Supplementary Material

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1 Hydrogen Basis Sets

The s contraction for the hydrogen basis sets is given in Table 1. The Gauss-Slater (GS) primitives for the double-zeta ($2z$) atomic natural orbital GS (ANO-GS) basis for hydrogen are provided in Table 2. The GS primitives for the triple-zeta ($3z$) ANO-GS basis for hydrogen are provided in Table 3. The Gaussian primitives for the quintuple-zeta ($5z$) Gaussian basis for hydrogen are provided in Table 4. Each basis was constructed using the methods of Ref. [1].

Table 1: s contraction for hydrogen basis sets. The contraction was constructed using the method of Ref. [1].

Exponent	Coefficient
0.05559917	0.070858475
0.11675826	0.283134279
0.24519235	0.347654627
0.51490394	0.233232914
1.08129828	0.119346810
2.27072639	0.053366645
4.76852541	0.022054957
10.01390336	0.011743843
21.02919706	0.000820785

Table 2: Primitives for $2z$ ANO-GS basis for hydrogen. The primitives were constructed using the method of Ref. [1].

Function	Exp.
GS-1S	1.946875
GS-2P	1.968750

Table 3: Primitives for $3z$ ANO-GS basis for hydrogen. The primitives were constructed using the method of Ref. [1].

Function	Exp.
GS-1S	0.925000
GS-1S	1.968750
GS-2P	1.887500
GS-2P	2.553125
GS-3D	2.659375

Table 4: Primitives for $5z$ Gaussian basis for hydrogen. The primitives were constructed using the method of Ref. [1].

Function	Exp.
1S	0.0692135
1S	0.1736131
1S	0.4543641
1S	1.3072524
2P	0.2370069
2P	0.6258464
2P	1.6114234
2P	5.1965679
3D	0.5106775
3D	1.3660613
3D	3.2652161
4F	0.6792030
4F	2.0042817

2 Setup and Reference Data

The geometries, zero point energies, and experimental atomization energies for the molecules of the G2 set [5] are provided in Table 5.

Table 5: Geometries, zero point energies, and experimental atomization energies for the molecules of the G2 set [5]. Some experimental error bars were not available (N/A).

System	Geometry	ZPE (kcal/mol)	Expt. Atomization Energy (kcal/mol)
LiH	[6]	1.99 [6]	56 ± 0.01 [7]
BeH	[6]	2.92 [6]	46.9 ± 0.01 [7]
CH	[6]	4.04 [6]	79.9 ± 0.02 [7]
CH_2 ($^3B_1$)	[6]	10.55 [6]	179.6 ± N/A [7]
CH_2 ($^1A_1$)	[6]	10.29 [6]	170.6 ± N/A [7]
CH_3	[6]	18.55 [6]	289.3 ± 0.2 [7]
CH_4	[6]	27.74 [6]	392.5 ± 0.1 [7]
NH	[6]	4.64 [6]	79 ± 0.4 [7]
NH_2	[6]	11.84 [6]	170 ± 0.3 [7]
NH_3	[6]	21.33 [6]	276.7 ± 0.1 [7]
OH	[6]	5.29 [6]	101.4 ± 0.3 [7]
H_2O	[6]	13.26 [6]	219.35 ± 0.01 [7]
HF	[6]	5.86 [6]	135.2 ± 0.2 [7]
SiH_2 ($^1A_1$)	[8]	7.3 [7]	144.4 ± 0.7 [7]
SiH_2 ($^3B_1$)	[9]	7.5 [7]	123.4 ± 0.7 [7]
SiH_3	[8]	13.2 [7]	213.8 ± 1.2 [7]
SiH_4	[8]	19.4 [7]	302.6 ± 0.5 [7]
PH_2	[8]	8.4 [7]	144.7 ± 0.6 [7]
PH_3	[6]	14.44 [6]	228.6 ± 0.4 [7]
H_2S	[6]	9.4 [6]	173.1 ± 0.2 [7]
HCl	[6]	4.24 [6]	102.24 ± 0.5 [7]
Li_2	[10]	0.5 [6]	23.9 ± 0.7 [7]

Table 5 – continued

System	Geometry	ZPE (kcal/mol)	Expt. Atomization Energy (kcal/mol)
LiF	[10]	1.3 [7]	137.6 ± 2 [7]
C_2H_2	[6]	16.5 [6]	386.9 ± 0.2 [7]
C_2H_4	[6]	31.66 [6]	531.9 ± 0.1 [7]
C_2H_6	[6]	46.23 [6]	666.3 ± N/A [7]
CN	[6]	2.95 [6]	178.1 ± 2.4 [7]
HCN	[6]	9.95 [6]	301.7 ± 2 [7]
CO	[6]	3.09 [6]	256.2 ± 0.2 [7]
HCO	[6]	8.09 [6]	270.3 ± 2 [7]
H_2CO	[6]	16.52 [6]	357.2 ± 0.1 [7]
H_3COH	[8]	31.72 [6]	480.8 ± N/A [7]
N_2	[6]	3.36 [6]	225.1 ± 0.4 [7]
N_2H_4	[8]	32.68 [6]	405.4 ± N/A [7]
NO	[6]	2.71 [6]	150.06 ± 0.04 [7]
O_2	[10]	2.25 [6]	117.96 ± 0.02 [7]
H_2O_2	[6]	16.44 [6]	252.3 ± N/A [7]
F_2	[10]	1.3 [6]	36.9 ± 0.1 [7]
CO_2	[6]	7.24 [6]	381.93 ± 0.01 [7]
Na_2	[8]	0.2 [7]	16.8 ± 0.3 [7]
Si_2	[10]	0.73 [6]	74 ± N/A [7]
P_2	[10]	1.11 [6]	116.1 ± 0.5 [7]
S_2	[10]	1.04 [6]	100.66 ± 0.07 [7]
Cl_2	[6]	0.8 [6]	57.18 ± 0.01 [7]
NaCl	[8]	0.5 [7]	97.3 ± 0.5 [7]
SiO	[6]	1.78 [6]	189.9 ± 2 [7]
CS	[10]	1.83 [6]	169.4 ± 6 [7]
SO	[6]	1.63 [6]	123.4 ± 0.3 [7]
ClO	[10]	1.22 [6]	63.42 ± 0.02 [7]
ClF	[6]	1.12 [6]	60.4 ± N/A [7]
Si_2H_6	[8]	30.5 [7]	500.1 ± N/A [7]
CH_3Cl	[6]	23.19 [6]	371 ± N/A [7]
H_3CSH	[8]	28.6 [7]	445.1 ± N/A [7]
HOCl	[6]	8.18 [6]	156.3 ± 0.5 [7]
SO_2	[10]	4.38 [6]	254 ± 0.2 [7]

3 Raw Data

3.1 Locality Approximation

This section contains the raw data for those systems handled with the locality approximation [11]. The diffusion Monte Carlo (DMC) total energies of the molecules from the G2 set and their atoms for a single determinant Slater-Jastrow (SJ) trial wavefunction composed of Hartree-Fock (HF) orbitals are given in Table 6. The DMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of variational Monte Carlo (VMC) optimized orbitals are given in Table 7. The DMC total energies of the molecules from the G2 set and their atoms for a CAS SJ trial wavefunction with an s and p active space are given in Table 8. The DMC total energies of the phosphorus containing molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of VMC optimized orbitals, a CAS SJ trial wavefunction with an s and p active space, and a CAS SJ trial wavefunction with an s, p, and d active space are given in Table 9.

Table 6: DMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of HF orbitals. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$2z$	$3z$	$5z$
H	-0.5000006(1)	-0.5000006(1)	-0.5000006(1)
Li	-0.1963297(5)	-0.1963297(7)	-0.196329(2)
C	-5.42251(7)	-5.42233(8)	-5.42236(7)
N	-9.79127(7)	-9.79109(5)	-9.79123(6)
O	-15.89289(8)	-15.89228(8)	-15.89254(8)
F	-24.18633(8)	-24.18594(7)	-24.18609(7)
Na	-0.1821457(7)	-0.1821441(7)	-0.182145(2)
Si	-3.76661(5)	-3.76662(5)	-3.76654(5)
P	-6.47660(7)	-6.47648(5)	-6.47645(7)
S	-10.13125(9)	-10.13103(9)	-10.1311(1)
Cl	-14.97223(6)	-14.97168(6)	-14.97179(6)
CH	-6.05266(7)	-6.05399(9)	-6.05422(8)
CH_2 ($^1A_1$)	-6.7061(1)	-6.70751(9)	-6.70792(9)
CH_3	-7.41421(9)	-7.41476(8)	-7.41490(8)
CH_4	-8.09421(9)	-8.09441(9)	-8.09451(8)
NH	-10.41946(8)	-10.42028(7)	-10.42068(8)
NH_2	-11.07601(9)	-11.07774(9)	-11.07834(9)
NH_3	-11.7593(1)	-11.76181(8)	-11.76266(9)
OH	-16.56031(9)	-16.56126(9)	-16.56142(9)
H_2O	-17.25949(8)	-17.26123(8)	-17.26175(9)
HF	-24.90895(8)	-24.91024(7)	-24.91083(8)
SiH_2 ($^1A_1$)	-5.00856(7)	-5.00925(7)	-5.00952(7)
SiH_2 ($^3B_1$)	-4.97656(7)	-4.97723(7)	-4.97709(6)
SiH_3	-5.6280(1)	-5.62910(8)	-5.62906(9)
SiH_4	-6.28261(9)	-6.28418(8)	-6.28428(7)
PH_2	-7.71744(8)	-7.71798(8)	-7.71812(8)
PH_3	-8.35619(7)	-8.35676(7)	-8.35696(7)
H_2S	-11.41932(8)	-11.41962(7)	-11.42012(7)
HCl	-15.64183(8)	-15.64178(8)	-15.64211(8)
Li_2	-0.43045(2)	-0.43053(3)	-0.43053(2)
C_2H_4	-13.74229(8)	-13.7433(1)	-13.74348(8)
C_2H_6	-14.98415(8)	-14.9851(1)	-14.9850(1)
CO	-21.7192(1)	-21.7232(1)	-21.7238(1)
H_2CO	-22.9038(1)	-22.9080(1)	-22.9082(1)
H_3COH	-24.12892(9)	-24.13207(8)	-24.13271(8)
N_2	-19.9296(1)	-19.9333(1)	-19.9338(1)
N_2H_4	-22.26561(9)	-22.27033(9)	-22.27206(8)
NO	-25.9062(1)	-25.9108(1)	-25.9117(1)
O_2	-31.9642(1)	-31.9679(1)	-31.9691(1)
H_2O_2	-33.1973(1)	-33.2013(1)	-33.2025(1)
F_2	-48.4134(1)	-48.4146(1)	-48.41757(9)
CO_2	-37.8168(1)	-37.8228(1)	-37.8235(1)
Na_2	-0.39102(2)	-0.39106(2)	-0.39104(2)
Si_2	-7.6498(1)	-7.6505(1)	-7.65031(9)
P_2	-13.1256(1)	-13.1273(1)	-13.1275(1)
S_2	-20.4191(1)	-20.4207(1)	-20.4214(1)

Table 6 – continued

System	$2z$	$3z$	$5z$
Cl_2	-30.0309(1)	-30.0305(1)	-30.03165(9)
SiO	-19.9535(1)	-19.96031(9)	-19.96104(8)
CS	-15.8151(1)	-15.8169(1)	-15.8185(1)
SO	-26.2105(1)	-26.2159(1)	-26.21669(9)
ClO	-30.9457(1)	-30.9475(1)	-30.9486(1)
ClF	-39.2434(1)	-39.24608(9)	-39.2478(1)
Si_2H_6	-11.3836(1)	-11.3857(1)	-11.38579(9)
CH_3Cl	-22.5236(1)	-22.5245(1)	-22.5249(1)
H_3CSH	-18.30598(9)	-18.3071(1)	-18.30752(9)
HOCl	-31.61547(9)	-31.6179(1)	-31.6193(1)
SO_2	-42.2986(1)	-42.3125(1)	-42.3152(1)

Table 7: The DMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of VMC optimized orbitals. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$2z$	$3z$	$5z$
H	-0.5000005(1)	-0.5000006(1)	-0.5000005(1)
Li	-0.1963295(4)	-0.1963292(4)	-0.1963296(3)
C	-5.42288(7)	-5.42292(7)	-5.42296(6)
N	-9.79213(6)	-9.79230(6)	-9.79229(6)
O	-15.8930(1)	-15.89305(8)	-15.89310(7)
F	-24.18619(5)	-24.18651(7)	-24.18636(8)
Na	-0.1821438(7)	-0.1821446(4)	-0.1821438(4)
Si	-3.76682(5)	-3.76676(4)	-3.76683(4)
P	-6.47688(9)	-6.47699(5)	-6.47686(5)
S	-10.1317(1)	-10.13184(8)	-10.13189(7)
Cl	-14.97253(6)	-14.97252(6)	-14.97261(6)
CH	-6.05388(8)	-6.05473(7)	-6.05476(9)
CH_2 ($^1A_1$)	-6.70711(9)	-6.70861(8)	-6.70860(7)
CH_3	-7.41489(7)	-7.41544(9)	-7.41549(7)
CH_4	-8.09523(7)	-8.09523(8)	-8.09523(8)
NH	-10.42146(8)	-10.42200(8)	-10.42186(7)
NH_2	-11.07824(9)	-11.07960(8)	-11.07962(8)
NH_3	-11.76205(8)	-11.76368(7)	-11.76378(7)
OH	-16.56188(9)	-16.56243(8)	-16.56264(9)
H_2O	-17.26195(8)	-17.26298(8)	-17.26313(8)
HF	-24.91098(7)	-24.91170(6)	-24.91175(7)
SiH_2 ($^1A_1$)	-5.00947(5)	-5.01034(5)	-5.01055(4)
SiH_2 ($^3B_1$)	-4.97846(4)	-4.97932(3)	-4.97952(3)
SiH_3	-5.62975(6)	-5.63077(6)	-5.63097(5)
SiH_4	-6.28405(6)	-6.28526(5)	-6.28548(5)
PH_2	-7.71870(8)	-7.71952(6)	-7.71994(6)
PH_3	-8.35790(7)	-8.35892(5)	-8.35921(6)
H_2S	-11.42111(8)	-11.42203(7)	-11.42238(7)
HCl	-15.64294(7)	-15.64345(7)	-15.64374(7)
Li_2	-0.43069(2)	-0.43069(5)	-0.43077(4)
C_2H_4	-13.74413(7)	-13.74453(6)	-13.74477(7)

Table 7 – continued

System	$2z$	$3z$	$5z$
C_2H_6	-14.98622(7)	-14.98643(7)	-14.98640(6)
CO	-21.72262(9)	-21.72572(9)	-21.72617(9)
H_2CO	-22.9080(1)	-22.91048(9)	-22.91083(9)
H_3COH	-24.13189(8)	-24.13417(7)	-24.1348(1)
N_2	-19.93256(9)	-19.93600(9)	-19.93638(9)
N_2H_4	-22.26927(9)	-22.27373(7)	-22.27469(8)
NO	-25.9119(1)	-25.91612(9)	-25.91693(9)
O_2	-31.9682(1)	-31.9707(1)	-31.9719(1)
H_2O_2	-33.2030(1)	-33.20627(8)	-33.20778(9)
F_2	-48.4216(1)	-48.42302(9)	-48.42522(8)
CO_2	-37.8259(1)	-37.8287(1)	-37.8291(1)
Na_2	-0.39104(1)	-0.39104(4)	-0.39106(2)
Si_2	-7.65138(6)	-7.65274(8)	-7.65279(7)
P_2	-13.12785(9)	-13.1300(1)	-13.13077(9)
S_2	-20.4211(1)	-20.4236(1)	-20.4248(1)
Cl_2	-30.03397(9)	-30.03514(9)	-30.03684(8)
SiO	-19.95896(9)	-19.96336(9)	-19.96385(7)
CS	-15.81932(9)	-15.82302(9)	-15.82387(8)
SO	-26.21600(9)	-26.22047(9)	-26.22172(9)
ClO	-30.9600(1)	-30.96312(9)	-30.96463(9)
ClF	-39.24935(9)	-39.25234(7)	-39.25406(8)
Si_2H_6	-11.38585(8)	-11.38818(7)	-11.38840(7)
CH_3Cl	-22.5259(1)	-22.5266(1)	-22.5275(1)
H_3CSH	-18.30852(9)	-18.30988(8)	-18.31105(7)
HOCl	-31.62113(9)	-31.62387(9)	-31.62501(8)
SO_2	-42.3125(1)	-42.32256(8)	-42.32431(8)

Table 8: The DMC total energies of the molecules from the G2 set and their atoms for a CAS SJ trial wavefunction with an s and p active space. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$3z$
H	-0.5000006(1)
Li	-0.1963292(4)
C	-5.42823(6)
N	-9.79230(6)
O	-15.89305(8)
F	-24.18651(7)
Na	-0.1821446(4)
Si	-3.76711(4)
P	-6.47699(5)
S	-10.13184(8)
Cl	-14.97252(6)
CH	-6.06239(6)
CH_2 ($^1A_1$)	-6.71713(6)
CH_3	-7.41764(6)
CH_4	-8.09730(6)
NH	-10.42390(7)

Table 8 – continued

System	$3z$
NH_2	-11.08219(7)
NH_3	-11.76623(6)
OH	-16.56411(8)
H_2O	-17.26521(7)
HF	-24.91286(7)
SiH_2 ($^1A_1$)	-5.01238(4)
SiH_2 ($^3B_1$)	-4.97970(3)
SiH_3	-5.63114(4)
SiH_4	-6.28571(4)
PH_2	-7.72051(5)
PH_3	-8.36003(5)
H_2S	-11.42305(7)
HCl	-15.64382(5)
Li_2	-0.431584(5)
C_2H_4	-13.75239(8)
C_2H_6	-14.99037(9)
CO	-21.73788(7)
H_2CO	-22.9190(1)
H_3COH	-24.14011(5)
N_2	-19.95032(7)
N_2H_4	-22.27934(5)
NO	-25.92787(8)
O_2	-31.97692(9)
H_2O_2	-33.21410(9)
F_2	-48.43320(8)
CO_2	-37.83890(7)
Na_2	-0.39106(2)
Si_2	-7.65485(7)
P_2	-13.13441(8)
S_2	-20.42452(9)
Cl_2	-30.03679(9)
SiO	-19.96885(7)
CS	-15.83223(6)
SO	-26.22235(9)
ClO	-30.96605(8)
ClF	-39.25596(7)
Si_2H_6	-11.38838(7)
CH_3Cl	-22.52839(7)
H_3CSH	-18.3128(1)
HOCl	-31.6278(1)
SO_2	-42.33049(6)

3.2 T-Moves

This section contains the raw data for those systems handled with the size-consistent version of T-Moves [12]. The DMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of HF orbitals are given in Table 10. The DMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of VMC optimized

Table 9: The DMC total energies of the phosphorus containing molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of VMC optimized orbitals, a CAS SJ trial wavefunction with an s and p active space, and a CAS SJ trial wavefunction with an s, p, and d active space. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	1CSF	s,p CAS	s,p,d CAS
H	-0.5000006(1)	-0.5000006(1)	-0.5000006(1)
P	-6.47699(5)	-6.47699(5)	-6.47753(5)
PH_2	-7.71952(6)	-7.72051(5)	-7.72183(5)
PH_3	-8.35892(5)	-8.36003(5)	-8.36145(6)
P_2	-13.1300(1)	-13.13441(8)	-13.13814(7)

orbitals are given in Table 11. The DMC total energies of the molecules from the G2 set and their atoms for a CAS SJ trial wavefunction with an s and p active space are given in Table 12.

Table 10: DMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of HF orbitals. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$2z$	$3z$	$5z$
H	-0.5000006(1)	-0.5000006(1)	-0.5000006(1)
Li	-0.1963297(5)	-0.1963297(7)	-0.196329(2)
Be	-1.00918(5)	-1.00928(4)	-1.00926(5)
C	-5.42211(7)	-5.42206(7)	-5.42194(6)
N	-9.79121(5)	-9.79092(6)	-9.79123(6)
O	-15.89194(8)	-15.89176(8)	-15.89184(7)
F	-24.18514(7)	-24.18515(7)	-24.18527(7)
Na	-0.1821457(7)	-0.1821441(7)	-0.182145(2)
Cl	-14.97154(6)	-14.97117(6)	-14.97115(7)
LiH	-0.78787(3)	-0.78800(2)	-0.78799(1)
BeH	-1.58814(6)	-1.58861(4)	-1.58849(5)
CH_2 ($^3B_1$)	-6.72719(9)	-6.72762(7)	-6.72777(8)
LiF	-24.60333(8)	-24.60401(8)	-24.60477(7)
C_2H_2	-12.4878(1)	-12.48906(9)	-12.48920(7)
CN	-15.48083(8)	-15.4833(1)	-15.48371(8)
HCN	-16.20259(8)	-16.20468(8)	-16.20494(9)
HCO	-22.24632(9)	-22.25065(8)	-22.25173(9)
NaCl	-15.31021(6)	-15.31104(8)	-15.31135(7)

Table 11: The DMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of VMC optimized orbitals. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$2z$	$3z$	$5z$
H	-0.5000005(1)	-0.5000006(1)	-0.5000005(1)
Li	-0.1963295(4)	-0.1963292(4)	-0.1963296(3)
Be	-1.00921(5)	-1.00916(5)	-1.00924(4)
C	-5.42244(6)	-5.42258(5)	-5.42245(5)
N	-9.79214(6)	-9.79210(6)	-9.79218(6)
O	-15.89241(9)	-15.89249(7)	-15.89272(7)
F	-24.18526(5)	-24.18535(7)	-24.18548(7)
Na	-0.1821438(7)	-0.1821446(4)	-0.1821438(4)
Cl	-14.97209(6)	-14.97204(6)	-14.97212(5)
LiH	-0.78804(1)	-0.78804(1)	-0.788051(9)
BeH	-1.58833(4)	-1.58887(3)	-1.58883(3)

Table 11 – continued

System	$2z$	$3z$	$5z$
NaCl	-15.31167(5)	-15.31196(6)	-15.31202(7)

Table 12: The DMC total energies of the molecules from the G2 set and their atoms for a CAS SJ trial wavefunction with an s and p active space. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$3z$
H	-0.5000006(1)
Li	-0.1963292(4)
Be	-1.010186(5)
C	-5.42775(5)
N	-9.79230(6)
O	-15.89305(8)
F	-24.18651(7)
Na	-0.1821446(4)
Cl	-14.97252(6)
LiH	-0.788238(6)
BeH	-1.59014(2)
CH_2 ($^3B_1$)	-6.73142(8)
LiF	-24.61011(7)
C_2H_2	-12.50101(5)
CN	-15.50866(7)
HCN	-16.22003(6)
HCO	-22.26378(7)
NaCl	-15.31334(6)

4 Variational Monte Carlo

This section contains the VMC data for the G2 set. The VMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of HF orbitals are given in Table 13. The VMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of VMC optimized orbitals are given in Table 14. The VMC total energies of the molecules from the G2 set and their atoms for a CAS SJ trial wavefunction with an s and p active space are given in Table 15.

Table 13: VMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of HF orbitals. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$2z$	$3z$	$5z$
H	-0.5000002(3)	-0.5000002(3)	-0.5000003(3)
Li	-0.1963192(5)	-0.1963192(5)	-0.196312(3)
Be	-1.00835(8)	-1.00843(8)	-1.0082(1)
C	-5.41531(5)	-5.41496(5)	-5.41513(2)
N	-9.78553(5)	-9.78506(5)	-9.78529(5)
O	-15.88268(8)	-15.88277(8)	-15.88312(8)

Table 13 – continued

System	$2z$	$3z$	$5z$
F	-24.17448(9)	-24.17461(9)	-24.17472(9)
Na	-0.1821236(9)	-0.1821239(9)	-0.181993(6)
Si	-3.76315(2)	-3.76295(2)	-3.76298(2)
P	-6.47276(4)	-6.47260(4)	-6.47259(4)
S	-10.12444(5)	-10.12390(6)	-10.12434(6)
Cl	-14.96368(5)	-14.96340(5)	-14.96353(5)
LiH	-0.78727(5)	-0.78777(4)	-0.78784(3)
BeH	-1.58359(3)	-1.58575(2)	-1.58566(2)
CH	-6.04119(8)	-6.04419(7)	-6.04483(7)
CH_2 ($^3B_1$)	-6.71774(7)	-6.71864(7)	-6.71906(7)
CH_2 ($^1A_1$)	-6.69381(8)	-6.69681(7)	-6.69787(7)
CH_3	-7.40344(8)	-7.40419(8)	-7.40457(7)
CH_4	-8.08247(9)	-8.08310(8)	-8.08338(8)
NH	-10.40752(9)	-10.40999(9)	-10.41050(9)
NH_2	-11.0613(1)	-11.0651(1)	-11.06646(9)
NH_3	-11.74334(9)	-11.74816(8)	-11.74998(8)
OH	-16.5468(1)	-16.5490(1)	-16.5495(1)
H_2O	-17.24389(8)	-17.24777(7)	-17.24877(7)
HF	-24.89475(8)	-24.89747(7)	-24.89835(7)
SiH_2 ($^1A_1$)	-4.99763(9)	-4.99915(8)	-5.00002(8)
SiH_2 ($^3B_1$)	-4.96462(9)	-4.96581(8)	-4.96669(8)
SiH_3	-5.6151(1)	-5.61682(9)	-5.61788(9)
SiH_4	-6.27140(7)	-6.27356(7)	-6.27459(6)
PH_2	-7.70464(7)	-7.70603(7)	-7.70671(6)
PH_3	-8.34136(9)	-8.34312(8)	-8.34374(8)
H_2S	-11.40510(6)	-11.40659(6)	-11.40795(6)
HCl	-15.63025(8)	-15.63067(8)	-15.63146(8)
Li_2	-0.42921(6)	-0.42957(8)	-0.42973(8)
LiF	-24.59015(9)	-24.5933(1)	-24.5941(1)
C_2H_2	-12.46639(9)	-12.46942(8)	-12.46978(8)
C_2H_4	-13.71321(7)	-13.71452(9)	-13.71543(7)
C_2H_6	-14.95497(8)	-14.95623(7)	-14.95686(7)
CN	-15.4528(1)	-15.4574(1)	-15.4578(1)
HCN	-16.1773(1)	-16.1815(1)	-16.1819(1)
CO	-21.6859(1)	-21.6938(1)	-21.6948(1)
HCO	-22.2121(1)	-22.2195(1)	-22.2209(1)
H_2CO	-22.86719(7)	-22.87324(7)	-22.87426(7)
H_3COH	-24.0890(1)	-24.0942(1)	-24.0957(1)
N_2	-19.8952(1)	-19.9019(1)	-19.9026(1)
N_2H_4	-22.22205(8)	-22.23083(8)	-22.23405(7)
NO	-25.8669(1)	-25.8745(1)	-25.8759(1)
O_2	-31.92106(9)	-31.9270(1)	-31.9288(1)
H_2O_2	-33.14808(9)	-33.15601(9)	-33.15818(9)
F_2	-48.3613(1)	-48.3642(1)	-48.3685(1)
CO_2	-37.7654(1)	-37.7788(1)	-37.7800(1)
Na_2	-0.39054(5)	-0.39066(4)	-0.39062(4)
Si_2	-7.63400(8)	-7.63601(7)	-7.63606(8)
P_2	-13.10120(9)	-13.10558(9)	-13.10629(9)
S_2	-20.3917(1)	-20.3959(1)	-20.3968(1)

Table 13 – continued

System	$2z$	$3z$	$5z$
Cl_2	-29.99928(8)	-29.99951(8)	-30.00062(8)
NaCl	-15.30170(8)	-15.30289(8)	-15.30341(8)
SiO	-19.9247(1)	-19.9345(1)	-19.93647(9)
CS	-15.7859(1)	-15.79042(9)	-15.79377(9)
SO	-26.1736(1)	-26.1814(1)	-26.18343(9)
ClO	-30.9076(1)	-30.9113(1)	-30.9130(1)
ClF	-39.2039(1)	-39.2073(1)	-39.2092(1)
Si_2H_6	-11.35963(8)	-11.36288(7)	-11.36485(7)
CH_3Cl	-22.4938(1)	-22.4950(1)	-22.4961(1)
H_3CSH	-18.27368(9)	-18.27634(5)	-18.27741(9)
HOCl	-31.57616(8)	-31.58107(7)	-31.58258(7)
SO_2	-42.23410(8)	-42.2544(1)	-42.2591(1)

Table 14: The VMC total energies of the molecules from the G2 set and their atoms for a single determinant SJ trial wavefunction composed of VMC optimized orbitals. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$2z$	$3z$	$5z$
H	-0.5000006(3)	-0.5000004(3)	-0.5000005(3)
Li	-0.196321(1)	-0.196324(1)	-0.196325(3)
Be	-1.0084(1)	-1.00850(7)	-1.00837(8)
C	-5.41616(5)	-5.41625(5)	-5.41625(5)
N	-9.78640(6)	-9.78660(5)	-9.78647(5)
O	-15.8832(1)	-15.88375(7)	-15.88404(8)
F	-24.17474(9)	-24.17534(9)	-24.17541(8)
Na	-0.1821236(9)	-0.182139(2)	-0.182141(3)
Si	-3.76433(2)	-3.76455(2)	-3.76457(2)
P	-6.4740(1)	-6.47435(3)	-6.47433(3)
S	-10.12575(4)	-10.12612(5)	-10.12647(5)
Cl	-14.96474(5)	-14.96515(5)	-14.96539(5)
LiH	-0.78780(2)	-0.78791(2)	-0.78795(2)
BeH	-1.58597(3)	-1.58761(2)	-1.58748(2)
CH	-6.04447(7)	-6.04668(7)	-6.04693(6)
CH_2 ($^3B_1$)	-6.72118(7)	-6.72238(6)	-6.72264(6)
CH_2 ($^1A_1$)	-6.69673(8)	-6.70002(7)	-6.70032(7)
CH_3	-7.40543(8)	-7.40662(7)	-7.40686(7)
CH_4	-8.08593(8)	-8.08620(8)	-8.08606(8)
NH	-10.41134(9)	-10.41286(8)	-10.41307(8)
NH_2	-11.0659(1)	-11.06868(9)	-11.06898(9)
NH_3	-11.74792(8)	-11.75212(8)	-11.75240(7)
OH	-16.5496(1)	-16.5510(1)	-16.5511(1)
H_2O	-17.24801(8)	-17.25070(7)	-17.25124(7)
HF	-24.89807(8)	-24.89954(7)	-24.89999(7)
SiH_2 ($^1A_1$)	-5.00102(8)	-5.00415(7)	-5.00467(6)
SiH_2 ($^3B_1$)	-4.97215(7)	-4.97453(6)	-4.97506(6)
SiH_3	-5.62188(9)	-5.62493(7)	-5.62549(7)
SiH_4	-6.27681(6)	-6.27942(5)	-6.27988(5)
PH_2	-7.70860(7)	-7.71172(6)	-7.71254(5)

Table 14 – continued

System	$2z$	$3z$	$5z$
PH_3	-8.34631(8)	-8.34997(7)	-8.35084(7)
H_2S	-11.40914(6)	-11.41219(5)	-11.41365(5)
HCl	-15.63249(8)	-15.63411(8)	-15.63494(7)
Li_2	-0.43001(5)	-0.4300(1)	-0.43013(6)
LiF	-24.59338(9)	-24.5945(1)	-24.5946(1)
C_2H_2	-12.47251(8)	-12.47386(8)	-12.47424(8)
C_2H_4	-13.72072(7)	-13.72361(6)	-13.72434(6)
C_2H_6	-14.96347(7)	-14.96475(6)	-14.96536(6)
CN	-15.4670(1)	-15.4713(1)	-15.47249(9)
HCN	-16.1850(1)	-16.18778(9)	-16.18830(9)
CO	-21.6953(1)	-21.7026(1)	-21.7035(1)
HCO	-22.2243(1)	-22.23171(9)	-22.23330(9)
H_2CO	-22.87806(7)	-22.88477(6)	-22.88603(6)
H_3COH	-24.09967(9)	-24.10596(9)	-24.10826(9)
N_2	-19.9025(1)	-19.9103(1)	-19.91182(9)
N_2H_4	-22.23354(7)	-22.24360(7)	-22.24677(7)
NO	-25.8773(1)	-25.8862(1)	-25.8888(1)
O_2	-31.92806(7)	-31.9350(1)	-31.9392(1)
H_2O_2	-33.16077(9)	-33.16910(8)	-33.17382(8)
F_2	-48.3752(1)	-48.3822(1)	-48.3866(1)
CO_2	-37.7880(1)	-37.7942(1)	-37.7949(1)
Na_2	-0.39087(3)	-0.39082(4)	-0.39101(3)
Si_2	-7.63878(5)	-7.64202(7)	-7.64348(7)
P_2	-13.10695(9)	-13.11214(8)	-13.11542(8)
S_2	-20.3953(1)	-20.4019(1)	-20.4059(1)
Cl_2	-30.0053(1)	-30.0087(1)	-30.01375(9)
NaCl	-15.30374(8)	-15.30468(7)	-15.30503(7)
SiO	-19.9338(1)	-19.94292(9)	-19.94447(9)
CS	-15.79466(9)	-15.80294(9)	-15.80576(8)
SO	-26.1840(1)	-26.19383(9)	-26.19689(9)
ClO	-30.9264(1)	-30.9332(1)	-30.9377(1)
ClF	-39.2141(1)	-39.22140(9)	-39.22499(9)
Si_2H_6	-11.36964(6)	-11.37477(6)	-11.37609(5)
CH_3Cl	-22.50049(9)	-22.50391(9)	-22.50675(9)
H_3CSH	-18.28229(9)	-18.28658(8)	-18.28989(8)
HOCl	-31.58679(7)	-31.59298(7)	-31.59752(7)
SO_2	-42.2567(1)	-42.2762(1)	-42.2831(1)

Table 15: The VMC total energies of the molecules from the G2 set and their atoms for a CAS SJ trial wavefunction with an s and p active space. Energies are in Hartrees. Error bar, which is shown in parentheses, is for the last digit.

System	$3z$
H	-0.5000004(3)
Li	-0.196324(1)
Be	-1.010191(8)
C	-5.42342(4)
N	-9.78660(5)

Table 15 – continued

System	$3z$
O	-15.88375(7)
F	-24.17534(9)
Na	-0.182139(2)
Si	-3.76508(2)
P	-6.47435(3)
S	-10.12612(5)
Cl	-14.96515(5)
LiH	-0.78818(1)
BeH	-1.58944(1)
CH	-6.05669(6)
CH_2 ($^3B_1$)	-6.72640(6)
CH_2 ($^1A_1$)	-6.71131(6)
CH_3	-7.41137(6)
CH_4	-8.09104(7)
NH	-10.41641(8)
NH_2	-11.07366(8)
NH_3	-11.75758(7)
OH	-16.5540(1)
H_2O	-17.25510(7)
HF	-24.90171(7)
SiH_2 ($^1A_1$)	-5.00884(4)
SiH_2 ($^3B_1$)	-4.97634(4)
SiH_3	-5.62691(5)
SiH_4	-6.28131(5)
PH_2	-7.71436(5)
PH_3	-8.35357(6)
H_2S	-11.41515(5)
HCl	-15.63556(8)
Li_2	-0.43156(1)
LiF	-24.6016(1)
C_2H_2	-12.49172(6)
C_2H_4	-13.74004(5)
C_2H_6	-14.97618(8)
CN	-15.49602(8)
HCN	-16.20797(8)
CO	-21.72140(9)
HCO	-22.24735(8)
H_2CO	-22.90135(6)
H_3COH	-24.11924(8)
N_2	-19.93310(8)
N_2H_4	-22.25696(6)
NO	-25.9055(1)
O_2	-31.9489(1)
H_2O_2	-33.18541(3)
F_2	-48.4023(1)
CO_2	-37.8128(1)
Na_2	-0.39099(1)
Si_2	-7.64737(6)
P_2	-13.12193(8)

Table 15 – continued

System	$3z$
S_2	-20.4049(1)
Cl_2	-30.0128(1)
NaCl	-15.30706(7)
SiO	-19.95375(9)
CS	-15.81754(3)
SO	-26.19852(9)
ClO	-30.93970(9)
ClF	-39.22866(9)
Si_2H_6	-11.37852(6)
CH_3Cl	-22.50929(9)
H_3CSH	-18.29484(7)
HOCl	-31.60189(7)
SO_2	-42.29272(9)

The deviation of the VMC atomization energies from experiment for a single determinant SJ trial wavefunction composed of HF orbitals is shown in Figure 1. The MAD from experiment for the $2z$, $3z$, and $5z$ bases are 12.0 kcal/mol, 9.4 kcal/mol, and 8.9 kcal/mol, respectively. The deviation of the VMC atomiza-

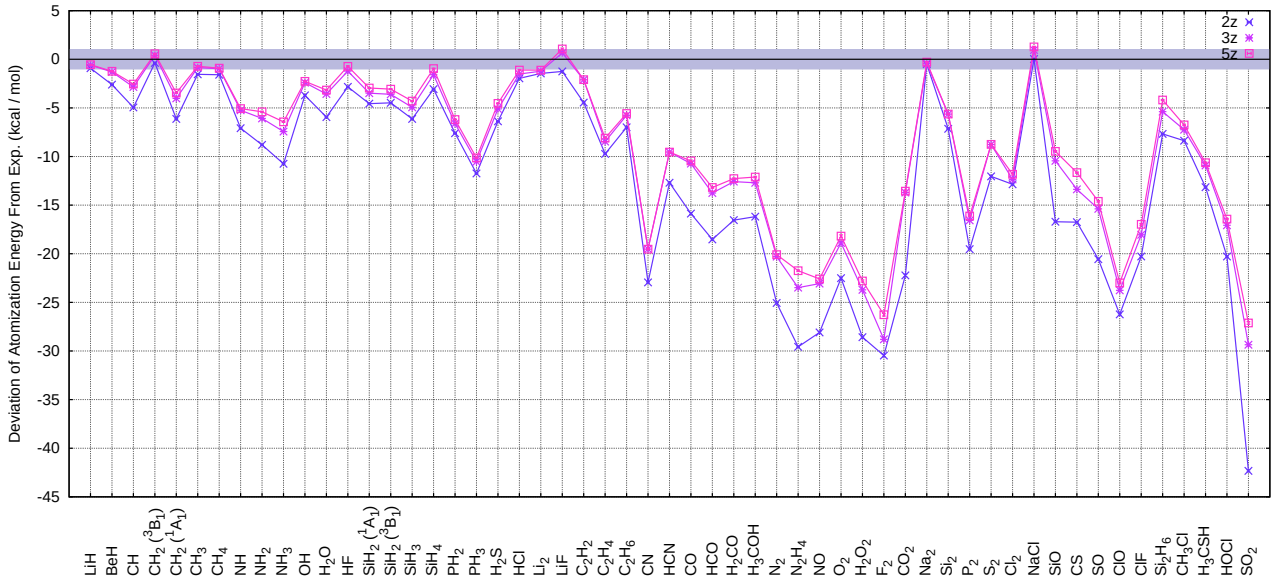

Figure 1: Deviation of the VMC atomization energies from experiment for a single determinant SJ trial wavefunction composed of HF orbitals. The MAD from experiment for the $2z$, $3z$, and $5z$ bases are 12.0 kcal/mol, 9.4 kcal/mol, and 8.9 kcal/mol, respectively.

tion energies from experiment for a single determinant SJ trial wavefunction composed of VMC optimized orbitals is shown in Figure 2. The MAD from experiment for the $2z$, $3z$, and $5z$ bases are 8.4 kcal/mol, 6.1 kcal/mol, and 5.2 kcal/mol, respectively. The deviation of the VMC atomization energies from experiment for the s and p valence CAS SJ trial wavefunctions is shown in Figure 3. The $5z$ single determinant results are included to demonstrate the benefit of using a CAS SJ trial wavefunction. This modest basis and CSF expansion results in a MAD from experiment of 2.9 kcal/mol.

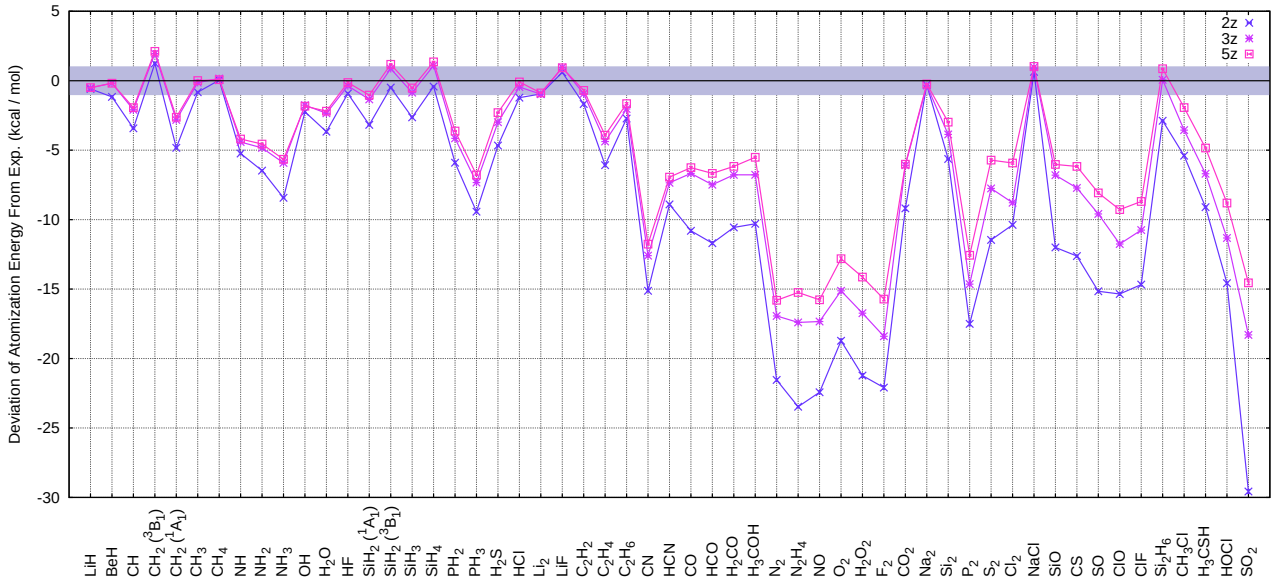

Figure 2: Deviation of the VMC atomization energies from experiment for a single determinant SJ trial wavefunction composed of VMC optimized orbitals. The MAD from experiment for the $2z$, $3z$, and $5z$ bases are 8.4 kcal/mol, 6.1 kcal/mol, and 5.2 kcal/mol, respectively.

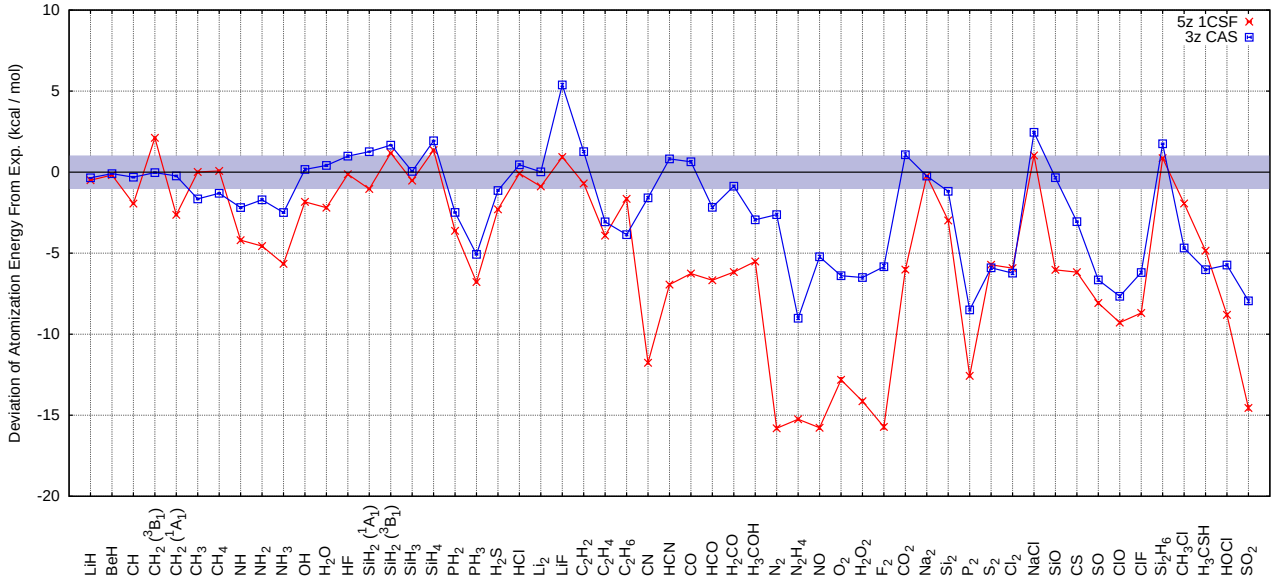

Figure 3: Deviation of the VMC atomization energies from experiment for a single determinant SJ trial wavefunction composed of VMC optimized orbitals and a CAS SJ trial wavefunction. The MAD from experiment for the single determinant SJ trial wavefunction is 5.2 kcal/mol. The MAD from experiment for the CAS SJ trial wavefunction is 2.9 kcal/mol.

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