SUPPORTING INFORMATION

FOR

Multi-Configuration Pair-Density Functional Theory

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Table S1. Main group atomic vertical excitation energies (eV) computed with cc-pVTZ[1]/cc-pVQZ[1] basis sets

Atom	Active Space[a]	CASSCF	CASPT2[b]	tBLYP	tPBE	tGVWN3	BLYP		PBE		GVWN3		Exp.
							Var.[c]	WABS[d]	Var.	WABS	Var.	WABS	
Be	2,4	2.9/2.9	2.8/2.8	2.6/2.5	2.6/2.5	2.6/2.6	2.5/2.5	2.5/2.5	2.3/2.3	2.3/2.3	2.4/2.4	2.4/2.4	2.73[e]
	2,5	2.9/2.9	2.8/2.8	2.6/2.6	2.6/2.6	2.6/2.6							
	2,8	2.9/2.9	2.8/2.8	2.6/2.6	2.6/2.6	2.6/2.6							
C	4,4	1.6/1.6	1.3/1.2	1.0/1.0	1.1/1.1	1.0/1.0	0.3/0.3	0.7/0.7	0.4/0.4	0.8/0.8	0.6/0.6	1.3/1.3	1.26[f]
	4,5	1.6/1.6	1.3/1.3	1.0/1.0	1.1/1.1	1.0/1.0							
	4,8	1.5/1.5	1.3/1.3	1.1/1.1	1.2/1.2	1.1/1.1							
N^+	4,4	2.2/2.2	1.9/1.9	1.5/1.5	1.5/1.5	1.4/1.4	0.6/0.5	1.1/1.1	0.6/0.6	1.2/1.2	0.9/0.9	1.9/1.9	1.89[f]
	4,5	2.3/2.3	2.0/2.0	1.5/1.5	1.5/1.5	1.5/1.5							
	4,8	2.2/2.2	2.0/2.0	1.6/1.6	1.7/1.7	1.6/1.6							
N	5,4	2.8/2.8	2.5/2.4	1.8/1.8	1.9/1.9	1.8/1.8	0.9/0.9	1.4/1.4	1.1/1.1	1.6/1.6	1.5/1.5	2.3/2.3	2.38[f]
	5,5	2.2/2.2	2.5/2.4	1.9/1.9	2.0/2.0	2.0/2.0							
	5,8	2.5/2.5	2.5/2.5	2.0/2.0	2.1/2.1	2.0/2.0							
O^+	5,4	3.7/3.6	3.4/3.4	2.4/2.4	2.5/2.5	2.5/2.5	1.4/1.4	2.1/2.1	1.5/1.5	2.3/2.3	2.1/2.1	3.2/3.2	3.32[g]
	5,5	3.1/3.1	3.4/3.4	2.6/2.6	2.6/2.6	2.6/2.6							
	5,8	3.0/3.0	3.4/3.3	2.6/2.6	2.7/2.7	2.7/2.7							

Table S1 (continued). Main Group Atomic Vertical Excitation Energies (eV) Computed with cc-pVTZ/(cc-pVQZ) Basis Sets

Atom	Active Space[a]	CASSCF	CASPT2[b]	tBLYP	tPBE	tGVWN3	BLYP		PBE		GVWN3		Exp.
							Var.[c]	WABS[d]	Var.	WABS	Var.	WABS	
O	6,4	2.2/2.2	2.0/1.9	1.2/1.2	1.3/1.3	1.2/1.2	0.7/0.6	1.3/1.3	0.7/0.7	1.4/1.4	0.9/0.9	1.8/1.8	1.96[f]
	6,5	2.1/2.1	2.0/2.0	1.4/1.5	1.3/1.3	1.2/1.2							
	6,8	2.1/2.1	2.1/2.0	1.4/1.5	1.5/1.5	1.4/1.4							
MAE[h]	(n,4)	0.3/0.3	0.07/0.04	0.5/0.5	0.5/0.5	0.5/0.5	1.2/1.2	0.8/0.8	1.2/1.2	0.7/0.7	0.9/0.9	0.12/0.13	
	(n,5)	0.2/0.2	0.08/0.04	0.4/0.4	0.4/0.4	0.4/0.4							
	(n,8)	0.2/0.2	0.09/0.04	0.4/0.4	0.3/0.3	0.4/0.4							

[a] The active space choices are given for each atom with the notation n/m, where n is the number of active electrons, and m is the number of active orbitals. Active Spaces (n,4) include the valence $2s$ and $2p$ orbitals, where n is the number of valence electrons. Active spaces (n, 5) and (n, 8) include correlating $3s$ and $3s$ with $3p$, respectively.

[b] An imaginary level shift[2] of 5.4 eV was for all CASPT2 calculations to keep out intruder states.[2]

[c] Variational Kohn-Sham DFT calculations.

[d] Weighted Average Broken Symmetry (WABS) Kohn-Sham DFT calculations.

[e] Kramida, A.; Martin, W. C. *J. Phys. Chem. Ref. Data*, **1997**, *26*, 1185–1194.

[f] Moore, C. E. *CRC Series in Evaluated Data in Atomic Physics*; Gallager, J. W., Ed.; CRC Press: Boca Raton, FL, 1993.

[g] Martin, W. C.; Kaufman, V.; Musgrove, A. *J. Phys. Chem. Ref. Data* **1993,** *22*, 1179–1212.

[h] The MAE includes all results in Table S1

[1] Dunning, Jr., T.H. *J. Chem. Phys.* **1989,** *90*, 1007-1023.

[2] Forsberg, N.; Malmqvist, P. -Å. *Chem. Phys. Lett.* **1997**, *274*, 196-204.

Table S2. Transition metal atomic excitation energies (eV) computed with ANO-RCC-VTZP[1]/ANO-RCC-VQZP[1] basis sets

Atom	Excitation	Active Space[a]	CASSCF	CASPT2[b]	tBLYP	tPBE	tGVWN3	BLYP		PBE		GVWN3		Exp.
								Var.[c]	WABS[d]	Var.	WABS	Var.	WABS	
Mn	$^6S \rightarrow {}^8P$	7,9	2.2/2.0	2.3/2.3	2.4/2.2	2.2/2.0	2.4/2.2	2.9/2.9	2.9/2.9	2.3/2.3	2.3/2.3	2.6/2.5	2.6/2.5	2.15[e]
Mo	$^7S \rightarrow {}^5S$	6,6	1.7/1.6	1.7/1.6	1.8/1.8	2.0/2.0	1.9/1.8	0.9/1.0	1.1/1.2	1.3/1.3	1.6/1.6	1.4/1.4	1.6/1.7	1.34[f]
		6,7	1.7/1.6	1.6/1.6	1.8/1.8	2.0/2.0	1.9/1.8							
		6,12	1.7/1.7	1.5/1.5	1.7/1.7	1.9/1.9	1.8/1.7							
Ru	$^5F \rightarrow {}^3F$	8,6	1.0/1.0	1.0/1.0	0.9/1.0	1.1/1.0	0.9/1.0	0.6/0.6	0.8/0.8	0.7/0.8	0.9/1.1	0.7/0.6	0.9/0.9	0.78[g]
		8,7	0.9/0.9	1.0/0.9	1.0/1.0	1.0/1.0	1.0/1.0							
		8,12	1.0/1.0	0.9/0.8	1.0/1.0	1.0/1.0	1.0/0.9							
Sc^+	$^3D \rightarrow {}^1D$	2,6	0.4/0.4	0.3/0.3	0.5/0.5	0.5/0.5	0.4/0.4	0.2/0.2	0.3/0.3	0.2/0.2	0.5/0.5	0.2/0.2	0.5/0.5	0.30[e]
		2,7	0.4/0.4	0.3/0.3	0.5/0.5	0.5/0.5	0.4/0.4							
		2,12	0.4/0.4	0.3/0.3	0.5/0.5	0.5/0.5	0.4/0.4							
Co	$^4F \rightarrow {}^2F$	9,6	2.3	0.4	1.0	0.9	0.8	0.3/0.4	0.2/0.7	0.1/0.5	0.1/0.7	0.2/0.4	0.3/0.7	0.89[e]
		9,12	1.0	1.1	0.9	0.7	0.6							
	MAE[h]	FV[3]	0.4/0.18	0.3/0.14	0.2/0.2	0.2/0.3	0.2/0.2	0.3/0.4	0.2/0.3	0.11/0.14	0.2/0.2	0.2/0.2	0.3/0.2	
	MAE[h]	(*n*,7)	0.2/0.19	0.17/0.13	0.3/0.3	0.4/0.4	0.3/0.3							
	MAE[h]	(*n*,12)	0.17/0.2	0.4/0.07	0.2/0.2	0.3/0.3	0.2/0.2							

[a] The active space choices are given for each atom with the notation *n*/*m*, where *n* is the number of active electrons, and *m* is the number of active orbitals. The full valance active space choices for each atom including the *d* and *s* orbitals. For Mo and Ru, these include the 4*d* and 5*s* orbitals. For Mn, these include the 4*s*, 4*p*, and 4*d* orbitals. For Sc^+ and Co, these are the 3*d* and 4*s* orbitals. The (*n*, 7) active spaces include a correlating *s* orbital. The (*n*, 12) includes a correlating *s* and *d* shell.

[b] An imaginary level shift[2] of 0.2 a.u. was for all CASPT2 calculations to keep out intruder states.

[c] Variational Kohn-Sham DFT calculations.

[d] Weighted Average Broken Symmetry (WABS) Kohn-Sham DFT calculations.

[e] Sugar, J.; Corliss, C. Atomic Energy Levels of the Iron-Period Elements: Potassium through Nickel, *J. Phys. Chem. Ref. Data*, **1985**, *14, Suppl. 2*, 1-664.

[f] Sugar, J.; Musgrove, A. *J. Phys. Chem. Ref. Data*, **1988**, *17*, 155–239.

[g] Moore, C. E. *Ref. Data Ser. 35, Vol. III (Reprint of NBS Circ. 467, Vol. III, 195*8), Nat. Bur. Stand.: 1971; p 245.

[h] MAE includes all data in Table S2.

[1] Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575-6579.

[2] Forsberg, N.; Malmqvist, P. -Å. *Chem. Phys. Lett.* **1997**, *274*, 196-204.

[3] Full valence

Table S3. Singlet to singlet vertical electronic excitations in eV. A cc-pVTZ basis set[1] was used for all species except for N_2 and butadiene for which an aug-cc-pVTZ basis set[1,2] was used.

System	AS[a]	CASSCF	CASPT2[b]	tBLYP	tPBE	tGVWN3	BLYP	PBE	GVWN3	Exp.
Be $^1S \rightarrow {}^1P$	2,4	6.2/6.1	5.7/5.7	4.2/4.3	4.4/4.4	4.3/4.3	5.0/4.9	5.0/5.0	5.0/5.0	5.28[c]
$N_2\ \sigma_g \rightarrow \pi_g$	6,6	11.9/11.9	9.4/9.4	8.6/8.6	8.6/8.6	8.6/8.6	9.1/9.1	9.1/9.1	9.1/9.1	9.31[d]
$N_2\ \pi_u \rightarrow \pi_g$	6,6	10.9/10.9	9.8/9.8	9.5/9.5	9.6/9.6	9.6/9.6	9.6/9.6	9.7/9.7	9.7/9.7	9.92[d]
trans-1,3-butadiene $\pi \rightarrow \pi^*$	4,4	7.6/7.5	6.8/6.9	5.6/5.8	5.7/5.9	5.9/6.1	5.3/5.3	5.5/5.5	5.5/5.5	5.92[e]
Pyrazine $n \rightarrow \pi^*$	10,10	5.3/5.3	4.1/4.1	3.9/3.9	3.9/3.9	3.8/3.8	3.6/3.6	3.6/3.6	3.6/3.5	4.20[f]
Cyclopentadiene $\pi \rightarrow \pi^*$	4,4	7.3/7.3	5.5/5.4	4.1/4.1	4.1/4.1	4.1/4.1	4.9/4.9	5.0/5.0	5.0/5.0	5.26[g,h]
Formaldehyde $n \rightarrow \pi^*$	8,6	4.4/4.4	4.0/4.0	4.0/4.0	4.0/4.0	4.0/4.0	4.0/4.0	3.9/3.9	3.8/3.8	4.00[i]
MAE[j]		1.4/1.3	0.3/0.3	0.6/0.5	0.5/0.5	0.5/0.5	0.3/0.3	0.3/0.3	0.3/0.3	

[a] For Be and N_2, active spaces are the full valence active spaces. For *trans*-1,3-butadiene, cyclopentadiene, and pyrazine the active space includes the π electrons, π bonding/antibonding orbitals, and additional nitrogen lone pairs/orbitals for pyrazine. For formaldehyde, the active space includes all the electrons, lone pair orbitals, and bonding/antibonding orbitals of the carbonyl. The basis sets are aug-cc-pVTZ (aug-cc-pVQZ)[1,2] for N_2 and butadiene and cc-pVTZ (cc-pVQZ)[1] for the other systems.

[b] An imaginary level shift of 0.2 hartrees was used for all CASPT2 calculations to keep out intruder states.[3]

[c] Kramida, A.; Martin, W. C. *J. Phys. Chem. Ref. Data*, **1997**, *26*, 1185–1194.

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[e] Doering, J. P.; McDiarmid, R. *J. Chem. Phys.* **1980**, *73*, 3617-3624.

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[h] McDiarmid, R.; Sabljić, A.; Doering, J. P. *J. Chem. Phys.* **1985**, *83*, 2147-2152.

[i] Wiberg, K. B.; de Oliveira, A. E.; Trucks, G. *J. Phys. Chem.* **2002**, *106*, 4192-4199.

[j] The MAE includes only the quadruple zeta results in the SI table. For N_2, an equilibrium geometry of 1.098 Å was used.[4] All other geometries were optimized according to specifications in Table S5 with M06-L.[5]

[1] Dunning, Jr., T.H. *J. Chem. Phys.* **1989,** *90*, 1007-1023.

[2] Kendall, R.A.; Dunning, Jr., T.H.; Harrison, R.J. *J. Chem. Phys.* **1992**, *96*, 6796-6806.

[3] Forsberg, N.; Malmqvist, P. -Å. *Chem. Phys. Lett.* **1997**, *274*, 196-204.

[4] Lofthus, A.; Krupenie, P. H. *J. Phys. Chem. Ref. Data* **1977**, *6*, 113-307.

[5] Zhao, Y.; Truhlar, D. G. J. *Chem. Phys.* **2006**, *125*, 194101.

Table S4. Dissociation Energies (eV) of Various Diatomic Molecules

Atom	AS[a]	CASSCF	CASPT2[b]	tBLYP	tPBE	tGVWN3	BLYP		PBE		GVWN3		Exp.
							Var.[e]	WABS[f]	Var.	WABS.	VAR.	WABS.	
H_2	2,2	4.1/4.1	4.6/4.6	4.9/4.9	4.7/4.7	5.0/5.0	4.8/4.8	4.8/4.8	4.5/4.5	4.5/4.5	4.9/4.9	4.9/4.9	4.75[g]
N_2	6,6	8.8/8.9	9.4/9.6	9.4/9.4	9.8/9.8	11.1/11.2	10.4/10.4	10.4/10.4	10.6/10.6	10.6/10.6	11.9/11.9	11.9/11.9	9.74[h]
F_2	2,2	0.7/0.7	1.5/1.6	1.9/1.9	2.1/2.1	2.8/2.8	2.2/2.2	2.2/2.2	2.4/2.3	2.4/2.3	3.5/3.5	3.5/3.5	1.66[i]
Cr_2	12,12*	0.0/0.0[c]	1.0[d]/1.0	0.5/0.5	0.6/0.7	2.3/2.3	2.1/2.2	2.5/	1.6/1.7	2.1/	3.5/3.6	3.7/	1.47[j]
	12,12**	0.0	1.3	0.5	0.6	2.3	2.2	-	1.7	-	3.5	-	
CaO	8,8	3.9/4.2	3.5/4.4	4.0/4.2	4.2/4.5	5.2/5.5	4.7/5.3	4.7/5.3	5.0/5.5	5.0/5.5	6.1/6.9	6.1/6.9	4.22[k]
NiCl	11,12	2.7	3.9	3.4	4.1	4.8	3.4	3.7	3.7	3.7	4.5	4.6	3.97[l,m]
MAE[n]		0.9	0.3	0.4	0.4	0.9	0.6	0.5	0.5	0.6	1.6	1.6	

[a] The active space (AS) choice for H_2 and N_2 includes the bonding electrons and bonding/antibonding orbitals. For F_2, the active space includes one 2*p* electron and orbital on each atom contributing to the ^{2}P configuration of the neutral atom. These first row diatomic molecules were computed with cc-pVTZ/cc-pVQZ[1,2] basis sets. For Cr_2, the active space includes the 3*d* and 4*s* electrons and orbitals on each atom. The (12,12)* series were calculated with a cc-pVTZ-DK/cc-pVQZ-DK[3] basis sets and the (12,12)** series was calculated with the ANO-RCC-VTZP[4] basis set. The AS for CaO includes the 4*s* electrons on Ca, and the 2*s* and 2*p* electrons on O. In addition to these orbitals, there is a correlating 4*p* shell on Ca. The basis set used on CaO were the cc-pV5Z[5] and the aug-cc-pV5Z[2] for Ca and O, respectively. Lastly, for the NiCl, the active space includes the *d* electrons on Ni and one 2*p* electron and orbital on Cl that contributes to the ^{2}P configuration of the neutral atom; the basis sets used were ANO-RCC-VTZP.[4]

[b] All CASPT2 calculations were done with an imaginary shift of 5.4 eV and an IPEA value of 6.80 eV.

[c] For CASSCF, the dissociation energy is zero because Cr_2 is not bound.

[d] CASPT2 calculation with IPEA value of 6.8 eV and imaginary shift of 5.4 eV. For Cr_2, these standard values predict an incorrect equilibrium bond distance of 2.1 Å with ANO-RCC-VTZP and 2.6 Å (exp. = 1.679 Å)[j]

[e] Variational Kohn–Sham DFT calculations.

[f] Weighted Average Broken Symmetry (WABS) Kohn–Sham DFT calculations.

[g] Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

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[m] Zhang, W.; Truhlar, D. G.; Tang, M. *J. Chem. Theory Comput.* **2013**, *9*, 3965-3977.

[n] A combined MAE is calculated and includes all data in Table S4

[1] Dunning, Jr., T.H. *J. Chem. Phys.* **1989,** *90*, 1007-1023.

[2] Kendall, R.A.; Dunning, Jr., T.H.; Harrison, R.J. *J. Chem. Phys.* **1992**, *96*, 6796-6806.

[3] Balabanov, N.B.; Peterson, K.A. *J. Chem. Phys.*, **2005**, *123*, 064107.

[4] Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575-6579.

[5] Koput, J. ; Peterson, K.A. *J. Phys. Chem. A*, **2002**, *106*, 9595-9599.

Table S5. Optimized Geometries

M06-L[1]/6-311+G(d,p)[2-4] optimized geometries

Butadiene

C	-0.387860	0.610999	0.000000
C	0.387860	-0.610999	0.000000
C	-0.140864	-1.839758	0.000000
C	0.140864	1.839758	0.000000
H	1.216961	1.989699	0.000000
H	-0.476926	2.729738	0.000000
H	-1.471766	0.494436	0.000000
H	1.471766	-0.494436	0.000000
H	0.476926	-2.729738	0.000000
H	-1.216961	-1.989699	0.000000

Pyrazine

C	1.128456	-0.695924	0.000029
C	1.128454	0.695927	0.000042
N	-0.000003	1.406203	0.000015
C	-1.128454	0.695927	-0.000028
C	-1.128452	-0.695930	-0.000043
N	0.000000	-1.406203	-0.000015
H	2.062214	-1.254579	0.000050
H	2.062211	1.254584	0.000073
H	-2.062215	1.254577	-0.000047
H	-2.062213	-1.254581	-0.000076

Formaldehyde

C	-0.523993	0.000000	0.000003
O	0.673370	0.000002	-0.000001
H	-1.121513	0.939152	-0.000005
H	-1.121489	-0.939164	-0.000005

M06-L/6-31+G(2d,p)[3-6] optimized geometries

Cyclopentadiene

C	-0.284536	-1.173722	0.000051
C	0.989408	-0.729261	0.000059
C	0.989635	0.728954	-0.000056
C	-0.284171	1.173810	-0.000058
H	-0.613148	-2.204482	0.000106
H	1.880976	-1.344585	0.000107
H	1.881394	1.344002	-0.000100
H	-0.612467	2.204671	-0.000119
C	-1.207959	0.000187	-0.000001
H	-1.875488	0.000328	0.872248
H	-1.875529	0.000253	-0.872216

[1] Zhao, Y.; Truhlar, D. G. J. *Chem. Phys*. **2006**, *125*, 194101.

[2] Krishnan, R. ; Binkley, J.S.; Seeger, R.; Pople, J.A. *J. Chem. Phys*. **1980**, 72, 650-654.

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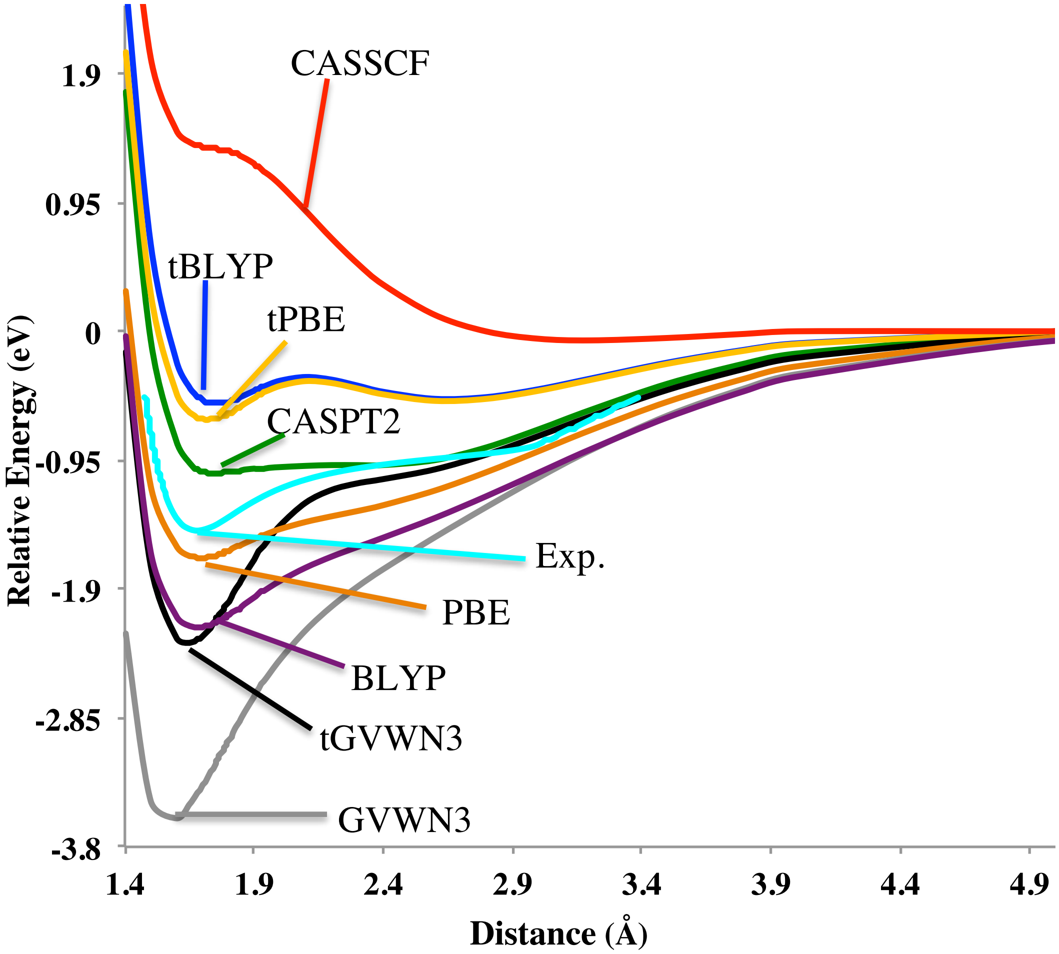

Figure S1. Potential energy curves with all functionals for Cr_2 computed with a cc-pVQZ-DK[1] basis set and DKH second order Hamiltonian. A (12,12) active space was used that includes the 3 *d* and 4 *s* electrons and orbitals on each atom. A 6.80 eV IPEA value along with an imaginary shift of 5.4 eV was used in the CASPT2 calculations to keep out intruder states.[2,3] The experimental curve is shown for experimentally measurable distances and is shifted to a common asymptote by the experimentally determined dissociation energy.[4]

[1] Balabanov, N.B.; Peterson, K.A. *J. Chem. Phys.*, **2005**, *123*, 064107.

[2] Ruiperez, F.; Aquilante, F.; Ugalde, J. M.; Infante, I. *J. Chem. Theory Comput.* **2011**, *7*, 1640-1646.

[3] Forsberg, N.; Malmqvist, P. -Å. *Chem. Phys. Lett.* **1997**, *274*, 196-204.

[4] Casey, S. M.; Leopold, D. G. *J. Phys. Chem.* **1993**, *97*, 816-830.

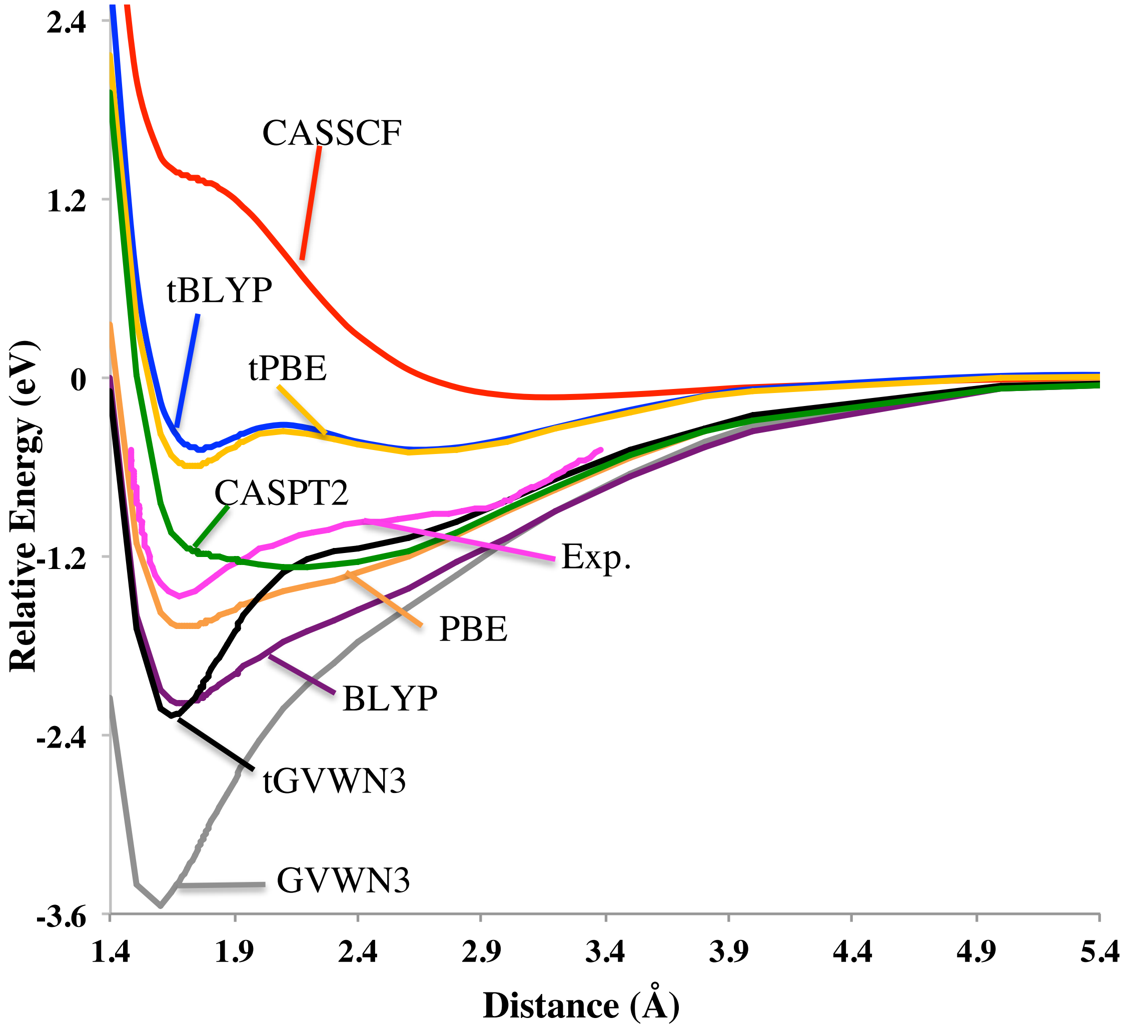

Figure S2. Potential energy curves with all functionals for Cr_2 computed with an ANO-RCC-VTZP[1] basis set and DKH second order Hamiltonian. A (12,12) active space was used that includes the 3 *d* and 4 *s* electrons and orbitals on each atom. A 6.80 eV IPEA value along with an imaginary shift of 5.4 eV was used in the CASPT2 calculations to keep out intruder states.[2,3] The experimental curve is shown for experimentally measurable distances and is shifted to a common asymptote by the experimentally determined dissociation energy.[4]

[1] Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575-6579.

[2] Ruiperez, F.; Aquilante, F.; Ugalde, J. M.; Infante, I. *J. Chem. Theory Comput*. **2011**, *7*, 1640-1646.

[3] Forsberg, N.; Malmqvist, P. -Å. *Chem. Phys. Lett*. **1997**, *274*, 196-204.

[4] Casey, S. M.; Leopold, D. G. *J. Phys. Chem*. **1993**, *97*, 816-830.

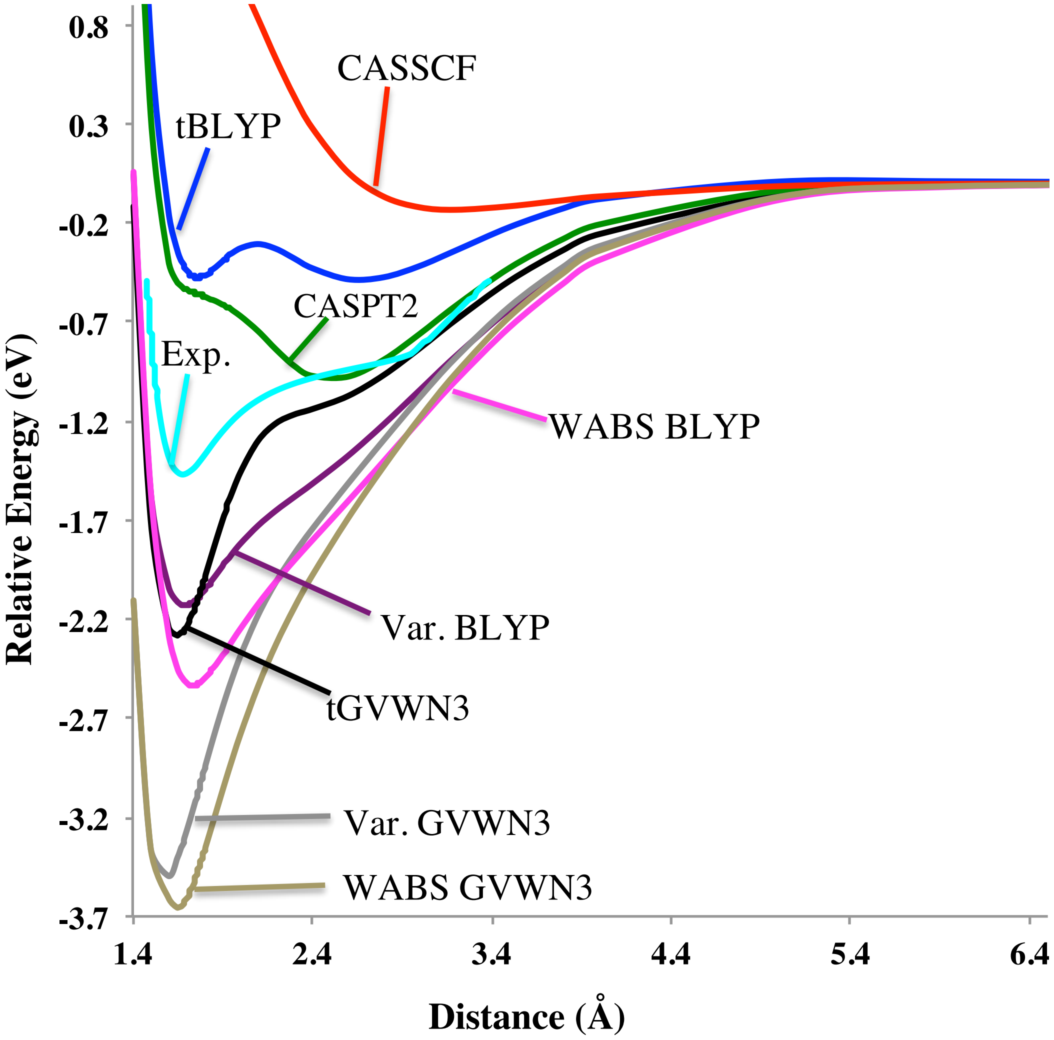

Figure S3. Potential energy curves without PBE for Cr_2 computed with a cc-pVTZ-TK[1] basis set and DKH second order Hamiltonian. A (12,12) active space was used that includes the 3 *d* and 4 *s* electrons and orbitals on each atom. A 6.80 eV IPEA value along with an imaginary shift of 5.4 eV was used in the CASPT2 calculations to keep out intruder states.[2,3] The experimental curve is shown for experimentally measurable distances and is shifted to a common asymptote by the experimentally determined dissociation energy.[4]

[1] Balabanov, N.B.; Peterson, K.A. *J. Chem. Phys.*, **2005**, *123*, 064107.

[2] Ruiperez, F.; Aquilante, F.; Ugalde, J. M.; Infante, I. *J. Chem. Theory Comput.* **2011**, *7*, 1640-1646.

[3] Forsberg, N.; Malmqvist, P. -Å. *Chem. Phys. Lett.* **1997**, *274*, 196-204.

[4] Casey, S. M.; Leopold, D. G. *J. Phys. Chem.* **1993**, *97*, 816-830.

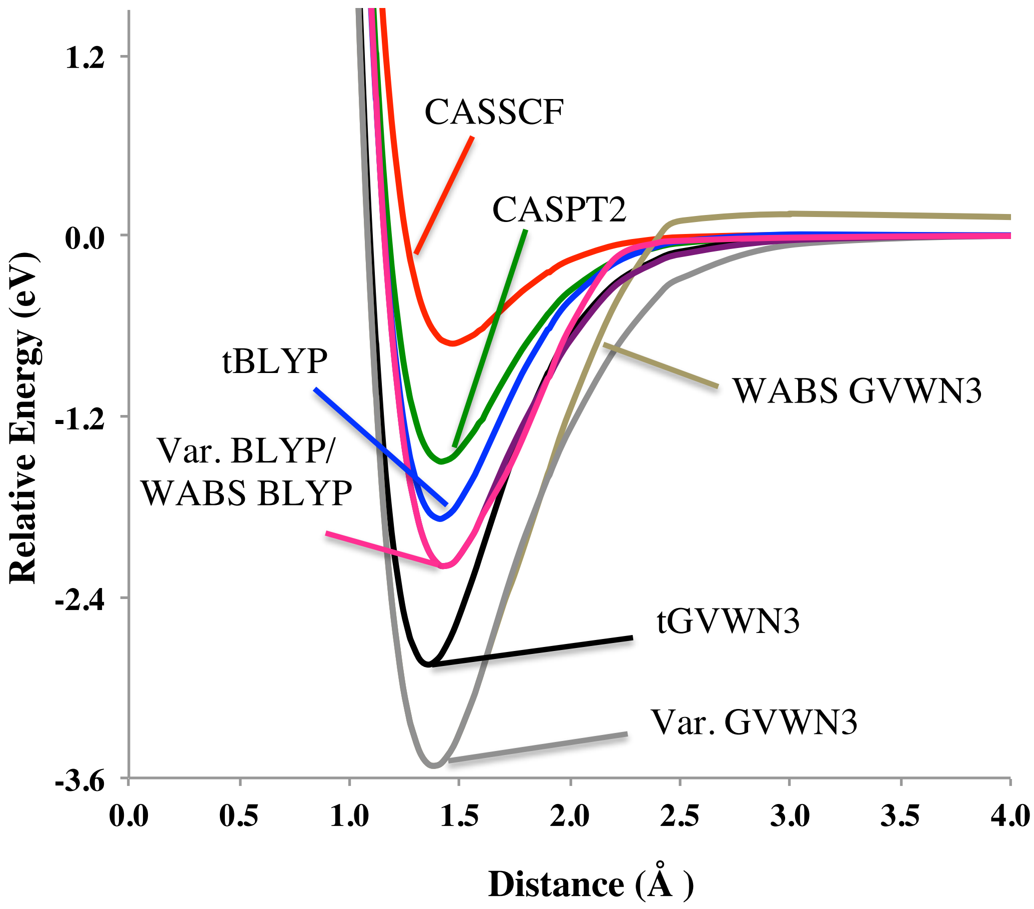
1.2
0.0
-1.2
-2.4
-3.6
Relative Energy (eV)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Distance (Å)
CASSCF
CASPT2
tBLYP
Var. BLYP/
WABS BLYP
WABS GVWN3
tGVWN3
Var. GVWN3

Figure S4a

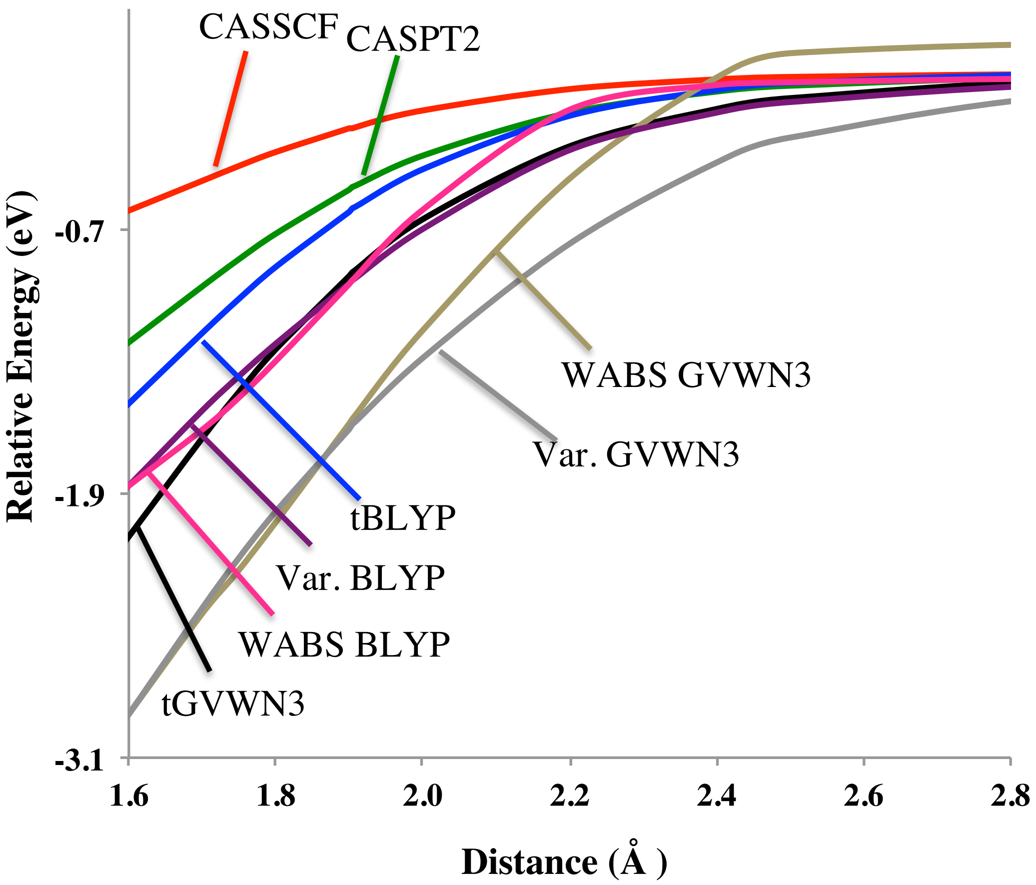

Figure S4b

Figure S4. Potential energy curves of F_2 without PBE computed with a cc-pVTZ[1] basis set and a (2,2) active space. Each atom has one 2 *p* electron and orbital. (a) Part a shows the whole range of distances. (b) Part b is a blowup of the region from 1.6 to 2.8 Å.

[1] Dunning, Jr., T.H. *J. Chem. Phys.* **1989,** *90*, 1007-1023.

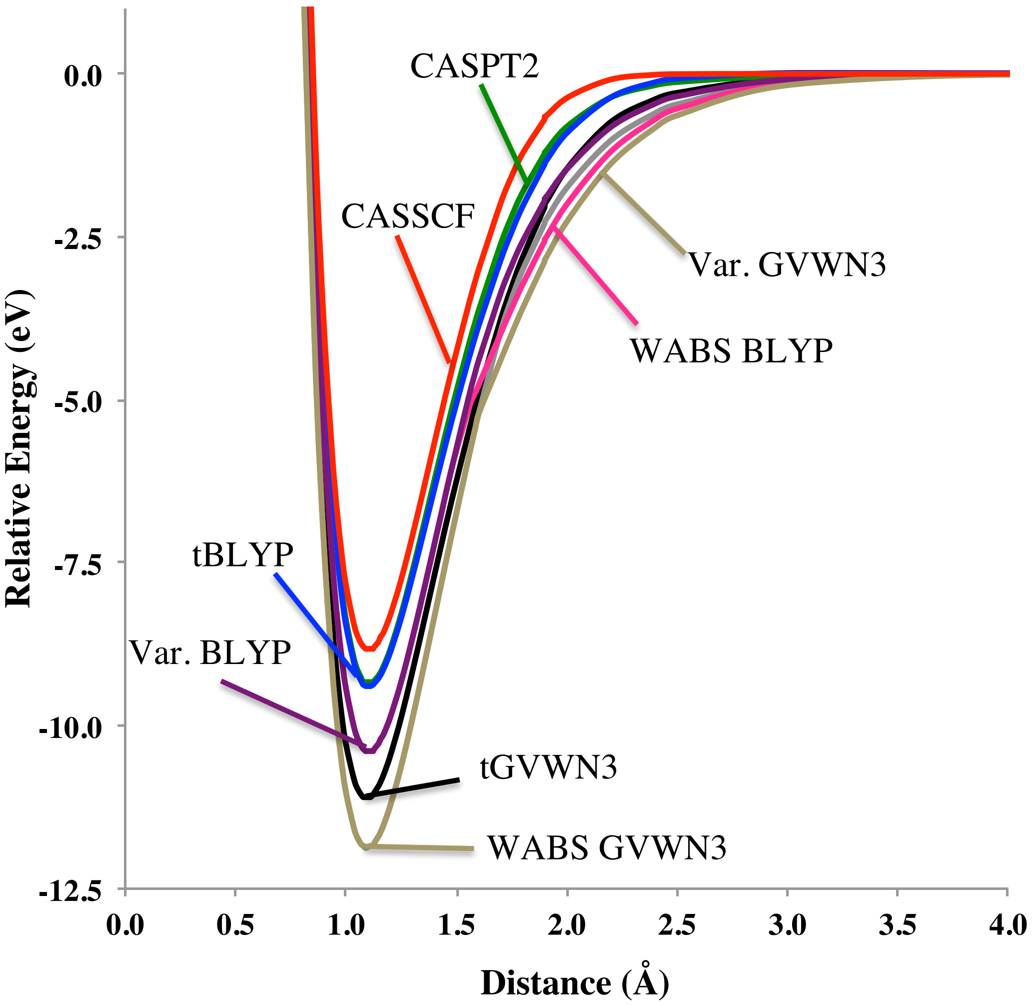
Relative Energy (eV)
0.0
-2.5
-5.0
-7.5
-10.0
-12.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Distance (Å)
CASPT2
CASSCF
Var. GVWN3
WABS BLYP
tBLYP
Var. BLYP
tGVWN3
WABS GVWN3

Figure S5a

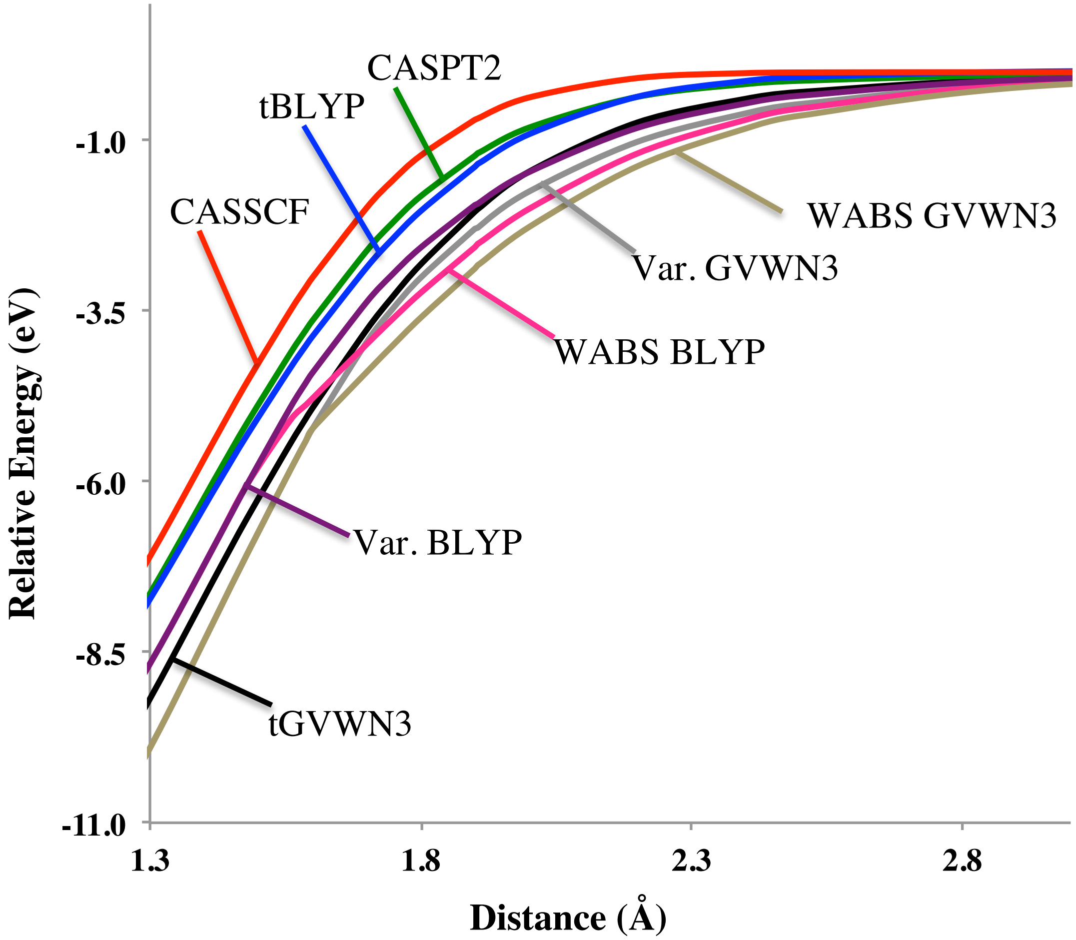

Figure S5b

SI Figure 5. Potential energy curves of N_2 without PBE computed with a cc-pVTZ[1] basis set and a (6,6) active space. The active space corresponds to the bonding electrons and orbitals. (a) Part a shows the whole range of distances. The tBLYP and CASPT2 overlap at equilibrium, as well as the variational and WABS BLYP. (b) Part b is a blowup of the region from 1.3 to 2.8 Å.

1. Dunning, Jr., T.H. *J. Chem. Phys.* **1989,** *90*, 1007-1023.

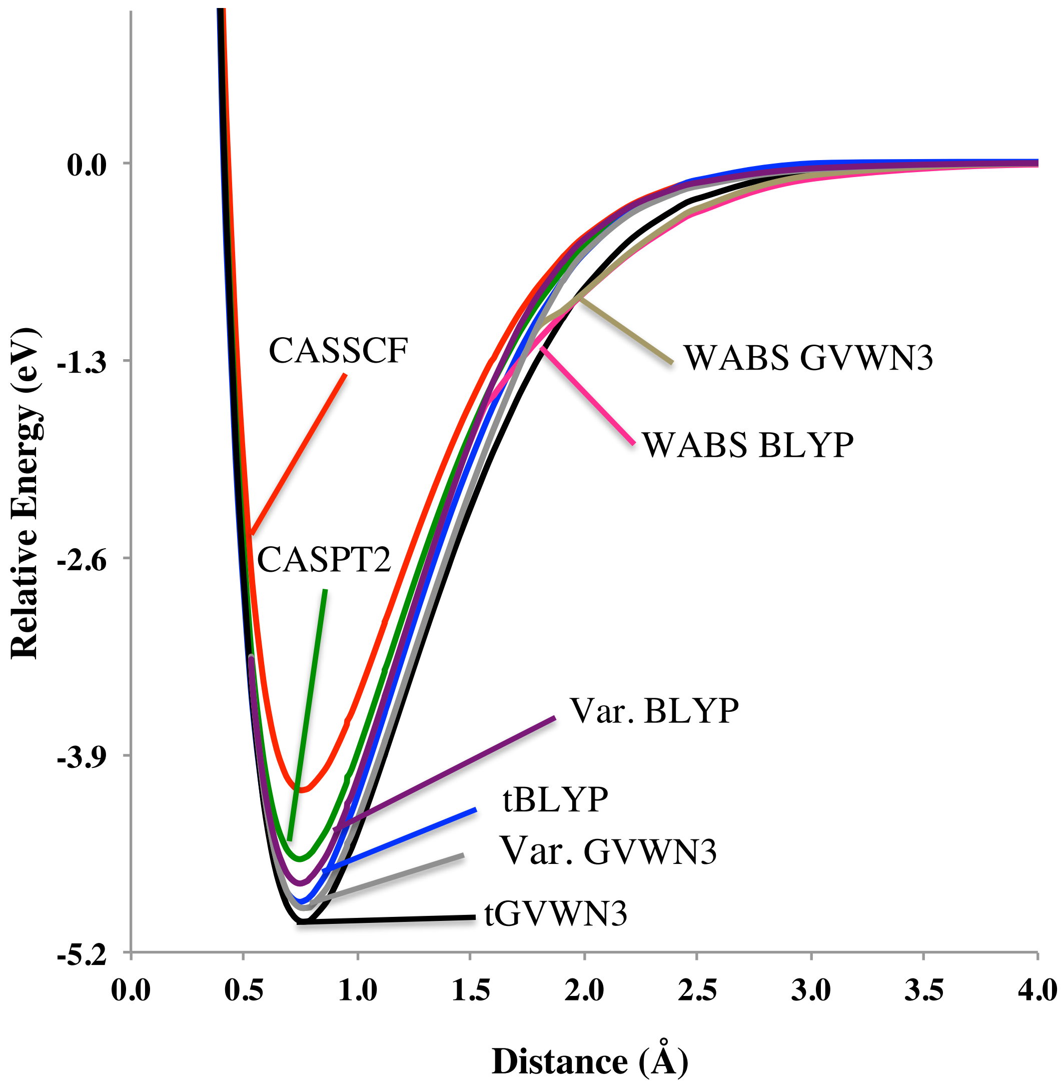
CASSCF
WABS GVWN3
WABS BLYP
CASPT2
Var. BLYP
tBLYP
Var. GVWN3
tGVWN3
Relative Energy (eV)
0.0
-1.3
-2.6
-3.9
-5.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Distance (Å)

Figure S6a

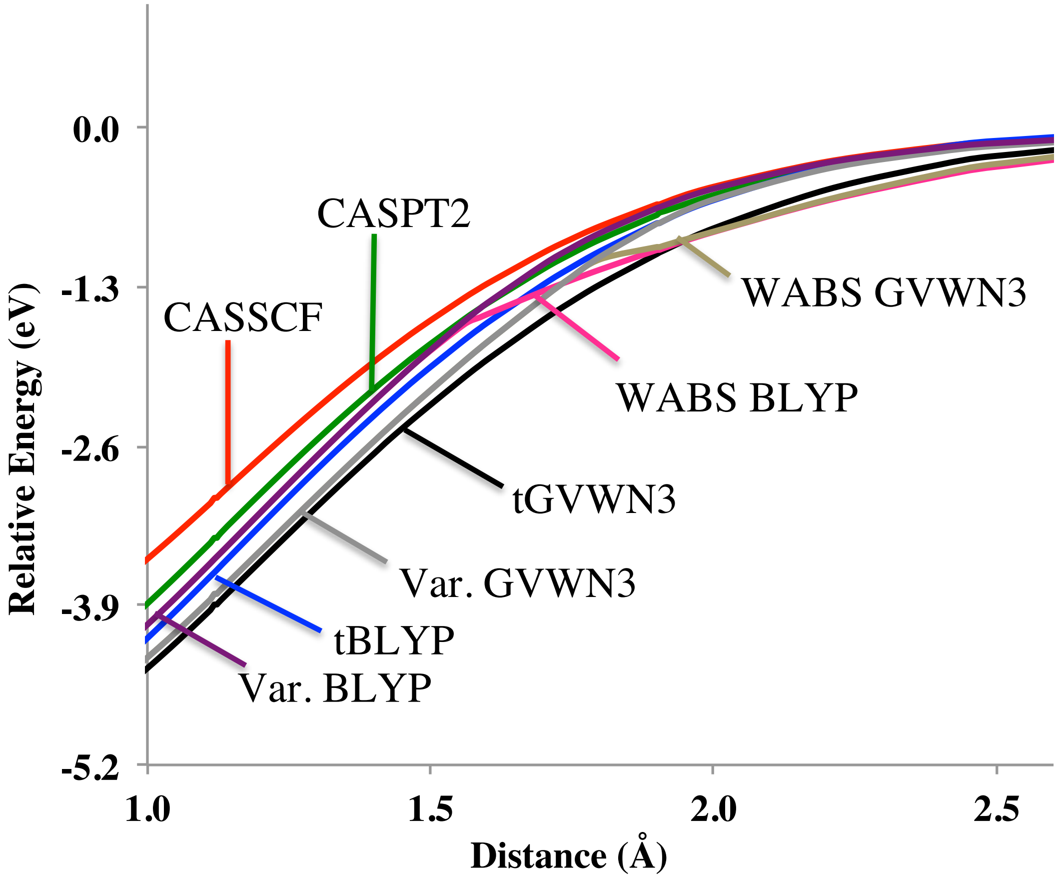

Figure S6b

Figure S6. Potential energy curves of H_2 without PBE computed with a cc-pVTZ[1] basis set and a (2,2) active space that includes the sigma bonding electrons and orbitals. (a) Part a shows the whole range of distances. The variational and WABS BLYP curves overlap at equilibrium. (b) Part b is a blowup of the region from 1.3 to 2.8 Å.

1. Dunning, Jr., T.H. *J. Chem. Phys.* **1989,** *90*, 1007-1023.

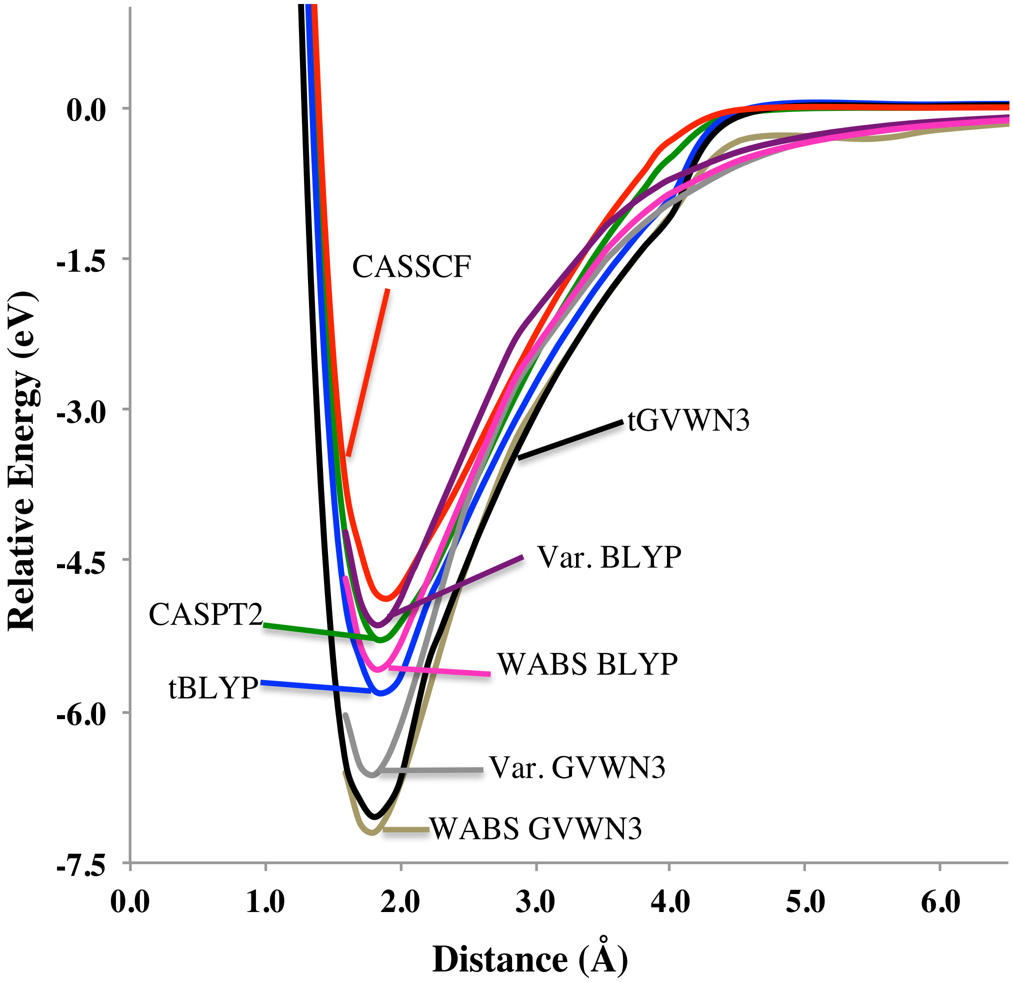
Relative Energy (eV)
0.0
-1.5
-3.0
-4.5
-6.0
-7.5
Distance (Å)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
CASSCF
tGVWN3
Var. BLYP
CASPT2
WABS BLYP
tBLYP
Var. GVWN3
WABS GVWN3

Figure S7a

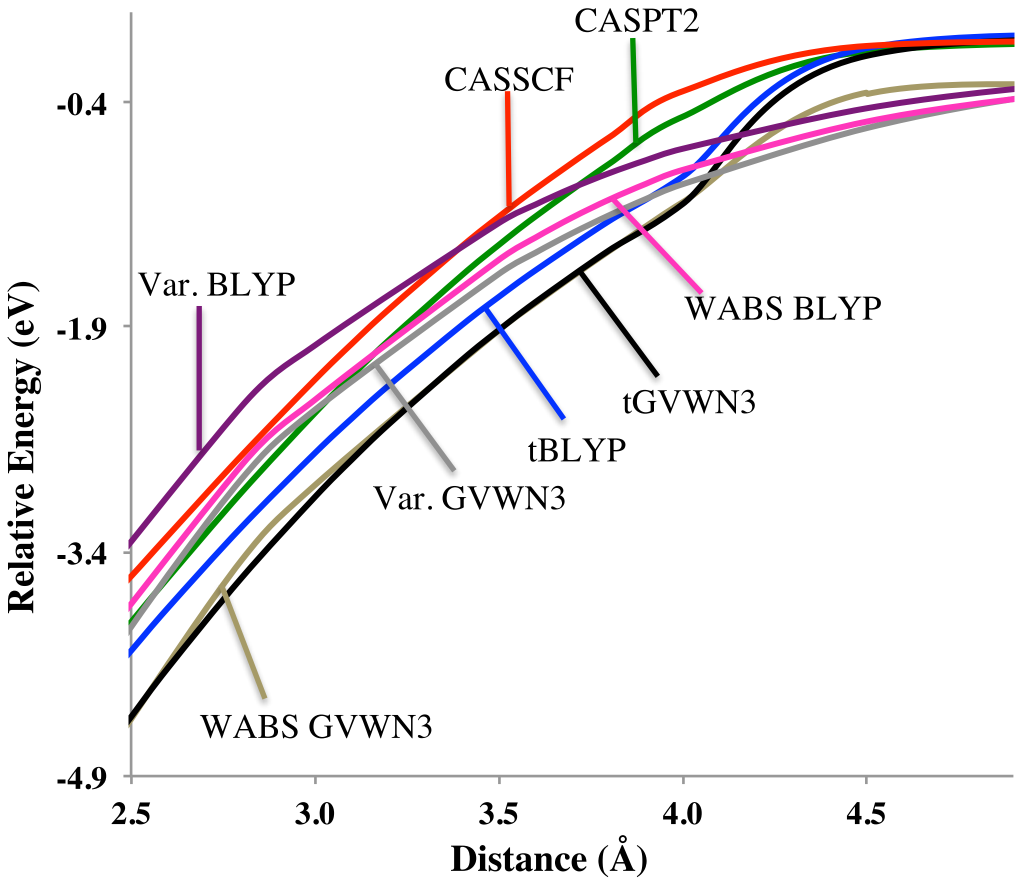

Figure S7b

Figure S7. Potential energy curves for CaO without PBE. The (8,8) active space includes the 4*s* electrons and orbitals on Ca and the 2*s* and 2*p* orbitals and electrons on O. Also, there is an additional set of 4*p* correlating orbitals on Ca. The basis sets used was cc-pVTZ[1]. (a) Part a shows the whole range of distances. (b) Part b is a blowup of the region from 2.5 to 5.0 Å.

[1] Dunning, Jr., T.H. *J. Chem. Phys.* **1989,** *90*, 1007-1023.

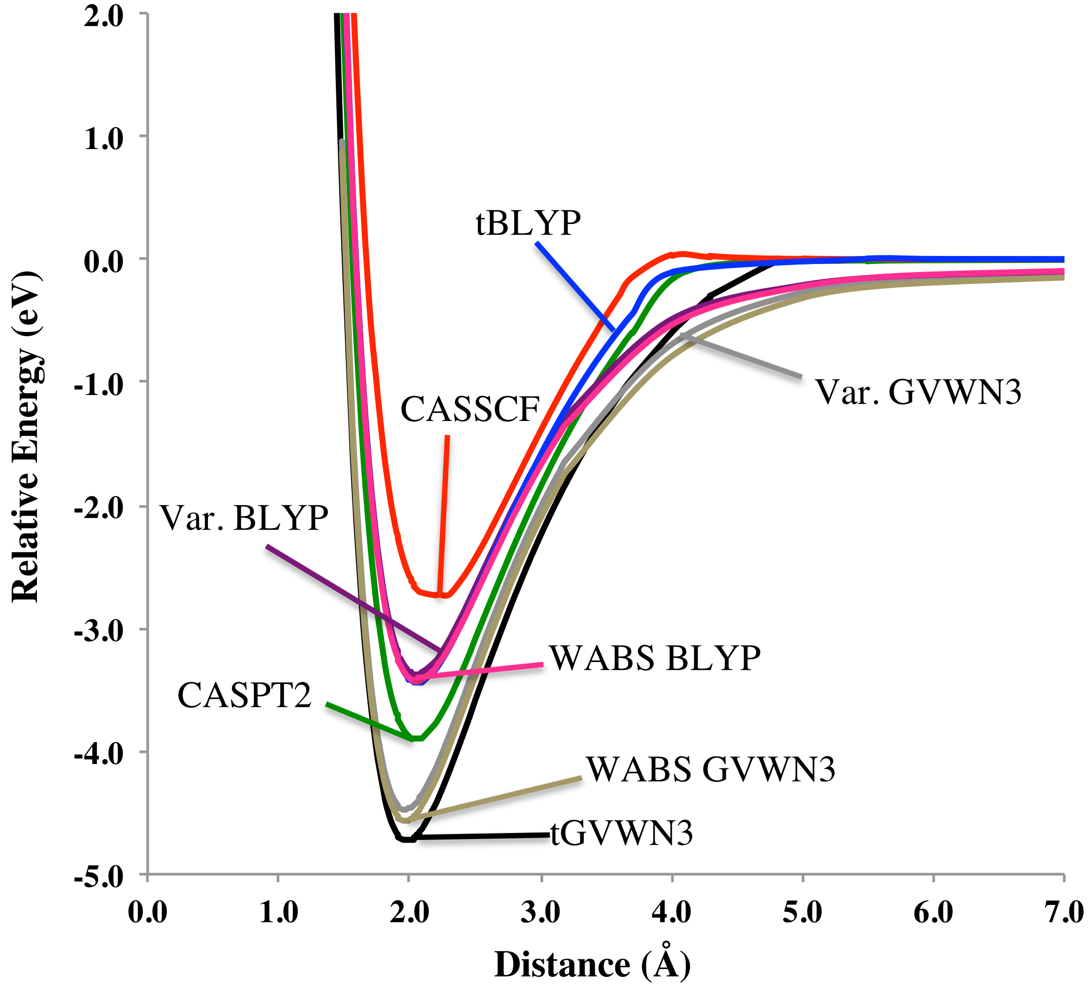
Relative Energy (eV)
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Distance (Å)
tBLYP
Var. GVWN3
CASSCF
Var. BLYP
WABS BLYP
CASPT2
WABS GVWN3
tGVWN3

Figure S8a

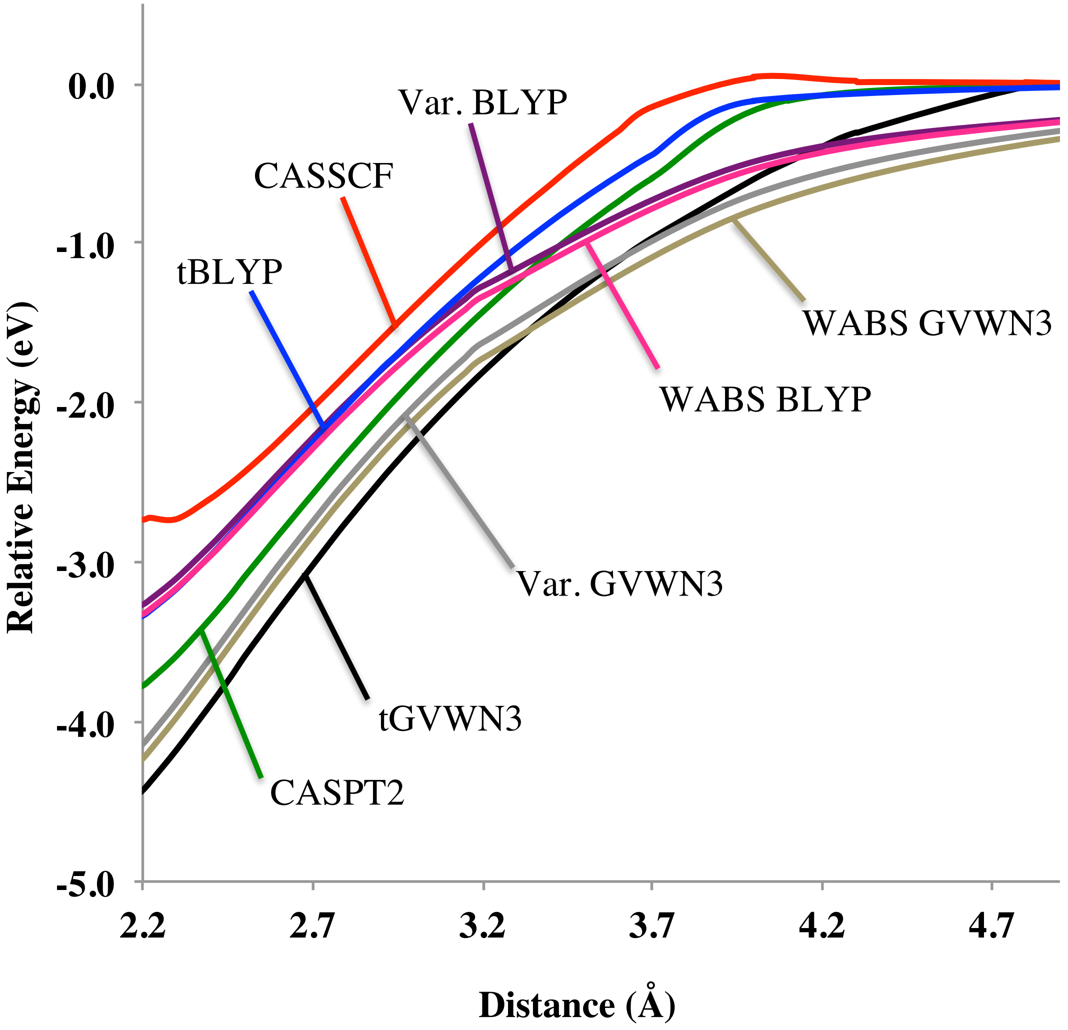

Figure S8b

Figure S8. Potential energy curves for the $^2\Pi$ state of NiCl. The basis set used was ANO-RCC-VTZP[1] for Ni and Cl. a) Part a shows the whole range of distances. At equilibrium, the electronic structure is ionic, with Ni^+ having a $3d^9$ configuration. At dissociation, Ni is in its $3d^8 4s^2$ ground state. b) Part b is a blowup of the region from 2.2 to 4.7 Å.

[1] Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575-6579.