Examining the Performance of DFT Methods in Uranium Chemistry: Does Core Size Matter for a Pseudopotential?

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We have investigated the performance of DFT in U(VI) chemistry. A large, representative selection of functionals has been tested, in combination with two ECPs developed in Stuttgart that have different-sized cores (60 and 78 electrons for U). In addition, several tests were undertaken with another 14 electron pseudopotential, which was developed in Los Alamos. The experimental database contained vibrational wavenumbers, thermochemical data, and ^{19}F chemical shifts for molecules of the type $UF_{6-n}Cl_n$. For the prediction of vibrational wavenumbers, the large-core RECP (14 electrons) gives results that are at least as good as those obtained with the small-core RECP (32 electrons). GGA functionals are as successful as hybrid GGA for vibrational spectroscopy; typical errors are only a few percent with the Stuttgart pseudopotentials. For thermochemistry, hybrid versions of DFT are more successful than GGA, LDA, or meta-GGA. Marginally better results are obtained with a 32 electron ECP than with 14; since the experimental uncertainties are at least 25 kJ/mol for each reaction, the best functionals give results that are essentially indistinguishable from experiment. However, large-basis CCSD(T) results match experiment better than any DFT that we examined. Our findings for NMR spectroscopy are rather disappointing; no combination of pseudopotential, functional, and basis yields even a qualitatively correct prediction of trends in the ^{19}F chemical shifts of $UF_{6-n}Cl_n$ species. Results yielded by the large-core RECP are, in general, slightly less bad than those obtained with the small core. We conclude that DFT cannot be recommended for predictions of NMR spectra in this series of compounds, though this conclusion should not be generalized. Our most important result concerns the good performance of the large-core Stuttgart pseudopotential. Given its computational efficiency, we recommend that it be used with DFT methods for the prediction of molecular geometries, vibrational frequencies, and thermochemistry of a given oxidation state. The hybrid GGA functionals MPW1PW91 and PBE0 give the best results overall.

Introduction

There has been a resurgence of interest in actinide chemistry during the past few years, for both practical and theoretical reasons. From the practical point of view, the production of atomic weapons and the generation of electricity in atomic power stations have both produced large quantities of radioactive waste. The development of satisfactory methods for the storage and treatment of these wastes is one of the most pressing environmental challenges at present. It is clear that the development of these methods will require a thorough understanding of the fundamental factors that control actinide chemistry. Since most of the actinides are radioactive, experimental studies of their behavior are difficult. It is therefore tempting to enquire to what extent current theoretical methods are useful in this area.

From the theoretical point of view, the development of methods that can treat actinide compounds satisfactorily is still a challenge. Not only are there large numbers of electrons to be treated; more importantly, both relativistic effects and electron correlation have to be taken into account to a high degree of accuracy. For reasons of computational efficiency, density functional theory (DFT) is very attractive, and several studies have shown that it can be applied satisfactorily to many problems in actinide chemistry.[1–5] The pseudopotential (or effective core potential, ECP) approach is also attractive for efficiency considerations, and again, it has been tested in actinide chemistry by several authors. It is essential to note that scalar relativistic effects can be included in the pseudopotential approach; the abbreviation RECP is often used to indicate that these effects have been incorporated.[6]

However, several questions remain open. There are many different versions of DFT; does it matter which one is chosen? Is the performance of the different functionals equally good (or bad) for different properties, or must one choose according to the property of particular interest? Within the pseudopotential approach, the number of electrons to be treated explicitly must be considered; is it sufficient to treat "only" the 5f, 6s, 6p, 6d, and 7s shells (14 electrons in the case of uranium), or is it prudent/essential to treat the 5s, 5p, and 5d shells as well, giving 32 electrons in the case of uranium? These two are generally described as "large-core" and "small-core" pseudopotentials, respectively. There are clearly good computational reasons to choose the 14 electron version if its performance is satisfactory. Note that we use the terms "small core" or "large core" to characterize the RECPs including 60 or 78 core electrons. These are sometimes described in the literature as "very small core" or "small core", respectively.

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The aim of this paper is to provide at least partial answers to these questions. We have limited ourselves to a consideration of the chemistry of U(VI), for two reasons, one practical and the other computational: there are more experimental data available for uranium than for other elements, and since all of these compounds are closed-shell, the effects of spin−orbit coupling are much smaller than those for many other actinide compounds, though we note that spin−orbit effects can be important for NMR shielding.[7] It should be clear that the ability of a particular theoretical approach to yield quantitatively useful data for U(VI) compounds is a necessary, but hardly sufficient, condition for its use in a more general context. We shall analyze the performance of DFT for the prediction of vibrational frequencies, thermochemical data, and NMR chemical shifts (of F bonded to U, the use of a pseudopotential on U rules out the calculation of chemical shifts for that nucleus). In particular, we shall compare two different sizes of pseudopotentials which have been prepared by the same group and more than a dozen different functionals. We shall pay little attention to molecular geometries since we are aware of only a single compound (UF_6) for which gas-phase data are available.

Many authors have already assessed the performance of different functionals in various areas of chemistry. Among recent work, we note a study by Truhlar and co-workers that concerned inorganometallic and organometallic compounds,[8] one by Jacquemin et al. concerning the properties of oligomers,[9] another by Truhlar and his colleagues on 3d transition-metal chemistry,[10] two by Bühl and his group devoted to the geometries of first-row and second-row transition-metal complexes,[11,12] and one by Merz and co-workers that considered essentially organic molecules.[13] Unfortunately, no consensus has yet emerged from these studies. The functional that is most suitable for a particular property or area of the periodic table may not be the best for another area or property, and in particular, debate continues on the need to include some exact exchange for the treatment of heavy atoms. Several methodological studies of the application of DFT to the vibrational spectra of actinide compounds have been published, of which the following deserve a special mention. De Jong and co-workers reported that large-core RECPs are not satisfactory for the uranyl ion.[1] Han and Hirao were less categorical. In their study of UO_2^{2+} and UF_6, they note that large-core RECPs may be a practical choice, provided that hybrid functionals are adopted.[2] Garcia-Hernandez et al., who also worked on UO_2^{2+} and UF_6, found that large-core RECPs are somewhat less accurate than all-electron methods.[3] Hay and Martin[4] and Schreckenbach et al. studied UF_6[14] and concluded that both local density and hybrid functionals can yield satisfactory results with a large core, though all-electron methods were more successful. Groenewold and colleagues have tested several different functionals in their work on complexes of the uranyl ion and report that the LDA approach is the most successful of their sample, though hybrid and GGA functionals were almost as accurate.[15,16] Very recently, Shamov et al. presented a comprehensive computational study of the structures and thermodynamics of uranium oxofluorides.[17] These workers tested MP2 and two different functionals using both small-core RECPs and all-electron approaches.

Despite this extensive activity devoted to "light" atoms,[8–12,14–17] it seemed to us that there was still a need in actinide chemistry for a systematic study that would test a wide selection of functionals, several different molecular properties, and, most importantly, the effect of core size within the pseudopotential approximation. We draw the readers' attention to three reviews, from different periods, of theoretical actinide chemistry.[14]

Computational Details

All calculations were performed at the DFT level of theory as implemented in the Gaussian 03 set of programs,[18] with the exception of a few "calibration" calculations undertaken at the CCSD(T) level of theory; these latter are described in the Thermochemistry section. Uranium was described by either a small-core (32 "valence" electrons) or a large-core (14 "valence" electrons) RECP extracted by the Stuttgart−Dresden−Bonn group, in combination with the associated basis sets (but g-type functions were, in general, excluded, except where indicated otherwise).[6,19] In the calculations of vibrational frequencies and reaction enthalpy changes, carbon, nitrogen, oxygen, and fluorine atoms were represented by pseudopotentials developed in Toulouse, together with basis sets of "double-ζ-plus-polarization" quality; diffuse s and p functions were added to the bases for O and F.[20] These basis sets have been used in several earlier publications on actinide chemistry.[5,21,22] We draw attention to our choice of exponents for d-type polarization functions; these are (roughly) optimized variationally for the compounds of interest at the B3LYP level of theory, and are sometimes much smaller than those obtained by wave function methods for these elements as isolated atoms [for example, 0.57 for F (optimized for UF_6) or 0.73 for O (UO_2^{2+})]. However, it is important to note that DFT energies are far less sensitive to the values of the polarization exponents than are wave-function-based energies. A standard DZP basis was used for the H atom (p-type exponent 0.9). Several test calculations were undertaken in which uranium was described by the 14 electron RECP developed in Los Alamos and the associated double-ζ basis set (noted LANL2DZ).[4] To enable us to compare the performance of the Los Alamos basis and pseudopotential for uranium with those developed in Stuttgart, the same description of C, N, O, F, and H atoms was adopted in these tests as in the calculations with the other pseudopotentials. In what follows, reference to a pseudopotential without further qualification will imply that the pseudopotential was developed in Stuttgart.

Four different basis sets were used for the fluorine and chlorine atoms in the calculations of the ^{19}F chemical shifts of the series of molecules $UF_{6-n}Cl_n$ ($n = 1-6$): the augmented correlation-consistent double-ζ and triple-ζ bases[23] and the 6-311G(3df) basis and the 6-311+G(3df) basis.[24] Since chemical shifts are conventionally quoted with respect to a standard reference compound, the same bases were also used for the study of CCl_3F. Geometries were systematically optimized for each compound with each functional and each basis prior to the NMR calculation. ^{19}F NMR chemical shifts were computed using the gauge-including atomic orbital (GIAO) approach.[25]

Within the general framework of DFT, there are so many different exchange and correlation functionals that it is neither feasible nor sensible to test every possible combination thereof. Preliminary tests revealed only modest changes in performance for different versions of functionals developed by a group of authors. Moreover, the choice of exchange functional appears to have relatively little influence. When a group of authors developed functionals for both correlation and exchange, it seemed more reasonable to test their combination rather than combine functionals developed with different philosophies.

Perdew and Schmidt have proposed a classification of different generations of DFT.[26] According to their classification, functionals can be placed in one of five categories (or generations), LSDA, GGA, hybrid GGA, meta-GGA, and hybrid meta-GGA. We refer interested readers to a recent review for explanations of these acronyms.[27] We decided to test a selection of functionals from the first four of these categories (only a

TABLE 1: Vibrational Wavenumbers Computed with Various Functionals Combined with the Large-Core RECP (RECP14) or Small-Core RECP (RECP32)[a]

	RECP14							RECP32						
	NUN	CUO	CUO	NUO^+	NUO^+	UO_3	UO_3	NUN	CUO	CUO	NUO^+	NUO^+	UO_3	UO_3
		(C−U)	(O−U)	(N−U)	(O−U)	sym	asym		(C−U)	(O−U)	(N−U)	(O−U)	sym	asym
exp corr.	1089	1062	881	1134	979	768	875	1089	1062	881	1134	979	768	875
B3LYP	1105	1107	876	1174	1003	766	906	1125	1142	886	1184	999	779	891
calc − exp	*16*	*45*	*−5*	*40*	*24*	*−2*	*31*	*36*	*80*	*5*	*50*	*20*	*11*	*16*
BP86	1059	1034	839	1102	957	736	868	1085	1091	862	1125	958	749	846
	−30	*−28*	*−42*	*−32*	*−22*	*−32*	*−7*	*−4*	*29*	*−19*	*−9*	*−21*	*−19*	*−29*
B3PW91	1122	1122	894	1193	1024	785	927	1142	1162	903	1206	1020	798	916
	33	*60*	*13*	*59*	*45*	*17*	*52*	*53*	*100*	*22*	*72*	*41*	*30*	*41*
B1B95	1137	1132	905	1203	1035	783	935	1156	1179	912	1222	1031	806	929
	48	*70*	*24*	*69*	*56*	*15*	*60*	*67*	*117*	*31*	*88*	*52*	*38*	*54*
BLYP	1038	1012	819	1078	932	712	840	1064	1064	842	1099	933	727	809
	−51	*−40*	*−62*	*−56*	*−47*	*−56*	*−35*	*−25*	*2*	*−39*	*−35*	*−46*	*−41*	*−66*
MPW1PW91	1138	1143	909	1215	1040	797	941	1142	1179	914	1226	1035	810	932
	49	*81*	*28*	*81*	*61*	*29*	*66*	*53*	*117*	*33*	*92*	*56*	*42*	*57*
PBE0	1141	1147	913	1218	1042	798	942	1161	1183	917	1229	1038	812	935
	52	*85*	*32*	*84*	*63*	*30*	*67*	*72*	*121*	*36*	*95*	*59*	*44*	*60*
B3LYP/LANL2DZ	1094	1072	837	1133	966	733	870							
	5	*10*	*−44*	*−1*	*−13*	*−35*	*−5*							
MPW1PW91/LANL2DZ	1126	1113	871	1177	1007	769	908							
	37	*51*	*−10*	*43*	*28*	*1*	*33*							
BLYP/LANL2DZ	1023	964	777	1023	883	681	787							
	−66	*−98*	*−104*	*−111*	*−96*	*−87*	*−88*							

[a] Wavenumber differences (calculated − experimental) appear in italics. Linearity has been imposed for the triatomic molecules.

limited number of hybrid meta-GGA functionals has been developed to date).

The simplest functional tested here belongs to the first category and is noted SVWN5[28,29] in the Gaussian terminology. Within the GGA framework, we tested BLYP,[30,31] BP86,[30,32] PW91,[33] and PBE;[34] this choice was determined by the considerations proposed above and by the popularity of these functionals. Six different hybrid GGA functional were investigated, B1B95,[35] B1LYP,[35,36] B3LYP,[31,37] B3PW91,[33,37] MPW1PW91,[38] and PBE0.[34] Finally, we studied two meta-GGA, TPSS[39] and VSXC.[40]

Results and Discussion

1. Vibrational Wavenumbers. There are relatively few simple uranium-containing molecules for which secure experimental vibrational data are available. The molecules need to be small and to allow a substantial number of functionals to be investigated without an excessive computational effort, and ideally, the experimental data should refer to isolated molecules (gas phase). The only compound known to us which meets all of our requirements is UF_6, for which high-quality (harmonic) gas-phase data have been published.[41] Data for NUN, CUO, NUO^+, and UO_3, trapped in rare-gas matrixes, have been published by Andrews and co-workers.[22,42–44] We described earlier how we estimated both the differences between observed and harmonic vibrational wavenumbers and the differences between matrix-isolated and gas-phase vibrational data for the three triatomic molecules;[45] in this work, we have made similar corrections (+1.1%) to the observed data for the two vibrational wavenumbers observed for UO_3 in a neon matrix. We limit ourselves here to the stretching motions of these molecules since the bending modes have not been observed experimentally. However, we shall need to consider the linearity of some of these molecules since CUO and NUN are nonlinear at some levels of theory, as discussed in more detail below.

In Table 1, we present the harmonic vibrational wavenumbers calculated with both the 14 and 32 electron RECP for NUN, CUO, NUO^+, and UO_3. A selection of results obtained with the LANL2DZ pseudopotential and basis set is presented. The differences between the calculated and corrected experimental values are also given. In order to assess the overall performance of each functional, we present several statistical measures in Table 2: the mean absolute error in vibrational wavenumbers, the mean error (allowing cancelation between negative and positive values), the maximum error found in this admittedly small sample, the slope of the regression line for a fit of the calculated to observed data (the fit was of the type $y = mx$), and the regression coefficient R^2.

While it is clearly not necessary to comment on each entry in Table 1, a few general remarks are appropriate. It is important to realize that the uncertainties in the "experimental" harmonic wavenumbers are on the order of 10 cm^{-1}; therefore, it is futile to analyze small differences too finely. Hybrid functionals that include some HF exchange systematically produce higher vibrational frequencies than their GGA counterpart, and the calculated frequencies are always too high for the molecules in this sample. For both the 14 and 32 electron ECP, B3LYP is the most accurate (slope closest to unity) of the hybrid functionals considered here. However, the differences in the regression coefficients between the various functionals are small and scarcely significant, given the size of the sample. It is noteworthy that the 14 electron ECP performs a little better (slope and R^2 both closer to unity) than the 32 electron version for each of the hybrid functionals considered here. The two GGA functionals both underestimate the vibrational wavenumbers, especially for BLYP.

The Los Alamos pseudopotential consistently produces longer bonds and lower vibrational frequencies than the Stuttgart large-core pseudopotential with the same number of active electrons. Since hybrid functionals generally overestimate vibrational frequencies, this reduction leads to results that are somewhat closer to experiment for B3LYP and MPW1PW91 with the LANL2DZ pseudopotential, though the dispersion in the results is a little greater. The combination of a GGA functional such

TABLE 2: Comparison between Computed Harmonic Vibrational Wavenumbers (cm^{-1}) and the Experimental Corrected Values, For Both Large-Core (RECP14) and Small-Core (RECP32) RECPs

		⟨Σ|err|⟩	⟨Σerr⟩	max. err	slope	R^2
RECP14	B3LYP	23	21	45	1.023	0.985
	BP86	28	−28	−32	0.971	0.993
	B3PW91	40	40	60	1.041	0.987
	B1B95	49	49	70	1.051	0.987
	BLYP	50	−50	−62	0.948	0.993
	MPW1PW91	56	56	81	1.059	0.986
	PBE0	59	59	85	1.061	0.986
	B3LYP/LANL2DZ	16	−12	−44	0.989	0.979
	MPW1PW91/LANL2DZ	29	26	51	1.028	0.983
	BLYP/LANL2DZ	93	−93	−111	0.905	0.980
RECP32	B3LYP	31	31	80	1.034	0.977
	BP86	19	−10	±29	0.990	0.981
	B3PW91	51	51	100	1.054	0.979
	B1B95	64	64	117	1.067	0.976
	BLYP	36	−36	−66	0.965	0.973
	MPW1PW91	64	64	117	1.067	0.975
	PBE0	70	70	121	1.073	0.978

as BLYP and LANL2DZ gives poor results since the GGA frequencies are systematically too low.

It has already been shown that NUN and CUO are predicted to be nonlinear when GGA functionals are used, though the bending is very modest when the RECP32 is used.[45] We now consider the case of NUN in more detail. With the RECP32 and BLYP functional, the equilibrium bond angle is 169°. Although two stretching modes are now IR-active, the predicted intensity of the symmetric mode is so low that its nonobservance is not incompatible with this prediction.[46] The RECP14 used with the BLYP functional predicts a bond angle of 165° and a very low intensity for the symmetric stretching mode. However, LANL2DZ combined with the same functional gives a bond angle of 151°, a symmetric stretching mode that would be sufficiently intense to have been observed, and a substantial lowering of the antisymmetric mode, almost doubling its error from 66 to 111 cm^{-1}. In a similar way, the combination of LANL2DZ and BP86 also predicts NUN to be significantly bent and to have two stretching modes that would have been observed.

The shape of UO_3 needs further comment. Its vibrational spectrum shows that it has C_{2v} symmetry,[22] but its angular properties are not experimentally determinable. Of the 17 different combinations of pseudopotentials and functional considered in Table 1, 16 predict a "T-shaped" planar geometry with two bond angles close to 100°. The sole exception is LANL2DZ/BLYP, which predicts a "Y-shaped" planar geometry with two bond angles close to 135°.

To complete these tests, we also examined the vibrational frequencies of the hexacoordinated molecule, UF_6. Data for the six independent vibrational wavenumbers for UF_6 may be found in the Supporting Information (Table S1). In this table, we present the harmonic vibrational wavenumbers computed with two different basis sets for fluorine atoms, our standard double-ζ-plus polarization plus diffuse pseudopotential-type basis or the aug-cc-pVDZ all-electron basis.

GGA functionals underestimate the vibrational frequencies, particularly for stretching motions. The underestimation is particularly acute for the Los Alamos pseudopotential. Hybrid functionals, in general, give vibrational frequencies that are closer to experiment than does the GGA. It is striking that the vibrational frequencies predicted by the hybrid functionals are consistently in this order: PBE0 > MPW1PW91 > B1B95 > B3PW91 > B3LYP. This same ranking was also observed for the smaller molecules whose results are presented in Table 1. Comparing the two Stuttgart RECPs, the ECP14 yields higher wavenumbers than the ECP32; the ECP14 values are generally too high for hybrid functionals, but the ECP32 results are usually underestimates. There is a slight tendency for the all-electron aug-cc-pVDZ basis for F to yield higher vibrational wavenumbers than the pseudopotential basis, but the differences are very modest. Overall, the performances of the two ECPs are similar.

The uncertainties in the experimental harmonic wavenumbers for UF_6 are estimated to be ± 6cm^{-1}.[41] It is therefore difficult to criticize any computational method for which the sum (over the six fundamental vibrations) of the unsigned differences $\bar{\nu}$(calc − obs) is less than 36 cm^{-1}. These are seven methods in Table S1 that satisfy this criterion, four which use the RECP14 and three which use the RECP32. Of these seven, six use the pseudopotential basis on F. However, several other methods yield results that are almost as satisfactory. For each of the hybrid functionals studied, there is at least one combination of fluorine basis and RECP that gives results which are essentially indistinguishable from experiment.

Several computational studies of the vibrational spectrum of UF_6 have already been published within the framework of DFT. Han and Hirao tested the two Stuttgart RECPs and six functionals.[2] They noted that "the performance of the pure GGA functionals is poor" and that with a given functional, the large-core RECP gave higher frequencies than the small core. Garcia-Hernandez et al. found that RECP32 and all-electron calculations gave very similar results and that with a LDA functional, "the stretching frequencies ν_1 to ν_3 are very well reproduced" (average unsigned error: 11 cm^{-1}).[3] Hay and Martin compared three functionals in combination with the Los Alamos methodology and reported that "SVWN and B3LYP results are in the best agreement with the observed vibrational frequencies".[4] It should, however, be noticed that most of their results were obtained with a rather small basis (6-31G*) on fluorine and that the addition of diffuse functions to this basis produced changes of as much as 46 cm^{-1} in the calculated wavenumbers. Schreckenbach et al. used all-electron methods and the BLYP functional; their results are in relatively good agreement with experiment as the sum of the unsigned differences is 55 cm^{-1}.[14] Batista et al. calculated the vibrational spectrum of UF_6 with four different functionals combined with the Stuttgart RECP32 and the Los Alamos pseudopotential.[47] They found that the RECP32 gives better results for each of the functionals; PBE0 clearly gave the best results of the functionals they tested. With the RECP32, the sum of the unsigned errors was 21, 51, 68, and 145 cm^{-1} for the PBE0, B3LYP, PBE, and SVWN functionals, respectively.

In our opinion, no functional emerges clearly as “the best” from these vibrational tests. The different GGA functionals give results whose overall quality is very similar, and the same comment can be made about the different hybrid functionals. The GGAs are a little more successful than the hybrids for NUN, CUO, NUO$^+$, and UO$_3$, but the hybrids perform substantially better for UF$_6$. We have not been able to find a reason for this change in behavior, but we stress that, overall, all of the functionals perform at least reasonably well with both of the Stuttgart pseudopotentials, with average errors of only a few percent and poor results only for one mode of CUO.

We conclude from the results in Tables 1 (NUN, CUO, NUO$^+$, and UO$_3$) and S1 (UF$_6$) that there is no particular reason to prefer the ECP32 to the ECP14 for the calculation of vibrational frequencies with DFT. We do not require that a 14 electron pseudopotential, combined with a given functional, reproduce the results obtained with the small-core pseudopotential and that same functional. It is clear that the universal functional has not yet been developed and that all of the functionals used here contain some residual errors. We are therefore pragmatically seeking a combination of functional and pseudopotential that gives consistently good results compared to experiment. At least for the compounds studied here, the 14 electron ECP is perfectly adequate; the results it yields are similar to those obtained with the ECP32 and are quite often even a little better. As we have already noted, several previous workers have criticized the performance of 14 electron pseudopotentials for the calculation of vibrational frequencies.[1–3,5,47] However, the 14 electron RECP used in several of those previous studies was that proposed in ref 4. To the best of our knowledge, the performance of the 14 electron Stuttgart pseudopotential studied here has not previously been extensively investigated. The Los Alamos pseudopotential gives results whose quality is uneven. They are quite satisfactory in some cases (hybrid functionals and the small molecules in Table 1) but clearly disappointing in other cases, notably for UF$_6$. We therefore agree with other workers[3,5,47] that this pseudopotential should not be used for the calculation of vibrational frequencies.

In has been noted on several occasions that hybrid functionals give better results for the vibrational frequencies of UF$_6$ than do GGA functionals.[2,3,47] However, we have observed here that GGAs perform better for smaller molecules such as NUN, CUO, NUO$^+$, and UO$_3$. Since we can find no reason to claim that one type of molecule is more typical than the other, we prefer to conclude that both GGA and hybrid functionals can give acceptable performance.

In the following section, we shall test the ability of these functionals and ECP to predict thermochemical data.

2. Thermochemistry. Privalov and co-workers have reported enthalpy changes associated with five different gas-phase reactions that involve compounds containing U(VI), UF$_6$, UO$_3$, UO$_2$F$_2$, and UO$_2$(OH)$_2$.[48] These reactions are

$$2UO_{3(g)} + UF_{6(g)} \rightarrow 3UO_2F_{2(g)} \quad (1)$$

$$UO_2F_{2(g)} + 2H_2O \rightarrow UO_2(OH)_{2(g)} + 2HF_{(g)} \quad (2)$$

$$UF_{6(g)} + 2H_2O_{(g)} \rightarrow UO_2F_{2(g)} + 4HF_{(g)} \quad (3)$$

$$UO_{3(g)} + H_2O_{(g)} \rightarrow UO_2(OH)_{2(g)} \quad (4)$$

$$UF_{6(g)} + 3H_2O_{(g)} \rightarrow UO_{3(g)} + 6HF_{(g)} \quad (5)$$

We have evaluated the standard enthalpy changes for each of these reactions with several different functionals, with the 14 electron and the 32 electron RECP. Schreckenbach and co-workers have very recently analyzed the energy changes of two of these reactions and several others, using both all-electron and RECP32 methodology.[17] Our results are presented in Table 3. As an indication of the overall quality of each functional, we present the sum of the absolute values of the differences between calculated and experimental enthalpy changes for these reactions.

TABLE 3: Comparison between Computed and Experimental Enthalpy Changes (kJ.mol^{-1}) for Reactions 1−5 for the Large-Core (RECP14) and Small-Core (RECP32) RECPs

		1	2	3	4	5	$\Sigma\lvert\text{calc} - \text{exp}\rvert$
	Exp.	−311	65	187	−184	435	
RECP14	B3LYP	−332	119	223	−153	495	192
	BP86	−241	109	253	−125	487	318
	B3PW91	−328	118	206	−149	473	162
	B1B95	−347	118	167	−139	424	165
	BLYP	−208	113	255	−119	487	336
	MPW1PW91	−354	119	205	−161	485	188
	PBE0	−353	118	212	−165	495	199
	SVWN5	−212	98	330	−172	602	454
	B3LYP/LANL2DZ	−319	109	156	−129	396	177
	MPW1PW91/LANL2DZ	−363	110	144	−144	398	217
	BLYP/LANL2DZ	−195	94	196	−101	391	281
RECP32	B3LYP	−283	98	250	−169	516	220
	B3LYP[a]	−274	97	309	−194	600	366
	BP86	−199	89	280	−151	520	347
	B3PW91	−290	95	229	−164	489	167
	B1B95	−312	97	219	−168	484	130
	BLYP	−193	94	287	−146	527	377
	MPW1PW91	−311	96	227	−173	495	142
	PBE0	−309	95	233	−176	504	155
	B1LYP	−304	99	241	−173	514	185
	TPSS	−208	97	299	−157	553	392
	PW91	−202	91	292	−157	540	372
	VSXC	−218	100	298	−158	556	386
	PBE	−203	91	286	−153	530	359
	CCSD(T)	−345	82	182	−180	441	66

[a] Data obtained with a basis on F containing no diffuse functions (see text).

Two main points emerge from the data in Table 3. First, it is clear that the GGA functionals (BP86, BLYP, PW91, or PBE) and the LSDA functional (SVWN5 in Gaussian notation) give poor results, as the average error is on the order of 60−70 kJ/mol per reaction for GGA and 90 kJ/mol for LSDA. In contrast, all of the hybrid functionals (B3LYP, B3PW91, B1B95, MPW1PW91, B1LYP, and PBE0) perform considerably better, with average errors on the order of 25−45 kJ/mol. The second main point is that for a given functional, the differences between the performances of the 14 and 32 electron ECPs are relatively modest, with a tendency for the 32 electron ECP to perform better with the hybrid functionals. The results obtained with the Los Alamos pseudopotential are broadly similar to those with the Stuttgart RECP14: neither systematically better nor worse for a given functional.

Comparing the different hybrid functionals, those with a single (generally empirical) parameter (B1B95, B1LYP, PBE0, and MPW1PW91) are a little more successful than those with three parameters (B3LYP, B3PW91). The “meta-functionals” TPSS and VSXC are the worst of all of those that we have tried in this area. To check whether use of a pseudopotential for the O and F atoms leads to errors, we tested an all-electron triple-ζ basis (10,6 contracted to 5,3 for O and F)[49] augmented with diffuse s and p functions for these atoms at the B3LYP level; the enthalpy changes with this TZP+ basis were always within 15 kJ/mol of those in Table 3 obtained with the pseudopotential, and the sum of the errors was, in fact, slightly greater.

TABLE 4: Experimental ^{19}F Chemical Shifts in $UF_{6-n}Cl_n$ Compounds[56]

	NMR Systems		^{19}F chemical shifts (ppm)
UF_6	A6		764.0
UF_5Cl	A4X	A4	762.0
		X	781.5
trans-UF_4Cl_2	A4		755.5
cis-UF_4Cl_2	A2X2	A2	760.0
		X2	785.8
mer-UF_3Cl_3	A2X	A2	753.0
		X	782.6
fac-UF_3Cl_3	A3		786.4
trans-UF_2Cl_4	A2		746.1
cis-UF_2Cl_4	A2		781.0
$UFCl_5$	A		774.3

TABLE 5: Calculated ^{19}F Nuclear Shieldings for $CFCl_3$ (experimental value: 188.7 ppm[57])

	auc-cc-pVDZ	6-311G (3df,3pd)	6-311++G (3df,3pd)	aug-cc-pVTZ
B3LYP	172.9	157.0	164.7	163.2
B3PW91	180.1			
MPW1PW91	187.3			
BP86	140.8	123.9	132.2	131.2
BLYP	132.0			
PBE0	186.4	172.5	179.7	178.2
B1LYP	178.7			

Although it might seem that an average error of 25−45 kJ/mol in a computed enthalpy change is disappointing, it is important to note that the experimental uncertainties in these data are substantial, about 50, 30, 15, 25, and 15 kJ/mol for reactions 1−5, respectively.[48] Under these circumstances, an average error of 25 kJ/mol implies that the computed results are essentially indistinguishable from the experimental values, one can hardly hope to do better than that. In an attempt to provide an independent assessment of the experimental data, we evaluated the enthalpy changes for each reaction using the CCSD(T) method and a relatively large basis, the 32 electron ECP for U, together with its associated basis augmented by 2g1h polarization functions, and the all-electron triple-ζ basis (cited above) augmented with diffuse s and p functions and 2d1f polarization functions for O and F and with 2p polarization functions for H. For these tests, we adopted the geometries and thermal corrections obtained at the B3LYP level with the TZP+ basis. These calculations were performed at the CCSD(T) level of theory as implemented in the MOLPRO set of programs.[50]

The overall performance of CCSD(T) with this basis is substantially better than any version of DFT since the sum of the errors is only 66 kJ/mol, half as large as that given by the best DFT functional (B1B95). The only appreciable difference between the experimental value and the CCSD(T) result (34 kJ/mol, all the others being less than 20 kJ/mol) is found for reaction 1, the reaction for which the experimental uncertainty is said to be the largest (50 kJ/mol). It thus seems probable that the CCSD(T) data that we have obtained are at least as reliable as the current experimental values. The agreement with experiment obtained at the CCSD(T) level improved slowly but steadily as the basis was enlarged, from 112 kJ/mol with a single polarization function on each atom, through 79 kJ/mol with two primary polarization functions, to 66 kJ/mol with the basis described above (two primary and one secondary polarization functions). It is a little surprising to note the large influence of triple excitations on these enthalpy changes; the sum of the errors at the CCSD level is nearly three times larger than that at CCSD(T), with the largest basis used here at −177 compared to 66 kJ/mol. We therefore may deduce that the CCSD method, even with the use of large basis sets, does not give better results for thermochemistry than several of the DFT functionals used with standard TZP bases.

Since the experimental data are not sufficiently precise to provide a stringent test of the different functionals, we tested their ability to reproduce the enthalpy data obtained at the CCSD(T) level. It turned out that the same relative ranking was obtained as when the experimental data were used as the measuring stick, and the sums of the errors were very similar (B1B95 140, MPW1PW91 154, PBE0 167, B3PW91 179, and B3LYP 232 kJ/mol with the 32 electron ECP). We thus believe that the ordering obtained has some meaning.

Privalov and co-workers reported computed enthalpy changes, obtained with four different methods, for the five reactions listed above.[48] While they also adopted a 32 electron ECP for U, the methodology that they employed differed from ours in several respects. We note that the sums of errors that they obtained are substantially larger than ours; for example, they report 469 kJ/mol for B3LYP, whereas we obtain 220 kJ/mol. We believe that the major part of the differences arises from the different basis sets used. Our standard basis on O and F contains diffuse s and p functions, which we believe to be important since these atoms will clearly bear substantial negative charges when bonded to U(VI). We tested the influence of these functions at the B3LYP level; the entry B3LYP[a] in Table 3 refers to results obtained with a basis without diffuse functions. Since the sum of the errors increases by 66% (from 220 to 366 kJ/mol) when these functions are deleted, we believe that their importance is firmly established for these systems. Schreckenbach and co-workers also emphasized the need to use suitable basis sets, even with DFT, if reliable thermochemical data are required. Like us, they found that both hybrid DFT and CCSD(T), in general, perform well.[17]

It is noticeable that the differences between calculated and experimental enthalpy changes obtained with the 32 electron ECP are always positive if the magnitude of the difference exceeds 10 kJ/mol. This observation implies that the reactants are described more accurately than the products. As already noted by Privalov and co-workers,[48] HF is a product in three of the reactions [2,3,5] but never a reactant, and the largest errors in the DFT calculations are generally found in just those reactions. We wondered whether the ability of a functional to predict an accurate bond energy for HF could indicate its reliability for the five reactions studied here, but in fact, that turns out not to be the case; the predicted values of D_e obtained with our TZP+ basis are 577, 564, 566, 572, and 575 kJ/mol for B1B95, MPW1PW91, PBE0, B3PW91, and B3LYP, respectively, which all compare reasonably well with the experimental value of 591 kJ/mol.[51] However, it is noticeable that the electron affinity of the F atom is, in general, predicted more accurately with those functionals that give the lowest overall errors for reactions 1−5; with the TZP+ basis, B1B95 321, MPW1PW91 317, PBE0 316, B3PW91 329, B3LYP 343, experiment 328 kJ/mol.[52] It is often said that DFT results converge quickly with the size of the basis; while this is indeed true in many cases, we note that the influence of diffuse functions is vital, even with DFT, for properties such as the electron affinity of the F atom. The difference between the TZP and TZP+ results is about 60 kJ/mol with DFT. The CCSD(T) results for both the electron affinity of the F atom and D_e(HF) both converge slowly with the size of basis but do not overshoot; we obtain 305 and 573 kJ/mol, respectively, with the largest basis used here.

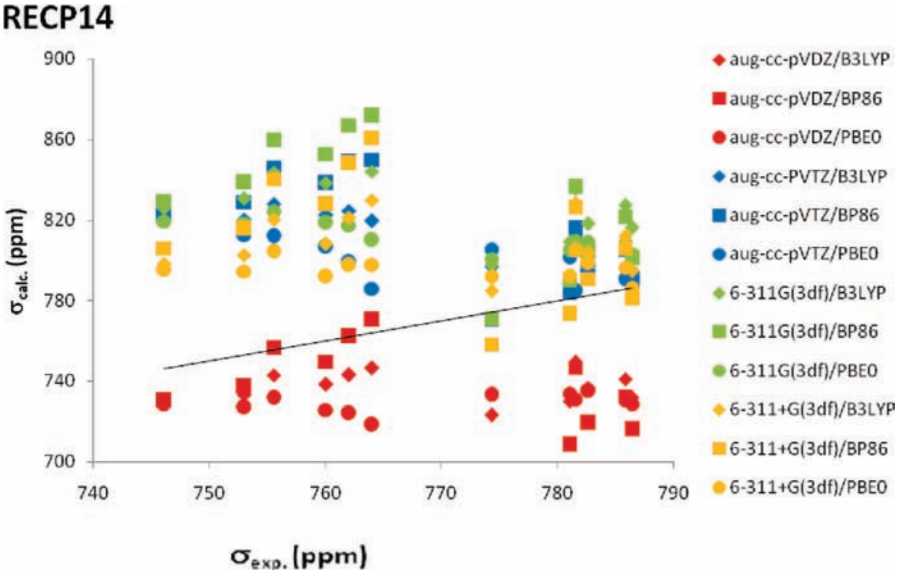

Figure 1. Calculated and experimental ^{19}F chemical shifts for $UF_{6-n}Cl_n$ compounds (with RECP14 on uranium).

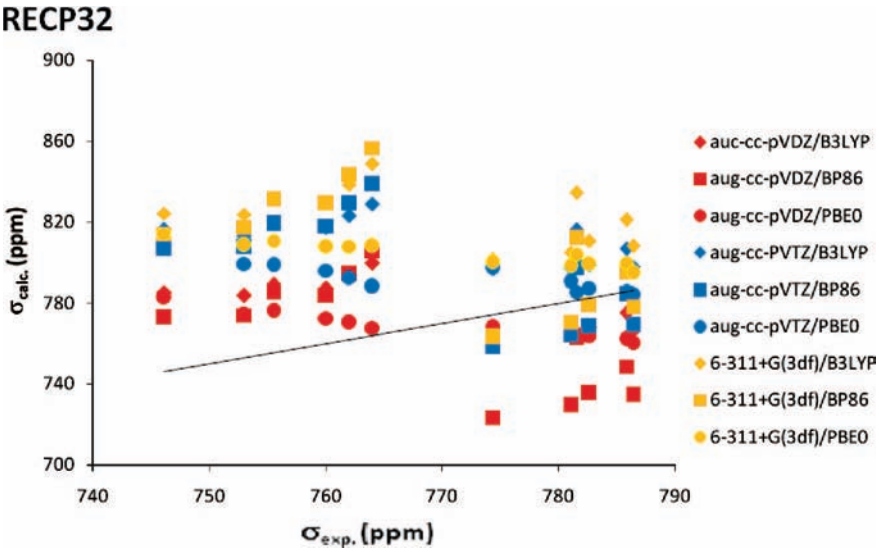

Figure 2. Calculated and experimental ^{19}F chemical shifts for $UF_{6-n}Cl_n$ compounds (with RECP32 on uranium).

TABLE 6: $\Sigma|(\delta_{UF_{6-n}Cl_n} - \delta_{UF_6})_{calc} - (\delta_{UF_{6-n}Cl_n} - \delta_{UF_6})_{exp}|$ with an aug-cc-pVDZ Basis Set on Fluorine and Chlorine Atoms and with RECP32 on Uranium

	aug-cc-pVDZ						
	B3PW91	MPW1PW91	BLYP	B1LYP	B3LYP	BP86	PBE0
UF_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
UF_5Cl	−1.4	3.2	−16.1	−2.6	−4.7	−9.1	4.6
	−29.3	−21.9	−71.4	−23.7	−31.0	−59.9	−21.1
cis-UF_4Cl_2	0.8	6.2	−30.1	−3.0	−8.2	−17.4	8.8
	−39.7	−29.4	−94.8	−35.7	−46.1	−78.5	−27.3
trans-UF_4Cl_2	6.6	13.3	−24.7	3.8	−1.8	−11.6	16.7
mer-UF_3Cl_3	5.2	16.1	−37.5	2.3	−4.7	−20.3	18.1
	−39.7	−24.8	−110.0	−36.5	−49.9	−88.4	−22.5
fac-UF_3Cl_3	−45.7	−32.8	−114.2	−42.4	−55.5	−93.2	−29.6
cis-UF_2Cl_4	−39.2	−23.3	−116.4	−36.0	−51.4	−93.0	−19.6
trans-UF_2Cl_4	17.2	28.1	−34.8	14.3	3.9	−14.5	32.9
$UFCl_5$	−30.3	−13.4	−118.9	−28.7	−46.2	−92.3	−9.3
$\Sigma|\Delta\Delta|$	255.1	212.5	768.9	229.0	303.4	401.4	210.5

It is important to note that the oxidation state of uranium does not change in any of the five reactions considered here. Hay and co-workers have recently studied the structural properties and thermochemistry of both UF_6 and UF_5 to calculate the bond dissociation energy (BDE) of a single bond in UF_6.[47] They used both 14 and 32 electron ECPs and several different versions of DFT. They showed that the combination of B3LYP and the Stuttgart ECP32 that we have used here gave a BDE that agrees well both with the value obtained from all-electron calculations and with experiment, but use of the Los Alamos 14 electron

TABLE 7: $\Sigma|(\delta_{UF_{6-n}}Cl_n - \delta_{UF_6})_{calc} - (\delta_{UF_{6-n}}Cl_n - \delta_{UF_6})_{exp}|$ with an aug-cc-pVTZ or a 6-311+G(3df) Basis Set on Fluorine and Chlorine Atoms and with RECP32 on Uranium

	aug-cc-pVTZ			6-311+G(3df)		
	B3LYP	BP86	PBE0	B3LYP	BP86	PBE0
UF_6	0.0	0.0	0.0	0.0	0.0	0.0
UF_5Cl	−3.7	−7.8	6.5	−8.4	−11.4	1.7
	−29.6	−59.3	−20.2	−31.9	−62.2	−21.5
cis-UF_4Cl_2	−7.4	−17	11.8	−15.0	−23.4	3.4
	−43.6	−76.4	−24.7	−49.7	−83.6	−30.2
trans-UF_4Cl_2	−0.9	−11.2	19.0	−8.0	−17.0	11.2
mer-UF_3Cl_3	−4.5	−20.1	22.2	−14.2	−28.1	11.5
	−48.7	−88.9	−19.3	−57.0	−96.1	−27.8
fac-UF_3Cl_3	−53.2	−92.3	−26.1	−63.2	−100.7	−35.9
cis-UF_2Cl_4	−48.9	−91.5	−14.6	−60.7	−102.8	−27.0
trans-UF_2Cl_4	5.4	−14.1	37.8	−6.7	−24.6	23.9
$UFCl_5$	−42.3	−90.8	−1.4	−57.7	−103.6	−18.4
$\Sigma|\Delta\Delta|$	288.2	569.8	203.6	372.5	653.5	212.5

pseudopotential[4] gave a BDE that differs by no less than 234 kJ/mol from the ECP32 result (80 instead of 314 kJ/mol). The obvious conclusion is that ECP14 is unreliable for thermochemistry, in contradiction with our observations above. We therefore tested the more recent ECP14 developed in Stuttgart[19] and found that it yielded a BDE for UF_6 with B3LYP that is smaller than the ECP32 value by 90 kJ/mol. Although this error is unacceptably large, it is much smaller than that associated with the Los Alamos pseudopotential,[4] presumably because the Stuttgart group derives their ECP from fits to data for several different electronic states.[53]

To conclude this section on thermochemistry, we observe that hybrid functionals perform considerably better than GGA and LDA, as already noted by Hay and co-workers[47] for the BDE of UF_6 and by Schreckenbach et al.[17] It is hard to criticize their performance as they give results for reactions in which U stays in the oxidation state (VI) that are indistinguishable from experiment (the experimental uncertainties are unfortunately rather large). Although the differences between the 14 and 32 electron RECPs are slight, at least for these reactions, the latter perform a little better overall. For both sizes of RECP, five hybrid functionals stand out, B1B95, MPW1PW91, PBE0, B3PW91, and B3LYP. These are also the most successful when checked against CCSD(T) data. It is important to note that the good performance of the RECP14 is not maintained for a reaction in which the oxidation state of U changes, though the RECP32 still performs well in this case.

3. NMR Spectroscopy. The calculation of nuclear magnetic shielding in the area of actinide compounds with RECP is still subject to debate. Schreckenbach and al. concluded a few years ago that "the ECP approach is beyond its limits" for such calculations.[54] In a recent paper, Straka and Kaupp point out that "it appears doubtful whether it is appropriate to use large-core pseudopotential in calculations of a sensitive property like nuclear shielding".[55] They concluded that "an effective core potential on uranium provides comparable accuracy in calculations of ligand NMR chemical shifts in uranium complexes as computationally more demanding relativistic all-electron ZORA methods, provided that a sufficiently small core size definition is used." Furthermore, they point out that "the opposite conclusions drawn by Schreckenbach et al. are due to the too large ECP core size used in that study." In this final section, we shall examine whether this conclusion, reached for an earlier 14 electron ECP,[4] is still valid for the more recent 14 electron ECP developed in Stuttgart.[19] We shall test the ability of both RECP and several functionals to calculate trends in ^{19}F nuclear shielding in $UF_{6-n}Cl_n$ complexes (Table 4). We also check the sensitivity of the results to the size of the basis set on F and Cl.

The reference used experimentally for ^{19}F NMR is $CFCl_3$. To compare our results for $UF_{6-n}Cl_n$ with experimental data, we computed $CFCl_3$ chemical shieldings and present the results in Table 5. We were surprised to find that agreement with experiment[57] deteriorates as the quality of the basis is improved from aug-cc-pVDZ to aug-cc-pVTZ for each of the functionals that we tested; while one coincidence or fortuitous cancelation of errors could be accepted, it seems remarkable that three "coincidences" could coincide in this way. However, the addition of diffuse functions to the 6-311G(3df) basis does produce a slight improvement in the computed chemical shift.

In our opinion, it is important to compare different theoretical approaches for the actinide compounds on an equal footing. Since ^{19}F shieldings are very sensitive to geometry (the variation of the ^{19}F nuclear shielding with the C−F bond length in $CFCl_3$ is about 4.3 ppm per pm, and for UF_6, it is some 25 ppm per pm of the U−F bond), we felt it necessary to optimize the structures of the reference and of the actinide compounds with each functional and each basis set. Chermette and co-workers have already observed that NMR chemical shifts can be very sensitive to geometry.[58] We find more pronounced variations of chemical shifts with the correlation functional than those described by Straka and Kaupp,[55] presumably due to the differences in the computational methodology that we employed. However, we note that the RECP32 data reported by Schreckenbach with the B3LYP functional are very similar to our own.[59] In view of this extreme sensitivity of the computed shieldings to geometry, is unrealistic to hope that the absolute values of computed chemical shifts will be reliable.

A representative selection of computed ^{19}F chemical shifts for $UF_{6-n}Cl_n$ compounds is displayed and compared with experiment in Figures 1 and 2 (data obtained with the RECP14 and RECP32, respectively). Results may be found for three different functionals (B3LYP, BP86, and PBE0) and the four different basis sets used for the results for $CFCl_3$ in Table 5. The straight lines in these figures represent a perfect match between experiment and computation; it is already clear that the dispersion of the calculated chemical shifts is very substantial. A larger selection of computed chemical shifts is presented in Tables S2 and S4 (for the RECP14) and S3 and S5 (for the RECP32) and in Figures S6 (RECP14) and S7 (RECP32) in the Supporting Information. Seven different functionals were tested with the aug-cc-pVDZ basis. The results obtained at this level show that the functionals can be separated into three groups, (i) the GGA functionals BLYP and BP86, (ii) the hybrid functionals B1LYP, B3LYP, and B3PW91, and finally, (iii) PBE0 and MPW1PW91. We chose to keep one functional from each group (BP86, B3LYP, and PBE0) to test larger bases, 6-311G(3df), 6-311+G(3df), and aug-cc-pvTZ.

Overall, we find the quality of the computed chemical shifts to be very disappointing. Although, as already noted above, we did not expect to find quantitative agreement for the shifts of the various uranium chlorofluorides, we did hope that the trends in these shifts would be at least semiquantitatively reproduced. The total variation in the ^{19}F chemical shift within this series is just over 40 ppm (see Table 4). In the event, all of the calculations fail even this test, which would seem not to be very demanding. It is not even possible to predict reliably the sign of the change in chemical shift from one member of the $UF_{6-n}Cl_n$ series to another. The failure to reproduce trends is shown most clearly by the data in Tables 6–9, where we compare the experimental and computed differences between

TABLE 8: $\Sigma|(\delta_{UF_{6-n}}Cl_n - \delta_{UF_6})_{calc} - (\delta_{UF_{6-n}}Cl_n - \delta_{UF_6})_{exp}|$ with an aug-cc-pVDZ Basis Set on Fluorine and Chlorine Atoms and with RECP14 on Uranium

	aug-cc-pVDZ						
	B3PW91	MPW1PW91	BLYP	B1LYP	B3LYP	BP86	PBE0
UF_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
UF_5Cl	2.1	6.2	−12.6	1.1	−1.3	−6.1	7.7
	−13	−6.2	−50.7	−8.5	−14.7	−41.0	−5.0
cis-UF_4Cl_2	2.4	9.0	−28.3	1.4	−4.1	−16.8	11.3
	−21.5	−11.7	−73.5	−18.0	−27.3	−59.7	−9.7
trans-UF_4Cl_2	12.8	20.0	−17.3	9.0	4.9	−5.0	21.8
mer-UF_3Cl_3	7.9	17.5	−38.9	15.0	−2.1	−22.0	19.5
	−18.1	−4.2	−89.2	−16.3	−28.4	−69.7	−2.1
fac-UF_3Cl_3	−28.3	−14.8	−96.8	−24.5	−37.0	−76.7	−12.2
cis-UF_2Cl_4	−21.4	−5.2	−102.5	−19.2	−33.5	−79.1	−1.5
transUF_2Cl_4	12.4	24.1	−42.7	10.4	0.5	−22.1	27.9
$UFCl_5$	−19.1	0.4	−115.5	−15.3	−33.7	−86.9	4.3
$\Sigma|\Delta\Delta|$	159.0	119.3	668.0	138.7	187.5	485.1	123.0

TABLE 9: $\Sigma|(\delta_{UF_{6-n}}Cl_n - \delta_{UF_6})_{calc} - (\delta_{UF_{6-n}}Cl_n - \delta_{UF_6})_{exp}|$ with an aug-cc-pVTZ, a 6-311G(3df), or a 6-311+G(3df) Basis Set on Fluorine and Chlorine Atoms and with RECP14 on Uranium

	aug-cc-pVTZ			6-311G(3df)			6-311+G(3df)		
	B3LYP	BP86	PBE0	B3LYP	BP86	PBE0	B3LYP	BP86	PBE0
UF_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
UF_5Cl	6.8	1.0	15.9	2.6	−2.4	9.6	−6.6	−10.7	1.8
	−25.4	−51.5	−18.6	−26.2	−52.8	−18.4	−19.1	−51.9	−10.5
cis-UF_4Cl_2	6.8	−7.7	25.1	−1.8	−14.7	12.6	−17.8	−29.2	−1.8
	−33.5	−66.3	−17.3	−38.8	−71.6	−23.6	−39.7	−76.7	−23.1
trans-UF_4Cl_2	16.5	4.0	34.5	7.8	−3.1	22.6	−1.2	−12.1	15.1
mer-UF_3Cl_3	11.6	−10.0	37.9	−2.6	−21.9	19.4	−16.2	−34.2	7.7
	−33.9	−76.2	−6.6	−44.5	−85.7	−19.8	−44.4	−88.8	−17.8
fac-UF_3Cl_3	−40.6	−83.6	−14.9	−50.3	−93.0	−29.2	−57.6	−102.2	−33.8
cis-UF_2Cl_4	−34.7	−82.9	−1.1	−52.1	−98.6	−22.2	−54.7	−104.6	−23.0
trans-UF_2Cl_4	19.3	−7.6	51.6	−0.5	−24.3	27.4	−13.8	−37.1	15.6
$UFCl_5$	−33.4	−89.8	9.4	−56.8	−110.8	−19.5	−55.4	−113.1	−15.9
$\Sigma|\Delta\Delta|$	262.5	480.6	232.9	284.0	578.9	224.3	326.5	434.4	166.1

the ^{19}F chemical shift for UF_6 and those for the other chlorofluorides. Inspection of these tables shows that quite large systematic errors are always present; for example, the second entry for *cis*-UF_4Cl_2 is always substantially negative for all functionals and both RECPs, as is the second entry for *mer*-UF_3Cl_3. However, the first entry for these two compounds is far more variable. This observation amounts to saying that the calculations for chemical shifts of fluorine atoms trans to F are much more successful than those for fluorine atoms trans to Cl. Straka and Kaupp were the first to make this observation,[55] which they have discussed in detail, though without finding a simple explanation.

Since we felt that the ability of the computations to reproduce trends in chemical shifts would be the best indication of quality, the data in Tables 6–9 enable us to rank the different functionals, basis sets, and the two RECPs. The following points emerge from an analysis of these tables. First, concerning the size of the ECP, the 14 electron RECP, in general, performs better than its larger 32 electron counterpart. Second, concerning the size of the basis set, there seems to be no advantage in increasing the size of the basis beyond aug-cc-pVDZ. Use of the substantially larger aug-cc-pVTZ basis produces either a trivial improvement or a substantial worsening in the sum of the differences. However, it should be noted that the 6-311G(3df) basis is far from saturated in the s, p space as addition of diffuse functions leads to substantial improvements for two functionals (PBE0 and BP86) but an appreciable worsening for B3LYP. Third, concerning the type of functional, the hybrid functionals perform much better than the GGA. Within the category of hybrid functionals, those with a single parameter (MPW1PW91, B1LYP, and PBE0) are a little more successful than those with three parameters (B3LYP and B3PW91), and B3PW91 performs a little better than B3LYP.

Conclusion

In this paper, we have investigated the performance of DFT as applied to uranium chemistry. We decided to limit ourselves to U(VI) since this is the oxidation state for which the largest amount of suitable data is available. We have analyzed the quality of the results yielded by a large, representative selection of functionals that belong to four different generations (LSDA, GGA, hybrid GGA, and meta-GGA). The experimental database consisted of vibrational wavenumbers, thermochemical data, and chemical shifts for ^{19}F in molecules of the type $UF_{6-n}Cl_n$. Two different pseudopotentials (Relativistic Effective Core Potential, RECP) were tested for uranium, with either 14 or 32 “active” electrons.

For the prediction of vibrational wavenumbers, the 14 electron RECP gives results that are at least as good as those obtained from the 32 electron RECP. We cannot recommend hybrid GGA functionals in preference to their simpler GGA counterparts for this property; the performance of both types is good, with errors of only a few percent. Reaction enthalpy changes are predicted well by both the RECP14 and RECP32, within the experimental uncertainties, provided that the oxidation state of uranium does not change during the reaction. We underline the observation by Hay and co-workers that the RECP32 can give good thermochemical results even when the oxidation state does change.[47] However, it is clear that GGA functionals are inadequate for thermochemistry, whereas hybrid GGAs are very satisfactory. The two meta-GGA functionals investigated both perform very poorly for thermochemistry. CCSD results obtained with a large basis are not better than those provided by several functionals, but the CCSD(T) results match experiment better than any version of DFT that we tested. Concerning the performance of the Los Alamos pseudopotential, it should be noticed that it gives results that are as good as those obtained with the 14 electron Stuttgart pseudopotential for thermochemistry but somewhat poorer for vibrational frequencies.

It is disappointing to observe that we were not able to make useful predictions for ^{19}F NMR spectra in $UF_{6-n}Cl_n$ molecules, no matter which combination of functional/ECP/basis was adopted. However, the pseudopotential approximation for U does not seem to be responsible for these failings, as Straka and Kaupp have already noted that their 32 ECP results were no worse than those obtained with all-electron methods.[55] We conclude that DFT cannot be recommended for predictions of NMR spectra in this type of compound, though, of course, there are examples of successful predictions of NMR chemical shifts for U(VI) complexes.[60]

Our most important result concerns the good performance of the Stuttgart large-core pseudopotential (14 electrons treated explicitly) for the properties considered here. Given its computational efficiency, we recommend that it be used with DFT methods.[61] Overall, the hybrid GGA functionals MPW1PW91 and PBE0 give the best results.

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Supporting Information Available: Additional theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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