

Considerations for Reliable Calculation of ^{77}Se Chemical Shifts

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Abstract: The theoretical chemical shifts of a large series of selenium compounds have been calculated using GIAO-MP2 and -DFT methods in several basis sets. Reliable chemical shifts are calculated for many compounds, especially with the mPW1PW91 exchange-correlation functional and either a triple- ζ basis set (tzvp: 13% mean absolute error) or a limited RECP set chosen for practical applications on complex molecules (BSL: 11.8% mean absolute error). Molecules with three-center-four-electron bonding or low-lying $n \rightarrow \pi^*$ states require additional diffuse functions and nonperturbative methods, respectively, but terminal selenium anions cannot be calculated reliably in the gas phase due to the neglect of solvation. When these cases are excluded, the mean absolute error decreases from 16.5% to 8.9% in GIAO-MP2/BSL but only slightly for DFT methods.

1. Introduction

Chemical shifts can be calculated using ab initio or density functional theory (DFT) through the gauge invariant atomic orbitals (GIAO) method with general applicability and reasonable accuracy.¹ For selenium compounds, early ab initio calculations showed that electron correlation was necessary for computation of accurate shielding constants.^{2,3} Møller–Plesset perturbation theory largely corrects the inaccuracy of GIAO-HF⁴ but is highly expensive and fails for some systems.⁵ Failures at the MP2 level can be corrected at higher levels of theory (CCSD(T)),⁶ but these methods are currently too expensive for practical application. DFT promises to be an economical means of calculating chemical shifts^{5,7} but systematic errors often result in the overestimation of the paramagnetic contribution to the shielding.⁸ Numerical corrections such as scaling factors,⁹ adjustments to the HOMO–LUMO gap,¹⁰ and level shifting of virtual orbital energies^{8,11} have been employed to improve DFT results.

GIAO shifts have been used successfully to explain experimental observations of complex molecules using simplified models.^{12,13} Bayse has recently shown that theoretical ^{77}Se NMR calculations of simple systems correlate

well to experimental shifts of selenoproteins.¹⁴ Continued interest in applications of theoretical ^{77}Se chemical shifts led us to examine the reliability of GIAO-MP2 and -DFT methods for a broad range of selenium functionalities. Basis set effects may be important for selenium due to the sensitivity of the nucleus to its electronic environment. Thus far, detailed studies of basis set effects have been limited to GIAO-HF methods or a few small molecules. The Schaefer et al. double- ζ basis set for selenium was selected for modification with diffuse and polarization functions. Chemical shifts were also calculated using Dunning's triple- ζ and correlation consistent basis sets. The reliability of GIAO shifts of geometries derived from effective core potential basis sets and GIAO-MP2//DFT chemical shifts are also examined for application to molecules of biological interest for which MP2 geometry optimizations would be prohibitively expensive.

2. Theoretical Details

Theoretical ^{77}Se NMR chemical shifts have been calculated for 64 selenium compounds using the GIAO-MP2 and -DFT (B3LYP,^{15,16} BLYP,^{17,16} B3P86,^{15,18} and mPW1PW91¹⁹) methods available in Gaussian98.²⁰ Configuration interaction wave functions were calculated for selected species using Gaussian98 (CIS) and GAMESS-UK²¹ (CISD). The reported

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chemical shifts are derived from the theoretical isotropic shielding referenced to that of Me_2Se calculated at the same level and basis set (eq 1).

$$\delta_i^{\text{calc}} = \sigma_{\text{ref}, \text{Me}_2\text{Se}}^{\text{calc}} - \sigma_{i, \text{Se}}^{\text{calc}} \quad (1)$$

For basis set I (BSI), selenium, phosphorus, sulfur, and chlorine basis sets are derived from the double- ζ plus polarization functions basis (DZP) of Schafer et al.²² The Se DZP basis set includes the diffuse selenium d-functions an early study showed were necessary for accurate energetics and geometries.²³ Hydrogen and first-row atoms were represented by Dunning's split valence triple- ζ (TZV) basis set²⁴ augmented with polarization functions on all non-carbon first-row atoms and hydrogens bonded to non-carbon heavy atoms. BSII adds a set of even-tempered diffuse s, p, and d functions to all non-carbon heavy atoms. BSIII modifies BSII by adding an additional set of s, p, and d diffuse functions to all heavy atoms. The effects of high angular momentum functions have been examined through the addition of f-type polarization functions to the selenium center ($\zeta_{f, \text{Se}}=5.8$). The exponent of these functions was optimized through MP2 geometry optimizations on SeH_2 . Additional f-type polarization functions were derived from this set of tight functions by dividing the exponent by four. GIAO calculations were also performed for a test set of 41 molecules with the mPW1PW91 functional and Dunning's TZVP, cc-pVDZ,²⁵ and cc-pVTZ²⁶ basis sets. The latter was modified by removing the f-type polarization functions on heavy atoms and the d-type polarization functions on hydrogen.

A basis set for geometry optimizations of large systems (BSL) was assembled from the relativistic effective core potential (RECP) basis set of Hurley et al.²⁷ for Se and the Wadt-Hay RECP for P, S, and Cl.²⁸ Oxygen, nitrogen, and fluorine were represented as in BSI. Hydrogens attached to non-carbon heavy atoms were represented as in BSII. Carbon and hydrogen atoms bonded to carbon were represented by the Dunning DZ basis set.²⁹ The RECP and carbon basis sets were modified by addition of a set of polarization functions. The selenium basis set also included an additional set of diffuse functions. The RECP basis set for selenium was used only for geometry optimization and was replaced with the all-electron Schafer et al.²² basis set used in BSI for GIAO calculations.

Relativistic effects have not been explicitly considered in these calculations, but effects due to the contraction of inner shell electrons are uniform and cancel in the calculation of the relative chemical shift.^{5,30} Structural changes due to relativistic effects should be incorporated in the BSL calculations through the RECP, but the difference between the BSI and BSL optimized geometries in this study is minor. Chemical shifts were calculated on structures corresponding to the minimum of the potential energy surface; rovibrational and dynamic effects have been ignored. The effects of conformational changes on the selenium chemical shift have been discussed in detail elsewhere.^{3,5} The lowest energy conformations were found for use in subsequent GIAO calculations.

Based upon previous studies of solvent dependence, the gas-phase theoretical chemical shifts presented in this work

should correlate well with most liquid- and solution-phase experimental results. Luthra et al.³¹ examined a series of selenides and diselenides to show a less than 20 ppm solvent-dependent shift in aprotic solvents. Protic solvents gave larger differences in certain cases. In another study, the chemical shifts of Me_2Se and PhSeEt in six protic and aprotic solvents ranging in polarity from cyclohexane to DMSO show standard deviations of roughly 7 ppm.³² For a selection of cationic selenium compounds and those with selenium adjacent to multiple bonds, the largest solvent-dependent difference between chloroform and trifluoroacetic acid was 21 ppm.³³ Larger solvent and phase dependencies occur in protic solvents with anionic solutes or when the solute can be protonated or deprotonated by the solvent.³³ For example, NaSeH shows an upfield shift with increasing hydrogen bonding ability of the solvent (−447 ppm (DMF), −495 ppm (EtOH), −529 (H₂O)). Alkylselenols are particularly sensitive to pH with shifts ranging from −150 to −200 ppm upon deprotonation.³³ Given these experimental observations of solvent dependence, correlation with gas-phase theoretical calculations should be maximized when weak intermolecular forces dominate solvation, but large discrepancies are expected when solvent effects are strong (i.e., anions, selenols).

3. Results and Discussion

Theoretical chemical shifts for selected basis sets and methods are listed with experimental values in Table 1. Tabulated results for all other basis sets and methods can be found in the Supporting Information. Detailed comparisons to previous theoretical studies will be omitted in the following discussion, but the overlapping data found in this study are generally comparable to previous work.^{2–8}

To gauge the overall quality of the calculated shifts, the experimental^{33–35} and theoretical data sets shown in Table 1 were plotted against one another. Plots for GIAO-MP2/BSI and GIAO-DFT(B3LYP)/BSI can be found in Figure 1 and are representative of plots of data for other basis sets and functionals. Regression and error data for additional methods and basis sets appear in Table 2. Three outliers appear in the GIAO-MP2 data (Figure 1a). These are $[\text{Se}_4]^{2+}$ (**41**), a known problem case for MP2,^{4,5} and related ions *cis*-(**42**) and *trans*- $[\text{Se}_2\text{S}_2]^{2+}$ (**43**). Several groups^{4,5} have examined the problems of GIAO-MP2 with the square $[\text{Se}_4]^{2+}$ cluster and conclude that DFT or multireference methods are required. Tuononen et al. have recently calculated very accurate chemical shifts for **41–43** using GIAO-DFT (BPW91 and B3PW91) and GIAO-CAS.³⁶ Omission of **41–43** from the GIAO-MP2 regression provides a near 1:1 correspondence and an overall upfield shift of 24.12 ppm based upon the y-intercept. Nakanishi and Hayashi¹² used similar plots of simple systems to calibrate method and basis set for their study of aryl selenides and obtained better correlation (B3LYP/6-311++G(3df,2pd), $R^2=0.998$) but used a limited reference set (11 compounds) and a single data point per compound. This study compares a test set of 41 compounds to averages of available experimental shifts in various solvents (Table 1).³⁷ Examination of individual data points shows that GIAO-MP2/BSI performs reasonably

Table 1. Experimental and Theoretical ^{77}Se Chemical Shifts for Various Selenium Compounds

	exp	solvent	GIAO-MP2 MP2/BSI	GIAO-MP2 MP2/BSL	GIAO-DFT B3LYP/ BSI	GIAO-MP2 B3LYP/ BSL	GIAO-DFT BSI	GIAO-DFT mPW1PW91/ BSL	GIAO-DFT mPW1PW91/ tzvp	GIAO-DFT mPW1PW91/ cc-pvdz
1	Me_2Se	0.0	0 (1970 ^a)	0.0 (2004 ^a)	0 (1691 ^a)	0 (1956 ^a)	0 (1804 ^a)	0 (1804 ^a)	0 (1805 ^a)	0 (1874 ^a)
2	MeSeEt	108 ^b	67	61	64	61	64	57	52	62
3	$\text{MeSeCH}_2\text{CH}_2$	192 ^c	179	179	183	176	218	194	176	168
4	$[\text{Me}_3\text{Se}]^+$	258, ^d 256 ^e	224	252	201	229	238	247	223	243
5	MeSeH	-130, ^f -155 ^g	-137	-128	-158	-121	-129	-125	-116	-124
6	$[\text{MeSe}]^-$	-332, ^{b,h} -330 ^d	-215	-274	-186	-243	-243	-290	-303	-243
7	H_2Se	-345(g), -288(l) ^d	-300	-276	-359	-264	-301	-299	-281	-290
8	$[\text{HSe}]^-$	-495, ^f -529 ^g , -518, ^h -447 ^h	-599	-578	-667	-554	-624	-614	-618	-570
9	Me_2SeO	819 ^d , 812 ^j	804	852	751	851	775	799	771	712
10	MeSeO_2H	1216 ^b	1272	1321	1237	1307	1248	1260	1232	1099
11	$[\text{MeSeO}_3]^-$	1045 ^k	1093	1136	984	1111	1027	1030	991	889
12	FSeO_3H	1001 ⁱ	1034	1069	989	1035	1040	1033	1003	915
13	MeSeSeMe	268, ^b 270, ^m 275, ⁿ 281, ^{o,d}	249	223	276	278	217	291	289	282
14	F_2CSe	688 ^p	574	577	673	591	684	725	690	576
15	AcSe^-	409 ^q	288	336	332	340	355	416	322	258
16	selenophene	605 ^{p,k}	583	602	546	588	581	591	567	539
17	1,2,3-selena- diazole	1502 ^r	1349	1360	1591	1484	1539	1534	1494	1458
18	Me_2SeCl_2	448 ^j	339	363	382	376	387	374	327	368
19	MeSeCN	120, ^s 123 ^t 125, ^o 133 ^u	88	117	70	104	84	114	89	88
20	CF_3SeCl	1077 ^v	1028	1048	1344	1150	1238	1246	1218	1130
21	Me_3PSe	-256, ^w -235, ^{x,y,z} -262	-322	-284	-310	-243	-311	-257	-265	-296
22	$\text{Se}(\text{SiH}_3)_2$	-666 ^{aa}	-633	-662	-666	-671	-634	-670	-691	-606
23	SeO_3	944 ^j	891	924	1316	886	1374	1364	1356	1262
24	$[\text{SeO}_3]^{2-}$	1263 ^{bb}	1385	1396	1297	1384	1303	1275	1268	1118
25	$[\text{SeO}_4]^{2-}$	1033, ^{bb} 1024 ^{cc} 1051 ^d	1185	1222	1098	1202	1131	1122	1090	960
26	$[\text{SeCN}]^-$	-322, ^h -273 ^{dd}	-404	-341	-497	-348	-448	-385	-413	-398
27	$[\text{Se}]^{2-}$	-511 ^f	-1040	-1040		-1054	-1206	-1206	-1203	-1135
28	SeOF_2	1378 ^f	1381	1420	1415	1382	1444	1442	1407	1335
29	SeOCl_2	1479, ^f 1501 ^v	1453	1443	1581	1434	1557	1509	1447	1466
30	SeCl_2	1758 ^{ee,ff,gg}	1785	1796	2548	2017	2275	2248	2162	2104
31	SeCl_4	1454 ^{l,ee}	1192	1187	1591	1341	1424	1368	1251	1353
32	$[\text{SeCl}_6]^{2-}$	863 ^{hh}	926	940	1298	1025	1136	1076	971	1053
33	SeF_4	1092, ⁱ 1083 ⁱⁱ	1221	1267	1215	1256	1226	1230	1161	1150

Table 1 (Continued)

34	SeF ₆	610, ⁱ 600 ⁱⁱ	neat	795	837	732	812	770	768	665	671
35	Se ₂ Cl ₂	1295/ ^{ee} ff, ^{gg} jj	CH ₂ Cl ₂ /heat	1214	1243	1588	1397	1444	1466	1433	1371
36	MeSSeSMe	784 ^{kk}		751	753	989	807	952	865	891	930
37	ClSSeSCl	1348 ^{gg}	neat	1018	1054	1276	1143	1164	1170	1115	1110
38	SeCO	-447 ^p	benzene	-490	-446	-574	-476	-502	-469	-479	-460
39	SeCS	102 ^p	benzene	-17	46	-27	10	47	114	98	63
40	CSe ₂	300, ^e 331 ^p	CH ₂ Cl ₂ /benzene	141	170	189	145	251	290	259	248
41	[Se ₄] ²⁺	1933 ^{ff}	SO ₂	323	744	2434	484	2311	2298	2226	2227
42	trans-[Se ₂ S ₂] ²⁺	1887 ^{mm}	SO ₂	831	917	2352	996	2254	2152	2057	2138
43	cis-[Se ₂ S ₂] ²⁺	2020 ^{mm}	SO ₂	658	898	2594	749	2469	2364	2279	2338

^a Absolute shielding of the reference Me₂Se/^b Reference 34a (NaSeMe), ^c Reference 34b (Me₃SeI, NaSeMe), ^d Reference 34c (Me₃SeI, NaSeMe, Na₂SeO₄), ^e Reference 34d (Me₃SeI), ^f Reference 34e ((NH₄)₂Se), ^g Reference 34f, ^h Reference 34g (NaSeH, KSeCN, NaSeMe), ⁱ Reference 34h (KSeH), ^j Reference 34i, ^k Reference 34j, ^l Reference 34k (K₂SeO₄), ^m Reference 34l, ⁿ Reference 34m, ^o Reference 34n, ^p Reference 34o, ^q Reference 34p (AcSeLi), ^r Reference 34q, ^s Reference 34r, ^t Reference 34s, ^u Reference 34t, ^v Reference 34v, ^w Reference 34u, ^x Reference 34w, ^y Reference 34x, ^z Reference 34y, ^{aa} Reference 34z, ^{bb} Reference 34aa (Na₂SeO₄, Na₂SeO₃), ^{cc} Reference 34bb ((NH₄)₂SeO₄), ^{dd} Reference 34cc (KSeCN), ^{ee} Reference 34dd, ^{ff} Reference 34ee, ^{gg} Reference 34ff, ^{hh} Reference 34gg ((NH₄)₂SeCl₆), ⁱⁱ Reference 34hh, ^{jj} Reference 34ii, ^{kk} Reference 34jj, ^{ll} Reference 34kk, ^{mm} Reference 35b.

well for many systems: 29% of the test set have errors less than 5%; 56% are below 15%. The mean absolute error of 21.0% is partially due to molecules such as **41**–**43** for which MP2 is known to fail. If the three outliers in the correlation plot are eliminated, the average error improves to 17.2%. Addition of a single set of f-type polarization functions to Se in BSI+f reduces the overall upfield shift of the theoretical data relative to experiment to 18.85 ppm and improves correspondence with experiment (slope = 1.001). The percentage of the test set with error below 15% decreases despite the slight improvement in the mean absolute error over BSI (Table 2). Diffuse functions in BSII increase the average error by ~2% for reasons explained below; errors for larger basis sets BSII+f and BSIII also exceed the error for BSI but by less than BSII.

The B3LYP XC functional commonly used in DFT studies has been documented to produce poor GIAO chemical shifts.⁷ Only 22% of the test molecules have error less than 5% and roughly half exceed 20% error. The B3LYP correlation plot (Figure 1b) has a slope of 1.198 consistent with the overestimation of the paramagnetic shielding in DFT. A skewed correlation plot is common for GIAO-DFT and is obtained to varying degrees for each functional in this study. Comparison of the B3LYP shifts with those obtained with BLYP and B3P86 (33.0 and 17.1% mean absolute error, respectively) suggests that the LYP correlation functional performs poorly in comparison to other functionals in the calculation of magnetic shielding properties. The mPW1PW91 functional shown to produce very accurate chemical shifts for ¹³C³⁸ gives an average absolute error comparable to B3P86 but has fewer species in excess of 15% error. GIAO-DFT(mPW1PW91) chemical shifts were also calculated using the TZVP, cc-pVDZ, and cc-pVTZ-fd basis sets. Each of these gives a lower mean absolute error than BSI and a slope closer to 1.0 for the correlation plot.

For GIAO studies of molecules of biological or catalytic interest, it may be practical to use RECP basis sets for heavy atoms such as Se, P, and Cl (as in BSL) to reduce the computational effort of the geometry optimization step. (Note that the ECP basis set for selenium must be replaced with an all-electron basis, here that of Schaefer et al. from BSI, for the GIAO calculations.) GIAO-MP2 calculations in BSL give the most ideal correlation plot of any method considered in this study (if [Se₄]²⁺ and its related ions are omitted). The mean absolute error also improves over MP2/BSI: 78% of test molecules have less than 20% error. Chemical shifts were also calculated from the B3LYP/BSL optimized geometry to obtain a mean absolute error ~2% greater than MP2/BSL likely due to the poor geometries generated with that functional.⁷ The mPW1PW91/BSL chemical shifts are even more accurate (11.8% average absolute error). Fifteen of the test molecules have less than 5% error, and only two molecules (MeSeEt and SeO₃) exceed 30% error. Large improvements in the theoretical chemical shift with mPW1PW91/BSL are also obtained for several species. SeCS has only 11.8% error in mPW1PW91/BSL but exceeds 100% error in virtually every other method and basis set. MeSeCN has roughly 30% error in BSI-III but is less than 10% for BSL. Less dramatically, the error for [Me₃Se]⁺ is reduced

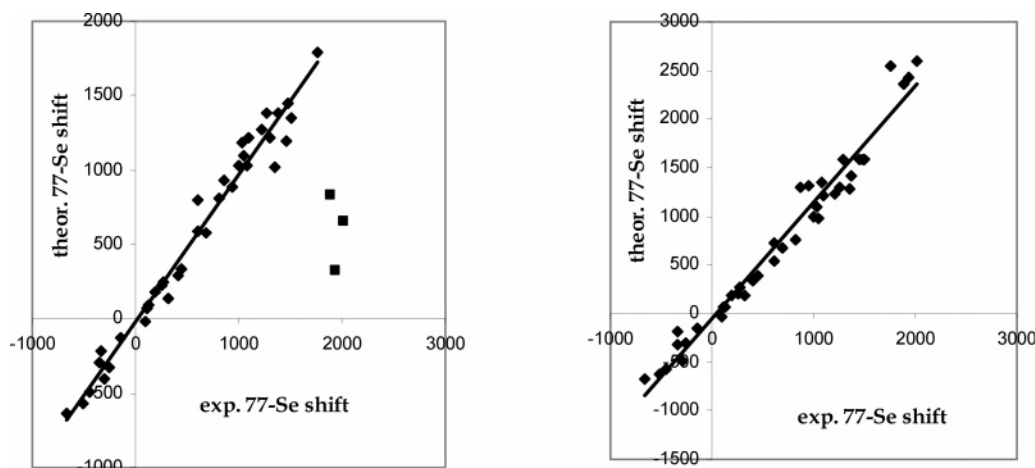


Figure 1. Plot of theoretical ((a) GIAO-MP2/BSI and (b) GIAO-DFT(B3LYP)/BSI) versus experiment ^{77}Se chemical shifts for the compounds in Table 1.

Table 2. Regression and Error Analysis for Experimental and Theoretical Data Presented in Table 1

method	geometry	slope	intercept	R^2	error ^b	error ^c
GIAO-MP2/BSI ^a	MP2/BSI	0.993	-24.116	0.975	20.9	17.2
GIAO-DFT ^d /BSI	B3LYP/BSI	1.198	-53.642	0.966	22.2	21.9
GIAO-DFT ^d /BSI	BLYP/BSI	1.242	-76.400	0.935	33.0	34.2
GIAO-DFT ^d /BSI	B3P86/BSI	1.149	-26.535	0.977	17.1	17.0
GIAO-DFT ^d /BSI	mPW1PW91/BSI	1.133	-24.739	0.975	17.0	16.7
GIAO-DFT ^d /tzvp	mPW1PW91/tzvp	1.078	-26.636	0.977	13.0	13.1
GIAO-DFT ^d /cc-pvdz	mPW1PW91/cc-pvdz	1.058	-33.051	0.972	15.1	15.1
GIAO-DFT ^d /cc-pvtz-fd	mPW1PW91/cc-pvtz-fd	1.072	-36.055	0.976	15.1	15.3
GIAO-MP2/BSI+f ^a	MP2/BSI+f	1.004	-18.847	0.975	20.1	16.7
GIAO-MP2/BSII ^a	MP2/BSII	1.025	-44.622	0.977	22.8	18.5
GIAO-MP2/BSII+f ^a	MP2/BSII+f	1.034	-37.647	0.978	21.0	17.3
GIAO-MP2/BSIII ^a	MP2/BSIII	1.034	-39.007	0.977	21.5 ^e	17.5 ^e
GIAO-MP2/BSL ^a	MP2/BSL	0.998	-5.567	0.975	16.5	13.4
GIAO-DFT ^d /BSL	mPW1PW91/BSL	1.100	-2.240	0.978	11.8	11.5
GIAO-MP2/BSL ^a	B3LYP/BSL	1.036	-5.888	0.980	18.3	14.9

^a Regression calculations in MP2 omit $[\text{Se}_4]^{2+}$, *cis*- and *trans*- $[\text{Se}_2\text{S}_2]^{2+}$. ^b Mean absolute error for all 41 molecules in the test set. ^c Mean absolute error for the test set omitting $[\text{Se}_4]^{2+}$, *cis*- and *trans*- $[\text{Se}_2\text{S}_2]^{2+}$. ^d GIAO-DFT calculations use the same functional as for the geometry optimization. ^e MP2/BSIII calculations omit $[\text{SeCl}_6]^{2-}$.

below 5% versus error exceeding 15% for shifts calculated in most all-electron basis sets.

In the data shown in Table 1, systems with large error (other than **41–43**) tend to be species with terminal anionic selenium (**6**, **8**, **15**, **26**), low-lying $n \rightarrow \pi^*$ excited states (**14**, **21**, **28**, **39**, **40**), or three-center-four-electron bonding (**18**, **31**, **32**, **33**, **34**). The average error for each of these groups is shown in Table 3. When these groups are excluded, the mean absolute error for the remaining ‘well-behaved’ species drops to $\sim 9\%$ with MP2 in BSI–BSIII. The error for systems with low-lying $n \rightarrow \pi^*$ excited states and 3c4e bonding decreases with the addition of f functions and diffuse functions, respectively, but that for species with anionic Se increases substantially when diffuse functions are added (MP2/BSI: 29.4%, MP2/BSII: 39.3%, MP2/BSIII: 39.9%). The large errors associated with these species lead to a net increase in error for the overall test set. For anions such as $[\text{MeSe}]^-$ or $[\text{Se}]^{2-}$ where the charge is localized on selenium, solvent interactions will serve to delocalize this charge and deshield the selenium nucleus. Therefore, gas-phase theoretical shifts tend to be upfield of the experimental values, more

so when diffuse functions are included. For example, the GIAO-MP2/BSI shift (-574 ppm) of $[\text{SeH}]^-$ agrees well with experimental data, but more diffuse basis sets shift it increasingly further upfield (BSII -698) because additional basis functions allow more charge to accumulate on Se (BSI $-0.972e$; BSII $-1.020e$). Similar basis set effects are observed for some systems with electronegative atoms. Methylselenenate $[\text{MeSeO}]^-$ (Table 5) shows a steady downfield shift with an increased basis set. The Mulliken charges show that as the basis set becomes more diffuse, the electron density on the oxygen increases, pulling charge and electron density toward oxygen (BSI: $-0.921e$; BSIII: $-1.277e$) to deshield the selenium nucleus. A similar basis set dependency is observed for MeSeF , MeSeCl , SeCl_2 , and other molecules with divalent selenium bonded to electronegative atoms.

Errors for compounds with 3c4e bonding are partially due to an incomplete basis set and are reduced with additional diffuse functions or larger basis sets (Table 3). For example, error for SeF_4 is consistently above 10% in all methods in BSI and BSL but decreases to 7.7% in MP2/BSII, 5.0% in

Table 3. Error Analysis for Species with Large Error

method	geometry	error ^b	error ^c	error ^d	error ^e
GIAO-MP2/BSI	MP2/BSI	29.4	45.3	17.2	9.0
GIAO-DFT ^a /BSI	B3LYP/BSI	40.0	44.1	23.1	14.4
GIAO-DFT ^a /BSI	BLYP/BSI	54.4	74.2	41.4	22.0
GIAO-DFT ^a /BSI	B3P86/BSI	29.3	26.3	21.0	12.5
GIAO-DFT ^a /BSI	mPW1PW91/BSI	28.1	22.2	18.4	13.5
GIAO-DFT ^a /tzvp	mPW1PW91/tzvp	22.3	7.0	10.7	12.6
GIAO-DFT ^a /cc-pvdz	mPW1PW91/cc-pvdz	27.4	19.3	11.3	12.7
GIAO-DFT ^a /cc-pvtz-fd	mPW1PW91/cc-pvtz-fd	32.3	23.1	11.1	11.4
GIAO-MP2/BSI+f	MP2/BSI+f	28.7	41.3	18.0	9.1
GIAO-MP2/BSII	MP2/BSII	39.3	48.6	13.8	9.2
GIAO-MP2/BSII+f	MP2/BSII+f	38.7	41.9	14.5	8.9
GIAO-MP2/BSIII	MP2/BSIII	39.9	44.9	12.8 ^f	8.8
GIAO-MP2/BSL	MP2/BSL	15.6	26.1	20.5	8.9
GIAO-DFT ^a /BSL	mPW1PW91/BSL	13.8	6.5	17.6	10.5
GIAO-MP2/BSL	B3LYP/BSL	17.2	33.6	19.0	9.9

^a GIAO-DFT calculations use the same functional as for the geometry optimization. ^b Mean absolute error for terminal anionic Se species.

^c Mean absolute error for molecules with low-lying $n \rightarrow \pi^*$ excited states. ^d Mean absolute error for species with 3c4e bonding. ^e Mean absolute error for the remainder of the test set also omitting **41–43**. ^f MP2/BSIII calculations omit $[\text{SeCl}_6]^{2-}$.

MP2/BSIII, and 1.9% in mPW1PW91/cc-pVTZ-fd. Augmentation with f-type Se polarization functions shows only a slight improvement for the molecules with low-lying $n \rightarrow \pi^*$ excited states. Of this class of molecule, SeCS gives some of the largest errors for any molecule in this study (116% in MP2/BSI). A plot of the MP2/BSI error for the series **38–40** versus the first CIS excitation energy is roughly linear suggesting that the excessive error is due to an overestimation of the contribution of the $n \rightarrow \pi^*$ excitation to the shielding which would be corrected with nonperturbative methods such as DFT or CCSD. The mPW1PW91 functional with the BSL and TZVP basis sets gives the lowest error (6.5 and 7.0% error, respectively).

The addition of f-type polarization functions in BSI+f and BSII+f results in downfield shifts of ~ 230 ppm for $[\text{Se}_4]^{2+}$, slight decreases in bond length, and significant MP2 energy corrections (Table 3). A diffuse exponent f-type polarization function (BSI+f': $\zeta=0.36$) was used to give a shift further downfield and an even shorter bond length, but the correlation energy recovered did not compare with that obtained using the tight f function of BSI+f.³⁹ Geometries of $[\text{Se}_4]^{2+}$ were calculated using CISD in BSI and BSI+f, giving Se–Se bond lengths in very close agreement with the X-ray structure (exp: 2.28 Å; CISD/BSI+f: 2.284 Å). The additional f function gives a significant reduction in energy for a variational calculation. Additional f functions in GIAO-MP2 (BSI+2f, BSI+3f) successively move the $[\text{Se}_4]^{2+}$ chemical shift downfield and reduce the bond length to within 0.03 Å of the experimental value. These data suggest that the problem with MP2 is fundamentally one of basis set which is partially corrected with f-type polarization functions. An s- or p-type function cannot mix with face-to-face interactions of the filled d orbitals in the core of each selenium. As a result, the ring must expand to relieve repulsions between electrons in these orbitals. Inclusion of f-type functions allow these AOs to distort away from the ring, depleting electron density in the ring and allowing a closer interaction of the d orbitals. The net result is a shorter

Table 4. Relative Energies and Chemical Shifts for $[\text{Se}_4]^{2+}$

	ΔE , kcal/mol ^a	δ , ppm ^b	$d(\text{Se}-\text{Se})$, Å
MP2/BSI	0.0	323	2.360
MP2/BSI+f	−523.70	552	2.355
MP2/BSI+f'	−83.36	889	2.326
MP2/BSI+2f	−698.65	973	2.336
MP2/BSI+3f	−767.16	1236	2.311
MP2/BSII	−270.99	286	2.364
MP2/BSII+f	−575.78	516	2.359
MP2/BSIII	−617.79	359	2.359
CISD/BSI	[0.0]		2.295
CISD/BSI+f	[−332.26]		2.284
B3LYP/BSI	(0.0)	2434	2.347
B3LYP/BSI+f	(−0.22)	2432	2.347
exp		1958	2.283 ^c

^a Relative to BSI, DFT results are in parentheses, CISD in brackets.

^b Relative to Me_2Se . ^c Reference 35a.

Se–Se bond length and an improved theoretical chemical shift in MP2.

The B3LYP chemical shifts and bond lengths in Table 4 (BSI, BSI+f) do not display large basis set dependence; the bond length remains the same, and there are only minor changes in the theoretical chemical shift. Schreckenbach et al.⁵ performed GIAO-DFT calculations on $[\text{Se}_4]^{2+}$ with the addition of one and two sets of f functions with no change in the absolute ⁷⁷Se shielding constant. The hybrid functional B3 consistently underestimates the theoretical shielding (compare B3LYP to BLYP; B3PW91 to BPW91 in ref 36). The hybrid functionals (B3 and mPW1PW91) underestimate the shielding by ~ 200 ppm, suggesting that the inclusion of the exact HF exchange results in excessive deshielding of these aromatic clusters.

The theoretical data in Table 5 for compounds that do not have experimental data available agree well with other known analogues. The quality of these comparisons is important if simplified model compounds¹⁴ are to be used for more complicated chemical systems. For the series of increasingly

Table 5. Theoretical ^{77}Se Chemical Shifts for Various Selenium Compounds

		GIAO-MP2 MP2/BSI	GIAO-MP2 MP2/BSL	GIAO-DFT B3LYP/BSI	GIAO-MP2 B3LYP/BSL	GIAO-DFT mPW1PW91/BSI	GIAO-DFT mPW1PW91/BSL
44	MeSeCCH	52	85	32	69	75	83
45	Me ₂ SeO ₂	973	1047	884	1020	931	944
46	MeSeOH	1153	1178	1291	1188	1212	1218
47	[MeSeO] ⁻	836	828	868	869	815	819
48	[MeSeO ₂] ⁻	1199	1251	1122	1250	1136	1157
49	MeSeO ₃ H	1083	1129	995	1100	1040	1043
50	Me ₂ Se(OH) ₂	486	520	457	512	471	480
51	Me ₂ Se(OMe) ₂	519	629	591	629	612	598
52	MeSeSe(O)Me	408	393	630	476	507	507
	MeSeSe(O)Me	990	1029	966	1070	957	998
53	MeSeSMe	333	348	423	386	385	388
54	MeSSe(O)Me	994	1038	979	1062	976	997
55	MeSeNH ₂	508	534	560	546	526	535
56	MeSeNMe ₂	726	717	775	742	746	737
57	H ₂ CSe	2763	2729	3259	2720	3210	3247
58	Me ₂ CSe	2173	2142	2358	2180	2340	2351
59	Me ₂ Se(OH)Cl	461	510	456	517	468	485
60	MeSeF	1961	1991	2261	2000	2131	2141
61	MeSeCl	920	959	1289	1097	1171	1187
62	SeCl ₆	446	472	638	499	546	506
63	SeF ₂	3414	3476	3957	3492	3734	3834
64	Se ₂ F ₂	1743	1584	1921	1819	1817	1817

unsaturated alkenes **2**, **3**, and **44** there is a roughly 110 ppm downfield shift from the alkane to the alkene and a ~120 ppm upfield shift from the alkene to the alkyne. A similar phenomenon has been observed in the experimental shifts of a series of 2-phenyl asymmetric selenides (MeSeCH₂CH₂-Ph 90 ppm, MeSeCHCHPh 186 ppm, MeSeCCPh 78 ppm). The experimental shift of methylphenylselenone is 977 ppm,⁴⁰ very similar to that of **45**. The theoretical shift of selenoacetone **58** (2173 ppm) corresponds well to the simplest known selenoketone (tBu)₂C=Se (2131 ppm).⁴¹ The upfield shift of methylselenonic acid **49** relative to methylseleninic acid **10** mirrors observations for CF₃SeO₂H (1231 ppm) and CF₃SeO₃H (981 ppm).³³ Our previous study reported that the theoretical shifts of the simple diselenide **13** and selenenyl sulfide **53** compare well to the experimental shifts of biologically relevant analogues.¹⁴ Known selenenyl sulfide oxides are found around 1050 ppm,⁴² very similar to the GIAO-MP2/BSIII data (1027 ppm).

Unfortunately, broad comparisons with experimental analogues break down when some of the simple systems in Table 1 are compared to their aryl derivatives. Lower oxidation state selenium compounds are more affected by aryl substitution than highly oxidized centers because the aromatic ring can delocalize electron density located on selenium. For example, methylselenenamide **55** and *N,N*-dimethylmethylselenenamide **56** are upfield of aryl selenenamides which typically appear between 600 and 950 ppm.⁴³ Two known organoselenium dichlorides, Ph₂SeCl₂ (586 ppm)⁴⁴ and MePhSeCl₂ (488 ppm),⁴⁰ appear downfield of **33** due to phenyl effects. In comparison to **51**, a bisbenzyl derivative, MePhSe(OBz)₂, has a ^{77}Se chemical shift of 663–672 ppm.^{40,44} Related selenoxide hydrates such as **50** have been proposed as intermediates in the racemization of selenoxides but have not been reported in NMR.

Conclusions

Theoretical chemical shifts have been calculated in several methods and basis sets to demonstrate the overall reliability of GIAO for a wide range of selenium functionalities. For ‘well-behaved’ systems, the mean absolute error is ~9.0% at the MP2 level and 10–15% for B3LYP, B3P86, and mPW1PW91. The mPW1PW91 hybrid functional gives the lowest mean error for the entire test set of compounds (11.8% BSL, 13.0% tzvp) and is the recommended functional based upon the results of this limited analysis of XC functionals. The larger error for DFT for this somewhat arbitrarily defined set of ‘well-behaved’ molecules is due to the established difficulties inherent in nonexact DFT.⁸ However, the successful calculation of chemical shifts for systems for which MP2 fails or performs poorly (**41**–**43** and species with low-lying $n \rightarrow \pi^*$ excited states) makes DFT an important tool nonetheless. The reliability of GIAO-DFT is limited in many of the same cases as MP2 but outperforms for [SeO₃]²⁻, [SeO₄]²⁻, SeCF₂, 1,2,3-selenadiazole, and [Se₄]²⁺ and related ions but underperforms in several notable cases (e.g., Me₂-SeO, SeO₃, SeCl₂, and MeSeSeMe). However, neither DFT nor MP2 was able to calculate an accurate chemical shift for MeSeEt which exceeds 30% error in every method and basis set. The consistency of the theoretical shifts for MeSeEt may indicate that solvent effects contribute significantly to the experimental chemical shift.

Of the basis sets examined in this study, it is difficult to suggest a generally reliable choice due to significant variance in performance with method and functional, but a basis set of at least triple- ζ quality would be recommended. Systems involving 3c4e bonding should be augmented with diffuse functions, and theoretical chemical shifts of terminal selenium anions should be treated with skepticism due to the

absence of solvation effects. The limited RECP basis set (BSL) gives surprisingly good results, a promising development for the reliable calculation of theoretical chemical shifts for the larger molecules of interest to synthetic, biological, and medicinal chemists.

Further applications of theoretical chemical shifts are currently being examined by this research group.

Supporting Information Available: Table of theoretical chemical shifts (GIAO-MP2 (BSI+f, BSII, BSII+f, BSIII, BSI/B3LYP/BSI) and GIAO-DFT (BLYP/BSI, B3P86/BSI, mPW1PW91/cc-pVTZ-fd)). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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