBL21/05		TMAE9/05		ML13/05		TMBL8/05		IP7/05	
	DZQ	TZQ	DZQ	TZQ	DZQ	TZQ	DZQ	TZQ	DZQ	TZQ
					LSDA					
SPWL	29.5	31.5	23.6	30.2	0.032	0.038	0.052	0.076	15.1	12.2
SVWN3	31.6	33.8	26.8	35.5	0.032	0.040	0.051	0.061	25.3	22.6
					GGA					
BLYP	8.8	11.2	5.3	7.4	0.028	0.016	0.160	0.047	10.9	8.7
BP86	11.0	13.5	9.9	9.6	0.026	0.017	0.199	0.038	13.8	11.5
BPBE	8.4	10.5	14.4	9.5	0.026	0.016	0.269	0.030	9.8	7.9
BPW91	8.3	10.4	15.9	9.5	0.026	0.016	0.263	0.039	10.5	8.5
G96LYP	7.7	9.6	9.9	5.5	0.027	0.015	0.195	0.040	9.5	7.0
HCTH	6.6	9.5	10.4	15.4	0.025	0.014	0.300	0.286	6.8	6.1
mPWLYP	10.1	12.9	4.4	10.0	0.027	0.016	0.136	0.045	65.1	9.2
mPWPBE	9.7	12.1	12.2	8.6	0.025	0.016	0.253	0.035	10.6	8.6
mPWPW91	9.6	12.0	13.6	8.6	0.025	0.016	0.247	0.036	11.2	9.1
OLYP	5.6	8.1	13.3	9.2	0.026	0.021	0.279	0.254	3.7	4.1
PBEPBE	10.8	13.5	10.8	9.3	0.025	0.014	0.236	0.034	10.1	8.7
XLYP	9.4	12.1	5.0	8.8	0.028	0.016	0.151	0.046	11.1	8.6
					Hybrid GGA					
B3LYP	8.0	7.9	27.0	20.5	0.021	0.014	0.310	0.300	9.0	7.2
B3P86	6.5	7.7	26.5	20.6	0.020	0.021	0.316	0.307	19.1	17.4
B3PW91	7.7	7.2	32.8	27.1	0.020	0.019	0.344	0.333	6.8	5.8
B97-1	8.9	7.0	28.4	11.2	0.024	0.019	0.275	0.291	3.9	6.5
B97-2	7.0	6.7	19.6	7.8	0.021	0.020	0.279	0.284	5.1	8.7
B98	9.7	7.3	28.2	13.1	0.024	0.012	0.288	0.299	4.4	5.8
BHandHLYP	25.5	22.8	45.3	41.9	0.027	0.030	0.404	0.372	5.3	6.4
MPW1K	19.2	17.2	41.6	39.2	0.017	0.025	0.423	0.403	5.0	7.8
mPW1PW91	10.0	8.7	34.8	32.7	0.018	0.019	0.358	0.346	5.7	5.1

MPW3LYP	8.8	7.8	27.9	20.2	0.020	0.014	0.309	0.300	8.3	6.4
MPWLYP1M	8.5	9.6	9.5	3.3	0.027	0.015	0.227	0.062	9.6	8.0
O3LYP	6.3	7.0	21.9	16.3	0.021	0.013	0.323	0.315	4.2	4.8
PBE1PBE	9.1	7.7	33.6	31.6	0.017	0.019	0.350	0.339	5.0	4.8
X3LYP	8.5	7.5	28.0	21.6	0.020	0.014	0.311	0.302	7.4	5.8
					Meta GGA					
BB95	12.1	14.6	17.6	12.3	0.025	0.016	0.334	0.325	7.2	6.8
mPWB95	13.7	16.3	18.1	15.5	0.025	0.017	0.357	0.351	7.5	495.1
MPWKCIS	8.8	15.1	11.3	7.7	0.027	0.015	0.334	0.326	13.8	11.7
PBEKCIS	10.1	13.7	8.8	9.2	0.026	0.015	0.373	0.371	13.5	11.9
TPSSKCIS	7.7	10.4	12.4	8.9	0.024	0.015	0.334	0.325	7.4	6.5
TPSSTPSS	7.3	9.8	13.7	10.0	0.024	0.014	0.313	0.287	6.9	5.9
VSXC	8.7	8.4	15.4	11.2	0.028	0.017	0.320	0.301	5.2	4.9
					Hybrid Meta GGA					
B1B95	8.2	8.0	32.6	29.1	0.017	0.020	0.599	0.597	4.4	5.7
BB1K	16.5	14.2	38.5	35.4	0.015	0.023	0.154	0.115	3.8	6.5
MPW1B95	9.8	8.6	32.5	28.5	0.016	0.020	0.135	0.101	3.3	5.9
MPWK1CIS	6.4	7.0	26.0	20.1	0.022	0.013	0.197	0.210	9.6	8.4
MPWKCIS1K	19.8	17.6	41.3	38.7	0.018	0.025	0.317	0.139	6.2	6.1
PBE1KCIS	8.7	7.7	31.7	26.2	0.019	0.017	0.244	0.065	8.1	7.0
TPSSTPSSh	6.5	7.7	23.4	16.3	0.021	0.014	0.263	0.057	4.4	5.0
TPSS1KCIS	6.4	6.9	25.4	16.4	0.020	0.014	0.275	0.072	5.3	5.0
					GGE					
BPWL	6.5	8.6	12.3	6.6	0.033	0.020	0.267	0.070	18.8	17.0
BVWN5	6.5	9.0	12.6	6.8	0.033	0.020	0.270	0.070	18.9	16.7
G96PWL	6.2	7.7	17.7	11.2	0.031	0.020	0.293	0.065	17.4	15.4
G96VWN5	6.2	7.7	17.9	11.5	0.031	0.020	0.294	0.065	17.4	15.5
mPWPWL	7.1	9.5	9.6	5.8	0.032	0.020	0.252	0.067	19.5	17.7
mPWVWN5	7.1	9.5	9.9	5.5	0.032	0.019	0.254	0.067	19.6	17.8
OPWL	6.3	7.6	19.1	13.7	0.030	0.017	0.337	0.319	10.2	9.6
OVWN5	6.4	7.5	19.3	13.9	0.029	0.017	0.338	0.320	10.3	9.8
PBEPWL	7.8	10.5	7.1	5.9	0.031	0.020	0.233	0.071	19.4	17.6

PBEVWN5	7.8	10.4	7.4	6.0	0.030	0.019	0.236	0.069	19.4	17.8
TPSSPWL	7.0	8.2	15.1	8.5	0.031	0.019	0.284	0.073	15.0	15.1
TPSSVWN5	7.0	8.1	15.3	8.8	0.031	0.019	0.286	0.075	15.1	15.2
					GGSC					
G96HLYP	6.4	8.3	13.6	7.1	0.029	0.017	0.251	0.051	12.8	10.7
MOHLYP	6.2	8.2	11.0	7.1	0.040	0.024	0.279	0.083	3.4	3.7

(1) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *submited*.

(2) Huber, K. P.; Herzberg, G. "Constants of Diatomic Molecules"(data prepared by J.W. Gallagher and R. D. Johnson, III). In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2003.

(3) Lipus, K.; Nelis, T.; Bachem, K.; Urban, W. *Mol. Phys.* **1989**, *68*, 1171.

(4) Ram, R. S.; Bernath, P. F.; Davis, S. P. *J. Mol. Spectros.* **1996**, *175*, 1.

(5) Phillips, J. G.; Davis, S. P.; Lindgren, B.; Balfour, W. J. *Astrophys. J. Suppl. Ser.* **1987**, *65*, 721.

(6) Taylor, A. W.; Cheug, A. S.-C.; Merer, A. J. *J. Mol. Spectrosc.* **1985**, *113*, 487.

(7) Merer, A. J. *Annu. Rev. Phys. Chem.* **1989**, *40*, 407.

(8) Yamada, C.; Fujitake, M.; Hirota, E. *J. Chem. Phys.* **1989**, *91*, 137.

(9) DaBell, R. S.; Meyer, R. G.; Morse, M. D. *J. Chem. Phys.* **2001**, *114*, 2938.

(10) Lagerqvist, V. A.; Selin, L. *Ark. Fys.* **1957**, *12*, 553.

(11) Pekeris, C. L. *Phys. Rev.* **1933**, *45*, 98.

(12) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(13) Davis, J. C. J. *Advanced Physical Chemistry*; The Ronald Press Company: New York, 1965.