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Fully relativistic correlated benchmark results for uranyl and a critical look at relativistic effective core potentials for uranium

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Abstract. A complete set of fully-relativistic benchmark results for the bond lengths and vibrational frequencies of uranyl at various levels of correlation treatment are presented. It is shown that the relativistic and correlation effects are of the same magnitude and should be treated on an equal footing. Results of uranyl calculations using various relativistic effective core potentials (RECP) are presented. Appropriate choices for RECPs for use in density functional theory (DFT) calculations in the local density approximation (LDA) and with the gradient-corrected B3LYP exchange-correlation functional are discussed. The conclusion is reached that small-core RECPs need to be used and that the best results as compared to the benchmark values are obtained by using a DFT functional that includes some fraction of Hartree-Fock Exchange.

Key words: Relativistic – Uranyl – Benchmark – CCSD(T) – RECP

Introduction

The uranyl cation, UO_2^{2+}, can form complexes with a variety of species including a wide range of anions (such as carbonate and nitrate). Both uranyl and these anions are present in nuclear waste tanks and the complexes formed are sufficiently mobile that they play an important role in the migration of actinide ions in groundwater. The solution chemistry of uranyl complexes is complicated because several ions can exist in equilibria with each other, the uncomplexed ion, and complete and partially hydrolyzed species, depending upon pH. This complicates the interpretation of experimental measurements, especially those needed to understand thermodynamic equilibria. Electronic structure calculations on molecular systems in combination with experimental observations can provide a fundamental understanding of the microscopic mechanisms of complexation and speciation, adsorption to surfaces of minerals, and mechanisms for changing between species, for example, redox chemistry. Such results can then be used in other models to predict, for example, environmental impact.

One important focus of the research at our laboratory is to gain insight into the chemistry and speciation of actinyl, specifically uranyl, complexes by studying these systems at the molecular level, both theoretically and experimentally. The size of the complexes that can be studied theoretically, and the accuracy of the results from the molecular quantum chemical studies, depend on the computational approach taken. Complexes that contain heavy atoms, in this case uranium, require the inclusion of relativity from the outset. In order to obtain quantitative results, correlation must be included. The currently available fully-relativistic correlated approaches require large computational resources and can, with the state of the art computers, only handle relatively small molecules. In order to study the large complexes relevant to experimental studies some approximations to the fully relativistic, highly correlated approach must be used. One approximation is to include scalar relativistic effects by the use of relativistic effective core potentials (RECPs). This approximation works well for closed-shell systems. Another approximation is to use density functional theory (DFT) to treat correlation effects as DFT exhibits much better scaling of the computational expense upon system size as compared to many-body molecular orbital-based correlation methods such as MP2 and CCSD(T).

A suitable computational approach should be able to compute the properties of the free uranyl ion, the core building block of uranyl complexes, with reasonable accuracy. To date, no experimental data are available for the bond length and vibrational frequencies of the isolated uranyl ion. Only recently a small number of

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isolated uranyl ions were produced but no spectroscopic data were obtained from this experiment [1]. The spectroscopic properties of the uranyl ion with various ligands, predominantly in the equatorial plane of the molecule, have been measured in solution and crystal lattices. Depending on the ligand the bond length can be tuned from 1.60 to 1.95 Å, and the vibrational modes range from 780 to 900 cm^{-1} for the symmetric stretch, from 800 to 1000 cm^{-1} for the asymmetric stretch, and from 190 to 210 cm^{-1} for the bending mode [2–4]. Zhou and coworkers [5] were able to observe the asymmetric stretch mode of the UO_2^+ ion in a neon matrix isolation IR spectroscopy experiment, but did not observe the UO_2^{2+}. In absence of experimental data for the free uranyl ion, high level calculations are needed in order to provide a benchmark for the more approximate methods needed for larger molecules. Part of the fully relativistic correlated benchmark results (CCSD(T) bond length and symmetric stretch frequency only) have been reported in the literature by one of us [6]. In this paper we present a complete set of benchmark numbers for the bond lengths and all frequencies at various levels of correlation treatment. We make a critical assessment of the results of uranyl calculations using various RECPs and methods for including correlation and compare them with the high-level benchmark results mentioned above. We focus our discussion on appropriate choices for RECPs in combination with some DFT functionals in uranyl calculations and compare our findings with those of Ismail et al. [7] and Han and Hirao [8].

Details of the calculations

The fully relativistic, highly correlated MP2, CCSD, and CCSD(T) calculations on the closed shell uranyl ion were obtained with the MOLFDIR program package [9]. The molecular calculations are performed in D_{4h}^* (equilibrium bond length and symmetric stretch), C_{4v}^* (asymmetric stretch), and C_{2v}^* (bend) double group symmetries. A Gaussian distribution is used to describe the spatial extent of the nucleus in both the nonrelativistic and the relativistic MOLFDIR all-electron calculation. The basis sets used in these calculations are of valence triple-zeta (VTZ) quality for uranium and the correlation consistent cc-pVTZ basis set [10] was used for oxygen; the basis sets and the nuclear Gaussian exponents used in the calculations are described in more detail in a previous paper by de Jong et al. [6]. In the Dirac-Hartree-Fock (DHF) and subsequent correlated calculations, the (SS|SS) class of integrals which describe the electronic repulsion energy between the small component densities has been excluded to make the calculations computationally feasible, and are accounted for by Visscher's correction to the total energy [11]. A second set of DHF calculations where the dominant term of the relativistic correction to the two-electron Coulomb repulsion term, the Gaunt interaction [12], was included, have also been performed. The Gaunt interaction term was shown to be small and was not included in the subsequent correlation calculations. In the MP2, CCSD, and CCSD(T) calculations, 24 electrons (U 6s, 6p, 6d, 5f and O 2s, 2p) are correlated in a total space of 200 spinors. The spectroscopic properties are obtained by fitting the calculated points of the potential energy curves to a fourth-order polynomial.

The RECP results are obtained using the NWChem software [13]. We use the term RECP to describe both effective core potentials and pseudopotentials. In our calculations we considered the RECPs of (1) Hay and Wadt (LANL2DZ, 78 core-electrons) generated at the Hartree-Fock (HF) [14] and Local Density Approximation (LDA) [15] level of theory, (2) Christiansen, Ross, Ermler (CRENBL [16], 78 core-electrons and CRENBS [17], 68 core-electrons thereby including the 5d orbitals into the valence shell), and (3) Küchle and Dolg (Stuttgart LC, 78 core-electrons [18] and Stuttgart SC [19], 60 core-electrons). We performed two different sets of calculations. In our first set of calculations we used the standard uranium basis sets provided with the RECPs, which gives us an overall impression of the RECP and its basis set. In the second set of calculations we used the same uncontracted basis set for all RECPs, ruling out any difference due to basis set effects and, hence, allowing for a direct comparison of the various RECPs themselves. The basis set chosen is the uncontracted Stuttgart-SC basis set extended with the two g-functions of the Stuttgart-LC basis set. For the oxygen we used both Dunning's aug-cc-pVDZ [10, 20] and the TZVP DFT-optimized basis set of Godbout et al. [21]. The results with these two oxygen basis sets are similar and have no effect on the subsequent interpretation of quality of the RECPs, the main goal of the RECP calculations. We will therefore only present the results obtained using the TZVP basis set. We do note that the frequencies for the asymmetric and symmetric stretch with the TZVP basis are slightly higher (around 10–15 cm^{-1}) than those of the aug-cc-pVDZ basis, whereas the bond lengths and bending frequencies are the same.

The RECP results were calculated at the SCF, MP2, and DFT levels of theory using NWChem. We correlated all electrons at the MP2 level of theory. At the DFT level we performed calculations in the local density approximation (LDA) with local Slater exchange [22] and the VWN correlation functional [23] and with the gradient-corrected hybrid functional B3LYP with the B3 exchange functional [24] and the Lee-Yang-Par (LYP) correlation functional [25].

In general, spherical basis sets were employed, with the exception of the CRENBS results. The s-functions in the CRENBS contracted basis are generated from the 3s component of the Cartesian d-functions, and hence we needed to employ Cartesian functions. We used no fitting of any kind in the DFT calculations although we advocate the use of the Dunlap fit [26] to reduce the cost of DFT calculations and have started work in our laboratory to generate accurate fitting basis sets for the actinide orbital sets. Because of the diffuse nature of the Stuttgart orbital sets, great care had to be taken in the numerical integration of the density and exchange and correlation functionals. Very large radial and angular grids were employed in order to achieve the desired convergence of $1.0d^{-8}$ in the total energy and $1.0d^{-4}$ in the geometric gradient.

Results and discussion

We first present a full list of benchmark results from our fully relativistic correlated calculation as shown in Table 1. If we compare the relativistic effects on the bond length and symmetric stretch with the correlation effects, 0.05 Å and -118 cm^{-1} vs 0.06 Å and -266 cm^{-1}, we see that both effects are of similar magnitude and that both have the same sets of signs leading to an increase in bond length and a decrease in the frequency. Hence, both relativity and correlation should be treated on the same footing in order to obtain accurate results. The inclusion of the relativistic correction to the two-electron interaction, the Gaunt interaction, has only a small effect on the geometry and vibrational spectroscopic properties. Our calculated uranyl bond length lies within the broad range of experimentally observed ones. The stretching frequencies are around 100 cm^{-1} higher than those found in experiments. However, Zhou et al. [5] showed that charge transfer from the ligands to the uranyl ion will lower these stretching frequencies.

Extensive Hartree-Fock and Dirac-Hartree-Fock calculations have shown that the valence orbitals and the bonding in uranyl changes significantly when relativity is included [6]. We therefore tested the assumption that the relativistic effects in closed shell uranyl are predominantly scalar relativistic, in order to demonstrate that the RECP approach is valid. This test was done by using the AREP – REP approach implemented in MOLFDIR by Lee and Lee [27] which allows us to switch the variational inclusion of the one-electron spin-orbit interaction on and off. For these calculations, we used the large core CRENBL RECP, one-electron spin-orbit potential and basis sets of Ermler et al. [16]. We found that the effect on the bond length is only 0.001 Å and the frequencies changed by less than 1%. Hence, the influence of spin-orbit on the bond length and frequencies is very small, even though there is a significant change in the bonding itself (see [6] for a more extensive discussion).

In Tables 2 and 3 we show the results of calculations using different RECPs at the SCF, MP2, LDA, and B3LYP levels of theory. In Table 2 we used the same uncontracted uranium basis set for all RECPs, and in Table 3 we used the basis sets provided with the RECPs. The results of Table 2 allow us to compare directly the different RECPs. Both the CRENBL and Stuttgart-LC RECP give a calculated bond length that is more than 0.01 Å shorter than those of their small-core counterparts. Overall the bond lengths of the small-core RECPs agree well with the corresponding benchmark results in Table 1, comparing results from SCF with DHF, MP2 with DHF MP2, and DFT with DHF CCSD(T). At the

Table 1. Fully relativistic benchmark results for the equilibrium bond length (r_e in Å) and vibrational stretch and bend frequencies (cm^{-1}) of uranyl using the software suite MOLFDIR

Calculation type	r_e	$\nu_{\text{symmetric stretch}}$	$\nu_{\text{asymmetric stretch}}$	ν_{bend}
HF	1.599	1358	1419	236
DHF	1.651	1240	1326	241
DHF + Gaunt	1.652	1242	1338	236
DHF + MP2	1.739	944	1052	136
DHF + CCSD	1.697	1041	1186	180
DHF + CCSD(T)	1.715	974	1121	164

Table 2. Equilibrium bond length (Å) and vibrational frequencies (cm^{-1}) of uranyl for various uranium RECPs using an uncontracted uranium Stuttgart-SC basis set plus Stuttgart-LC g-functions, and the TZVP DFT basis set for oxygen

Property	Theory	LANL2DZ HF (78)	LANL2DZ DFT (78)	CRENBL (78)	CRENBS (68)	Stuttgart LC (78)	Stuttgart SC (60)
r_e	SCF	1.646	1.638	1.627	1.649	1.631	1.643
	MP2	1.736	1.718	1.711	1.718	1.715	1.727
	LDA	1.717	1.695	1.691	1.676	1.694	1.698
	B3LYP	1.704	1.685	1.679	1.679	1.684	1.696
$\nu_{\text{symmetric}}$	SCF	1228	1227	1258	1241	1250	1243
	MP2	923	939	947	955	940	939
	LDA	968	1018	1005	1070	1012	1027
	B3LYP	1011	1053	1047	1083	1045	1049
$\nu_{\text{asymmetric}}$	SCF	1280	1292	1311	1299	1301	1306
	MP2	1022	1048	1050	1070	1048	1051
	LDA	1061	1110	1096	1159	1103	1124
	B3LYP	1101	1142	1135	1170	1134	1142
ν_{bend}	SCF	270	245	278	255	271	257
	MP2	142	148	158	141	162	121
	LDA	93i	147	34	147	64	117
	B3LYP	139	196	166	185	168	163

Table 3. Equilibrium bond length (Å) and vibrational frequencies (cm^{-1}) of uranyl for various RECPs using the TZVP DFT basis set for oxygen and the uranium basis set optimized for the specific RECP

Property	Theory	LANL2DZ HF (78)	LANL2DZ DFT (78)	CRENBL (78)	CRENBS (68)	Stuttgart LC (78)	Stuttgart SC (60)
r_e	SCF	1.653	1.644	1.635	1.655	1.634	1.649
	MP2	1.753	1.734	1.725	1.736	1.722	1.743
	LDA	1.727	1.702	1.697	1.684	1.697	1.702
	B3LYP	1.713	1.691	1.686	1.685	1.687	1.701
$\nu_{\text{symmetric}}$	SCF	1237	1245	1240	1232	1240	1238
	MP2	930	940	932	927	932	938
	LDA	959	1014	997	1054	1009	1028
	B3LYP	1002	1052	1037	1070	1045	1048
$\nu_{\text{asymmetric}}$	SCF	1294	1314	1303	1293	1291	1314
	MP2	1021	1050	1026	1038	1038	1043
	LDA	1053	1107	1092	1146	1101	1131
	B3LYP	1096	1143	1129	1158	1130	1147
ν_{bend}	SCF	278	261	281	255	277	253
	MP2	164	154	121	144	179	71
	LDA	82i	150	18	143	95	111
	B3LYP	142	199	164	181	181	158

MP2 and DFT levels of theory, the LANL2DZ HF RECP gives bond lengths that are 0.01 Å longer than the other RECPs. For all of the vibrational frequencies, we see that all RECPs produce similar results at the SCF and MP2 level of theory, which are also in good agreement with the benchmark results. Most of the RECPs produce similar stretch frequencies at the LDA and B3LYP level, but the LANL2DZ-HF RECP gives frequencies about 40 cm^{-1} lower, and the CRENBS RECP leads to frequencies at the LDA level about 50–60 cm^{-1} higher. The LANL2DZ-HF RECP gives an imaginary bending frequency at the LDA level, i.e., it predicts that the uranyl ion is bent. After this problem was observed by us and others, Hay [15] constructed a new LANL2DZ RECP at the LDA level of theory (LANL2DZ-DFT) which improves the uranyl LDA results considerably. In addition to the LANL2DZ-DFT RECP, the bending frequencies of the other two 78-electron RECPs, CRENBL and Stuttgart-LC, also give bending frequencies that are too small. Christiansen [17] tried to remedy the large core deficiency by moving the 5d orbitals from the core into the valence space. This CRENBS RECP improves the LDA bending frequency considerably but it also leads to an overestimation of all frequencies for methods that include some fraction of Hartree-Fock exchange. At the B3LYP level of theory, all of the RECPs, even the large-core RECPs, perform reasonably well. The CRENBS and the LANL2DZ-DFT RECPs overestimate the bending frequency somewhat.

We conclude that the Hartree-Fock-based large-core RECPs do not always perform well at the LDA level of theory. A reasonable performance is obtained for the Hartree-Fock-based methods and B3LYP. Small-core RECPs yield good results for all methods including LDA. The calculations using the CRENBS RECP, which gives results consistent with the small-core RECPs, suggest that the inclusion of the rather diffuse 5d orbitals into the core is at least partly responsible for the poorer performance of the large-core RECPs. Hay's LDA-based RECP does improve the LDA results but shows poorer performance when we include some fraction of Hartree-Fock exchange at the B3 level. Hence, these LDA-based RECPs seem suitable for use only with the LDA functional.

We can conclude that the Hartree-Fock-based RECPs, especially the large core RECPs, do not always perform that well when LDA is used. A remedy would be to generate the RECPs at the LDA level of theory, as done by Hay. When we recover part of the Hartree-Fock exchange by using, for example, the B3LYP exchange-correlation potential we improve our DFT results considerably for all of the HF-based RECPs. The results obtained with the CRENBS RECP are in line with the other small-core RECPs. This suggests that the inclusion of the rather diffuse 5d orbitals in the core is at least partly responsible for the poorer performance of the large-core RECPs.

We now focus on the results in Table 3, where the basis sets optimized for each individual RECP are used. In general, the results of Table 3 match those of Table 2, and, again, the same problems with the LDA bending frequency are observed here. The differences are caused by the smaller basis sets that are supplied with some of the RECPs. For the Stuttgart-SC RECP we find a rather long MP2 bond length and a low bending frequency. The standard Stuttgart-SC basis sets do not have g-functions, in contrast with the Stuttgart-LC. If we add the Stuttgart-LC g-functions to the Stuttgart-SC basis set the MP2 bond length is shortened by 0.015 Å and the bending frequency increases from 71 to 144 cm^{-1}. The effect of these additional g-functions on the DFT results is negligible. Hence, g-functions should be added to the Stuttgart-SC basis set when MP2, configuration interaction, or coupled cluster calculations are performed. Addition of g-functions to the LANL2DZ-HF RECP also shortens this MP2 bond length by over 0.01 Å. As noted above, the calculations with the contracted CRENBS basis were performed by using a Cartesian basis. We performed the same calculations using the uncontracted spherical basis set. The bond length shortens by ~0.01 Å, the changes in the stretch frequencies are negligible, and the bending frequencies increase by ~20 cm^{-1}.

Our results demonstrate that considerable care must be given to the choice of the uranium RECP and basis set in combination with the level of theory used in the calculation. Similar observations have been made by Ismail et al. [7] and Han and Hirao [8] when they performed test calculations for RECPs with various DFT functionals. Their calculations show that the best gradient-corrected functional is one that includes, to some extent, Hartree-Fock exchange. Ismail et al. found good agreement with the then available benchmark results using the Stuttgart-SC RECP. They also find that the large-core RECP of Hay et al. [28], a different RECP than used in our work, produces bond lengths which are ~0.02 Å shorter than those obtained with the Stuttgart-SC RECP, similar to what we found. The large-core and small-core Stuttgart RECP results obtained by Han and Hirao are similar to ours, with the exception of the large-core Hartree-Fock bond distance which oddly seems to be 0.02 Å too short. They also observe that the best DFT results are obtained when some fraction of Hartree-Fock exchange is introduced in the exchange-correlation potential, as was observed in our calculations. However, the differences between the LDA and B3LYP values are not that large in terms of the geometries or stretching frequencies and are most pronounced for the bending frequency.

Conclusions

We have presented a complete set of fully relativistic results for the bond lengths and all frequencies of uranyl at various levels of correlation treatment, which can be used as benchmark numbers for approximate calculations. In addition, we have also presented results of uranyl calculations using various RECPs and methods for including correlation. From our results, it is clear that small-core RECPs that include at least the 5d function in the valence space need to be used in order to obtain results consistent with the benchmark numbers. The best RECP results are obtained by using the Stuttgart-SC RECP. We also observe that the best results are obtained using a gradient-corrected DFT functional. It has also been found that g-functions are needed in the Stuttgart small-core basis set when many-body correlation methods like MP2 are used. For uranyl a bond length reduction of 0.015 Å and an increase of 70 cm^{-1} in the bending frequency is found at the MP2 level of theory when such g-functions are included.

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