Multiconfigurational quantum chemical methods for molecular systems containing actinides

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Recent advances in computational actinide chemistry are reported in this *tutorial review*. Muticonfigurational quantum chemical methods have been employed to study the gas phase spectroscopy of small actinide molecules. Examples of actinide compounds studied in solution are also presented. Finally the multiple bond in the diuranium molecule and other diactinide compounds is described.

1. Introduction

Actinide chemistry presents a challenge for quantum chemistry mainly because of the complexity of the electronic structure of actinide atoms. The ground state of the uranium atom is, for example, $(5f)^3$ $(6d)(7s)^2$, $^5L_6$. The ground level is thus 13-fold degenerate and is described using 7 + 5 + 1 = 13 atomic orbitals. The challenge for quantum chemistry is to be able to handle systems with a high density of states involving many active orbitals and all this has to be done using relativistic methods that include spin–orbit coupling. It is true that much actinide chemistry involves highly ionized actinide ions with few atomic valence electrons usually occupying only the 5f shells. A good example is the uranium chemistry involving the U^{6+} ion (for example in the uranyl ion UO_2^{2+}). Such compounds are often closed shell species and can be treated using well established quantum chemical tools where only scalar relativistic effects are taken into account.

There is, however, an extensive actinide chemistry that involves ions of lower valency and even neutral atoms. If we consider also chemical processes we find situations where the oxidation number may change form zero to a large positive number. An example is the small molecule NUN that will be discussed in this review. The formal oxidation number of the uranium ion is six, even if in reality the UN bonds are strongly

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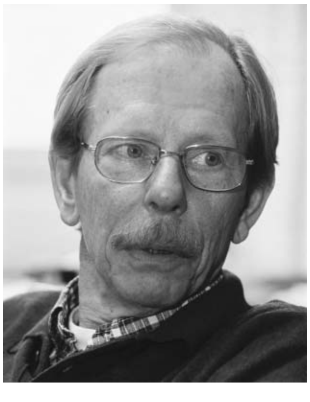

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Björn Olof Roos was born June 28, 1937 in Malmö, Sweden. He performed his academic studies at the University of Stockholm, where he received his PhD in April 1968. He then worked as a professor with salary from the Swedish Natural Science Research Council until 1983 when he was appointed Professor of Theoretical Chemistry at the University of Lund in southern Sweden. Roos is a member of the Royal Academy of Science and served on the Nobel Committee for Chemistry during the years 1986–2000. His research interest is in quantum chemistry. He has contributed to the development of new methods through the invention of the direct CI method in 1972, the Complete Active Space SCF method in 1980 and multiconfigurational second order perturbation theory in 1990. All these methods have been collected into the software MOLCAS. In recent year he has interested himself in heavy element chemistry, introducing relativistic effects into MOLCAS. He has applied his methods to a number of applications in organic spectroscopy, transition metal chemistry and in recent years in actinide chemistry. Roos has published about 350 articles in international journals.

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covalent. But consider the formation of this molecule, which is done by colliding uranium atoms with N_2: $U + N_2 \rightarrow NUN$.[1] Here, the oxidation number of U changes from zero to six along the reaction path and the spin quantum number from two to zero. The energy surface is 13-fold degenerate for the separate system but non-degenerate and closed shell at equilibrium. The quantum chemical description of the reaction path requires methods that can handle complex electronic structures involving several changes of the spin state and many close lying electronic states. This situation is rather common in uranium chemistry and many other similar situations can be found in the literature.

Another situation that involves actinide atoms in the zeroth oxidation state is the formation of actinide–actinide bonds. The molecule U_2 has recently been described theoretically.[2] The electronic structure is characterized by the existence of a large number of nearly-degenerate electronic states and wave functions composed of several electronic configurations.

The methods used to describe the electronic structure of such compounds must be relativistic and must have the capability to describe complex electronic structures. Such methods have been applied here. They will be described in section 2. The main characteristic is the use of multiconfigurational wave functions in an approach that includes relativistic effects. These methods have been applied for a large number of molecular systems with actinides and we shall give several examples from recent studies of such systems.

We shall start by describing in section 3 some triatomic molecules containing a uranium atom, which have been studied both in gas phase and in rare gas matrices. Most of the actinide chemistry occurs, however, in solution. In section 4 our recent attempts to describe actinide ions in solution will be presented. The extensive study of the multiple bond between two uranium atoms in the U_2 molecule and in other diactinides is reported in section 5. Several examples of inorganic compounds that include U_2 as a central unit are presented in section 6. The oxidation state in such compounds varies between zero and three and the wave functions are complex with a strong multiconfigurational nature.

2. The multiconfigurational approach

We shall here describe the methods that have been used in the applications to actinide-containing molecules. Many such systems, in particular those containing low valent actinide ions, cannot be well described using single configurational methods, like Hartree–Fock (HF), DFT, or Coupled Cluster. A multiconfigurational approach is needed, where the wave function is described as a combination of different electronic configurations. Here, a three step procedure will be used. In the first step we determine a multiconfigurational wave function using the Complete Active Space (CAS) SCF method. This wave function is in the second step used to estimate remaining (dynamic) correlation effects using multiconfigurational second order perturbation theory. Scalar relativistic effects are included in both these steps. Spin–orbit coupling is added in a third step where a set of CASSCF wave functions are used as basis functions to set up a spin–orbit Hamiltonian, which is diagonalized to obtain the final energies and wave functions. Below we shall describe each of these steps in more detail.

2.1 The complete active space SCF method

The CASSCF method was developed almost 30 years ago. It was inspired by the development of the Graphical Unitary Group approach to the full CI problem by I. Shavitt,[3] which made it possible to solve large full CI problems with full control of spin and space symmetry. This was in itself not very helpful because full CI is an approach that can only be used with very small basis sets and few electrons. It was, however, known that the important configurations (those with coefficients appreciably different from zero) in a full CI expansion used only a limited set of molecular orbitals. The following idea emerged, inspired by earlier work, especially the concept of a fully optimized reaction space (FORS) introduced by K. Ruedenberg in 1976:[4] The molecular orbital space is divided into three subspaces, inactive, active, and external orbitals. The inactive orbitals are assumed to be doubly occupied in all configuration functions (CFs) used to build the wave function. They thus constitute a Hartree–Fock sea in which the active orbitals move. Remaining electrons occupy a set of predetermined active orbitals. Once this is done, the wave function is fully defined as the full CI in the set of active orbitals. All CFs with a give space and spin symmetry are included in the multiconfigurational wave function. This is the concept of the Complete Active Space (CAS).[5]

To choose the correct active space for a specific application is not trivial and many times one has to make several experiments. It is difficult to set up any general rules because every chemical problem poses its own problems. There is also a tight connection to the choice of AO basis, which must be extensive enough to be able to describe the occupied MOs properly. The size of the active space is limited. The maximum size in most software is around 15 for the case where the number of orbitals and electrons are equal. This is the most severe limitation of the CASSCF method and makes it sometimes difficult or even impossible to carry out a specific study. In this article we shall exemplify how active orbitals are chosen in studies of actinide compounds, which poses special difficulties in this respect due to the large number of valence orbitals that may contribute to the chemical bonds (5f, 6d, 7s, and possibly 7p).

An extension to the CASSCF method exists that has not been used much so far but may become more interesting in the future: the Restricted Active Space (RAS) SCF method.[6] Here the active subspace is divided into three: RAS1, RAS2, and RAS3. The orbitals in RAS1 are doubly occupied but a limited number of holes is allowed. An arbitrary occupation is allowed in RAS2. A limited number of electrons is allowed to occupy the orbitals in RAS3. Many different types of RAS wave functions can be constructed. Leaving RAS1 fully occupied and RAS3 empty, we retrieve the CAS wave function. On the other hand, if we have no orbitals in RAS2 we obtain a wave function that includes all single, double, *etc.* excitations out of a closed shell reference function (the SDTQ-CI wave function). Maximizing the number of holes in RAS1 and the number of electrons in RAS3 to two with orbitals also in RAS2, we obtain what has been called a second order wave function in the active space.

The interesting feature of the RAS wave function is that it can work with larger active spaces than CAS, without exploding the CI expansion. It thus has the potential to perform multiconfigurational calculations that cannot today be performed with the CASSCF method. The problem is how one can add the effects of dynamic electron correlation. For CASSCF we can use second order perturbation theory (CASPT2, see below) but this is not yet possible for RASSCF wave functions. Recent developments in the research groups of the present authors indicate, however, that this may become possible in the near future through the development of a RASPT2 method. This will extend the applicability of the multiconfigurational methods to new classes of problems that cannot be treated today.

2.2 Multiconfigurational second order perturbation theory, CASPT2

The CASSCF wave function will, if the active space has been adequately chosen, include the most important CFs in the full CI wave function. In this way we include all near degenerate configurations, which describe static correlation effects, for example, in a bond breaking process. As a result, the CASSCF wave function will be qualitatively correct for the entire chemical process studied, which can be an energy surface for a chemical reaction, a photochemical process, *etc*. The energies that emerge are, however, not very accurate. We need to include in some way the part of the CF space that describes the remaining (dynamic) correlation effects. This is as necessary in the multiconfigurational approach as it would be if we started from the HF approximation.

How do we do that? In a single configurational approach, the obvious choices are preferably coupled cluster (CC) methods, or if the system is too large, second order perturbation theory (MP2), which is already quite accurate. A practical multiconfigurational CC theory does not exist yet. A method that has been used with great success since the 80's is *Multi-Reference CI (MRCI)* where the most important of the CFs of the CAS wave function are used as reference configuration in a CI expansion that includes all CFs that can be generated by single and double replacements of the orbitals in the reference CFs. The method is still used with some success due to recent technological developments. It becomes, however, time consuming for systems with many electrons and has also the disadvantage of lacking size-extensivity, even if this can be approximately corrected for.

Another way to treat the dynamic correlation effects is to use perturbation theory. Such an approach has the virtue of being size-extensive and ought to be computationally more efficient than the MRCI approach. Møller–Plesset second order perturbation theory (MP2) has been used for a long time to treat electron correlation for ground states, where the reference function is a single determinant. It is known to give accurate results for structural and other properties of closed shell molecules. Could such an approach work also for a multiconfigurational reference function like CASSCF? The approach was suggested soon after the introduction of the CASSCF method[7] but technical difficulties delayed a full implementation until the late 80's.[8] Today it is the most widely used method to compute dynamic correlation effects for multiconfigurational (CASSCF) wave functions. The principle is simple. We compute the second order energy with a CASSCF wave function as the zeroth order approximation. Having said that, one easily realizes that there are some problems to be solved that do not occur in MP2. We need to define a zeroth order Hamiltonian with the CASSCF function as an eigenfunction. It should preferably be a one-electron Hamiltonian in order to avoid too complicated a formalism. We need to define an interacting space of configurations. This is straightforward. They are given as:

$$\hat{\mathrm{E}}_{pq}\hat{\mathrm{E}}_{rs}|CASSCF\rangle. \tag{1}$$

This is an internally contracted configuration space, doubly excited with respect to the CAS reference function $|0\rangle = |CASSCF\rangle$. One or two of the four indices p, q, r, s must be outside the active space. The functions (1) are linear combinations of CFs and span the entire configuration space that interacts with the reference function. Labeling the compound index $pqrs$ as μ or v, we can write the first order equation as:

$$\sum_{v}\left[H_{\mu v}^{(0)}-E_0S_{\mu v}\right]C_v=-V_{0\mu}. \tag{2}$$

Here, $H_{\mu v}^{(0)}$ are matrix elements of a zeroth order Hamiltonian, which is chosen as a one-electron operator in the spirit of MP2. $S_{\mu v}$ is an overlap matrix: the excited functions are not in general orthogonal to each other. Finally, $V_{0\mu}$ represents the interaction between the excited function and the CAS reference function. The difference between eqn (2) and ordinary MP2 is the more complicated structure of the matrix elements of the zeroth order Hamiltonian. In MP2 it is a simple sum of orbital energies. Here it is a complex expression involving matrix elements of a generalized Fock operator, $\hat{F}$, combined with up to fourth order density matrices of the CAS wave function. We do not give further details here but refer to the original papers. The zeroth order Hamiltonian is written as a sum of projections of $\hat{F}$ onto the reference function $|0\rangle$

$$\hat{H}_0=\hat{P}_0\hat{F}\hat{P}_0+\hat{P}_{SD}\hat{F}\hat{P}_{SD}+\hat{P}_X\hat{F}\hat{P}_X, \tag{3}$$

where $\hat{P}_0$ projects onto the reference function, $\hat{P}_{SD}$ onto the *interacting configurations space* (1), and $\hat{P}_X$ onto the remaining configuration space that does not interact with $|0\rangle$. $\hat{F}$ has been chosen as the *generalized Fock operator*:

$$\hat{F}=\sum_{p,q}f_{pq}\hat{E}_{pq}, \tag{4}$$

with

$$f_{pq}=h_{pq}+\sum_{r,s}D_{rs}\left[(pq|rs)-\frac{1}{2}(pr|qs)\right]. \tag{5}$$

It has the property that $f_{pp} = -IP_p$ (IP = Ionization Potential) when the orbital p is doubly occupied and $f_{pp} = -EA_p$ (EA = Electron Affinity) when the orbital is empty. The value will be somewhere between these two extremes for active orbitals. Thus, we have for orbitals with occupation number one: $f_{pp} = -\frac{1}{2}\left(IP_p + EA_p\right)$. This formulation is somewhat unbalanced and will favor systems with open shells, leading for example to underestimated binding energies. The problem is that one would like to separate the energy connected with excitations out from an orbital from that of excitations into the orbital.

A modified zeroth order Hamiltonian has been suggested, which removes the systematic error and considerably improves both dissociation and excitation energies.[9] We can approximately write eqn (5) as an interpolation between the two extreme cases:

$$F_{pp} = -\frac{1}{2}\left(D_{pp}(IP)_p + \left(2 - D_{pp}\right)(EA)_p\right), \tag{6}$$

where D_{pp} is the diagonal element of the one-particle density matrix for orbital p The formula is correct for $D_{pp} = 0$ and 2, and also for a singly occupied open shell. Assume now that when we excite into an active orbital, we want its energy to replaced by $-EA$. This is achieved by adding a shift to eqn (6):

$$\sigma_p^{(EA)} = \frac{1}{2}D_{pp}\left((IP)_p - (EA)_p\right). \tag{7}$$

On the other hand, if we excite out of this orbital we want its energy to be replaced by $-IP$. The corresponding shift is:

$$\sigma_p^{(IP)} = -\frac{1}{2}\left(2 - D_{pp}\right)\left((IP)_p - (EA)_p\right). \tag{8}$$

The definition of $(IP)_\mathrm{p}$ and $(EA)_p$ is not straightforward. Therefore $(IP)_p - (EA)_p$ was replaced with an average shift parameter ε. The two shifts are then:

$$\sigma_p^{(EA)} = \frac{1}{2}D_{pp}\varepsilon \tag{9}$$

$$\sigma_p^{(IP)} = -\frac{1}{2}\left(2 - D_{pp}\right)\varepsilon \tag{10}$$

A large number of tests were performed, which showed that a value of 0.25 for epsilon was optimal. The mean error in the dissociation energies for 49 diatomic molecules was reduced from 0.2 to 0.1 eV. The effect was particularly impressive for triply bonded molecules: the average error for N_2, P_2, and As_2 was reduced from 0.45 eV to less than 0.15 eV. Similar improvements were obtained for excitation and ionization energies.[9]

Perturbation theory like MP2 or CASPT2 should only be used when the perturbation is small. Orbitals that give rise to large coefficients for the states (1) should ideally be included in the active space. Large coefficients in the first order wave function are the result of small zeroth order energy differences between the CAS reference state and one or more of the excited functions. We call these functions *intruder states*. In cases where the interaction term, $V_{0\mu}$, is small one can remove the intruder using a level shift technique that does not affect the contributions for the other states.[10] This method to solve the intruder state problem has been used successfully in a large number of applications.

The reference (zeroth order) function in the CASPT2 method is a predetermined CASSCF wave function. The coefficients in the CAS function are thus fixed and not affected by the perturbation operator. This often works well when the other solutions to the CAS Hamiltonian are well separated in energy but may be a problem when two or more electronic states of the same symmetry are close in energy. Such situations are quite common for excited states. One can then expect the dynamic correlation to affect also the reference function. This problem can be handled by extending the perturbation treatment to include electronic states that are close in energy. This is the *Multi-State CASPT2* method:[11]

Assume a number of CASSCF wave functions, ψ_i, $i = 1, N$, obtained in a state average calculation. The corresponding (single state) CASPT2 functions are: χ_i, $i = 1, N$. The functions $\psi_i + \chi_i$ are used as basis functions in a "variational" calculation where all terms higher than second order are neglected. The corresponding effective Hamiltonian has the elements:

$$(H_{eff})_{ij} = \delta_{ij}E_i + \langle\psi_i\hat{\mathrm{H}}|\chi_j\rangle, \tag{11}$$

E_i is the CASSCF energy for state i. This Hamiltonian is not symmetric. In practice a symmetrized matrix is used. This may cause problems if the non-Hermiticity is large and it is then advisable to extend the active space. One can expect this extension of the CASPT2 method to be particularly important for actinide compounds, where the density of states is often high.

2.3 Treatment of relativity

So far we have discussed a non-relativistic quantum chemistry. But actinide compounds cannot be studied theoretically without a detailed account of relativity. Thus, we need to extend the multiconfigurational method to the relativistic regime. Can this be made with enough accuracy for chemical applications without starting all over from the four-component Dirac theory? Much work has also been done in recent years to develop a 4-component quantum chemistry. It can today be made quite accurate, for example, when combined with the coupled-cluster approach for electron correlation. The problem is that an extension to multiconfigurational wave functions is difficult and would, if pursued, lead to lengthy and complex calculations, allowing only applications to small molecules. It is, however, possible to transform the 4-component Dirac operator to a 2-component form where one simultaneously analyzes the magnitude of the different terms and keeps only the most important. The presently most used such transformation leads to the second order Douglas–Kroll–Hess (DKH) Hamiltonian.[12] The DKH Hamiltonian can be divided into a scalar part and a spin–orbit coupling part. The scalar part includes the mass–velocity term and modifies the potential close to the nucleus such that the relativistic weak singularity of the orbital is removed. The effect on energies is similar to that of the Darwin term, but the resulting operator is variationally stable. This part of the relativistic corrections can easily be included in a non-relativistic treatment. Usually, only contributions to the one-electron Hamiltonian are included. For lighter atoms, the scalar relativistic effects will be dominating and calculations on, say, first row transition metal compounds, can safely be performed by adding only this term to the one-electron Hamiltonian used in non-relativistic quantum chemical methods. The scalar DKH Hamiltonian has recently been implemented into the CASSCF/CASPT2 version of the multiconfigurational approach.[13]

The scalar terms are only one part of the DKH Hamiltonian. There is also a true two-component term that as the dominating part has the spin–orbit interaction. This is a two-electron operator and therefore as such quite difficult to implement for molecular systems. However, some years ago an effective one-electron Fock-type spin–orbit Hamiltonian was suggested by Hess and coworkers[14] that significantly simplifies the algorithm for the subsequent calculation of spin–orbit matrix elements. Two-electron terms are treated as screening corrections of the, at least for heavy elements, dominating one-electron terms. Here, we use the Atomic Mean Field Integrals (AMFI), which, based on the short-range behavior of the spin–orbit interaction, avoids the calculation of multi-center one- and two-electron spin–orbit integrals and thus reduces the integral evaluation to individual atoms taking advantage of the full spherical symmetry. The approach reduces the computational effort drastically but leads to a negligible loss of accuracy compared to *e.g.* basis set or correlation limitations.

The treatment of the spin–orbit part of the DKH Hamiltonian is in the present work based on the assumption that the strongest effects of spin–orbit coupling arise from the interaction of *electronic states* that are close in energy. For these states independent CASSCF/CASPT2 calculations are performed. The resulting CASSCF wave functions are then used as basis functions for the calculation of the spin–orbit coupling. The diagonal elements of the spin–orbit Hamiltonian can be modified to account for dynamic correlation effects on the energy by, for example, replacing the CASSCF energies with CASPT2 energies. To be able to use the above procedure one needs to be able to compute matrix elements between complex CASSCF wave functions, which is not trivial because the orbitals of two different CASSCF wave functions are usually not orthogonal. A method to deal with this problem was developed by P.-Å. Malmqvist twenty years ago.[15] The method has become known as the CASSCF State Interaction (CASSI) method and is effective also for long CAS-CI expansions. It was recently extended to handle the integrals of the spin–orbit Hamiltonian.[16]

Is the method outlined above accurate enough for heavy element quantum chemistry? Today we have an extensive experience through a number of applications. A number of studies have been performed on atoms and small molecules, which show that the approach is capable of describing relativistic effects in molecules containing most atoms of the periodic system with good accuracy, maybe with exception of the fifth row elements Tl–At. Here the method gives larger errors than for any other atom in the periodic system.[17] The studies on actinide atoms and molecules show, however, that the method works well for the f-elements. A number of examples will be given later. As an illustration of how it works for atoms, we present in Table 1 the electronic spectra for some actinide atoms. These examples shows that atomic excitation energies (at least for the lower part of the spectrum) are reproduced with an accuracy better than 0.17 eV. There is one striking example, the $^6K_{19/2}$ state of neptunium, where the error is 0.31 eV. Could this be due to a misassignment of the experimental spectrum? As we shall see later, errors for molecular systems are in the range 0.0 to 0.2 eV (0–4 kcal mol^{-1}). Most of these errors are actually due to the use of the CASPT2 method for dynamic correlation and not to the method used to treat spin–orbit coupling.

2.4 Relativistic AO basis sets

It is not possible to use normal AO basis sets in relativistic calculations. The relativistic contraction of the inner shells makes it necessary to design the basis sets to take account of this effect. Specially designed basis sets have therefore been constructed using the DKH Hamiltonian. These basis sets are of the Atomic Natural Orbital type and are constructed such that semi-core electrons can also be correlated. They have been given the name ANO-RCC (Relativistic with Core Correlation) and cover all atoms of the periodic table (see ref. 18 and references therein). They will be used in most applications presented in this review. ANO-RCC are all-electron basis sets. We have not found that this is a problem in any of the applications presented here. Deep core orbitals are described by a minimal basis set and are kept frozen in the wave function calculations. The extra cost compared to using effective core potentials is therefore limited. Such potentials will, however, be used in some of the studies. More details will be given in connection with the specific application. The ANO-RCC basis sets can be downloaded from the home page of the MOLCAS quantum chemistry software (http://www.teokem.lu.se/molcas).

2.5 The effective bond order

We shall in the discussion of the bonding use the concept *effective bond order, EBO*. It is defined as follows: Each bonding orbital i has a natural orbital occupation number b_i. The corresponding antibonding orbital has the occupation number ab_i. The EBO is then defined as:

$$EBO = \sum_i (b_i - ab_i)/2$$

Table 1 Excitation energies (CASPT2/RASSI-SO) for some actinide atoms including spin–orbit coupling (in eV). Experimental values within parenthesis[a]

Th	Pa	U	Np
$^3F_2$ 0.00(0.00)	$^4K_{11/2}$ 0.00(0.00)	$^5L_6$ 0.00(0.00)	$^6L_{13/2}$ 0.32(0.43)
$^3P_0$ 0.28(0.32)	$^4K_{13/2}$ 0.38(0.46)	$^5L_7$ 0.38(0.47)	$^6L_{15/2}$ 0.69(0.86)
$^3F_3$ 0.34(0.36)	$^4K_{15/2}$ 0.82(0.93)	$^5L_8$ 0.81(0.95)	$^6L_{17/2}$ 1.10(1.24)
$^3P_2$ 0.39(0.46)	$^4K_{17/2}$ 1.32(1.39)	$^5L_9$ 1.30(1.40)	$^6L_{19/2}$ 1.56(1.60)
$^3P_1$ 0.41(0.48)	$^4I_{9/2}$ 0.13(0.10)	$^5L_{10}$ 1.84(1.84)	$^6L_{21/2}$ 2.09(1.99)
$^5F_1$ 0.55(0.69)	$^4I_{11/2}$ 0.45(0.51)	$^5K_5$ 0.14(0.08)	$^6K_{9/2}$ 0.33(0.25)
$^3F_4$ 0.59(0.62)	$^4I_{13/2}$ 0.83(0.92)	$^5K_6$ 0.47(0.53)	$^6K_{11/2}$ 0.61(0.64)
$^5F_2$ 0.66(0.79)	$^4I_{15/2}$ 1.28(1.27)	$^5K_7$ 0.85(0.91)	$^6K_{13/2}$ 0.93(0.97)
$^5F_3$ 0.80(0.93)	$^4G_{5/2}$ 0.37(0.20)	$^5K_8$ 1.29(1.32)	$^6K_{15/2}$ 1.31(1.30)
$^1D_2$ 0.83(0.90)	$^4G_{7/2}$ 0.57(0.58)	$^5K_9$ 1.78(1.68)	$^6K_{17/2}$ 1.73(1.61)
$^5F_4$ 0.96(1.09)	$^4G_{9/2}$ 0.84(0.91)		$^6K_{19/2}$ 2.21(1.90)
$^1G_4$ 1.02(1.01)	$^4G_{11/2}$ 1.17(—)		$^6I_{7/2}$ 0.41(0.43)
$^5F_5$ 1.11(1.22)	$^4H_{7/2}$ 0.43(0.37)		$^6I_{9/2}$ 0.69(0.82)
$^5P_1$ 1.37(1.44)	$^4H_{9/2}$ 0.69(0.76)		$^6I_{11/2}$ 1.03(1.20)
$^5P_2$ 1.41(1.46)	$^4H_{11/2}$ 1.01(—)		$^6I_{13/2}$ 1.39(1.41)

[a] From the NIST tables.[53]

This definition allows for fractional bond orders. If b_i is close to two and ab_i close to zero the contribution to EBO is one corresponding to the creation of a complete bond. If, on the other hand both b_i and ab_i are close to one, no bond is formed. The two electrons are then localized one on each atom. This happens for example in the U_2 diatomic molecule. Intermediate cases also exist in weakly bonded molecules as we shall see below. It is thus not certain that, what would formally be called a quintuple bond, really has five fully developed bonds. Some of them may be quite weak and the EBO may be appreciably smaller than five.

3. Spectroscopy of triatomic molecules containing one uranium atom

The chemistry of uranium with atmospheric components like carbon, nitrogen, and oxygen, in relation to the development of gas-phase separation involving atomic uranium, poses a challenge to both experimentalists and theoreticians. From the experimental point of view, few spectroscopical observations for actinide compounds are suitable for direct comparison with properties calculated for isolated molecules. Ideally, gas phase data are required for such comparisons. It has been found that even data for molecules isolated in cryogenic rare gas matrixes, a medium usually considered to be minimally perturbing, can be influenced by the host to such a degree that it is difficult to avoid the interaction between the matrix and the molecules. Calculations on isolated molecules may thus be of great help to understand the interpretation of the experimental measurements.

Over the years we have studied several triatomic compounds of general formula XUY, where X,Y = C,N,O and U is the uranium atom in the formal oxidation state VI, V, IV. We have determined the vibrational frequencies for the electronic ground state of NUN, NUO^+, NUO, OUO^{2+} and OUO^+[19] and compared them with the experimental measurements performed by L. Andrews and coworkers.[20]

The electronic spectrum of OUO was also studied extensively.[21,22] The OUO molecule was found to have a (5f ϕ)(7s), $^3\Phi_{2u}$, ground state. The lowest state of gerade symmetry, $^3H_{4g}$, corresponding to the electronic configuration $(5f)^2$ was found 3300 cm^{-1} above the ground state. The computed energy levels and oscillator strength were used for the assignment of the experimental spectrum,[23,24] in energy ranges up to 32000 cm^{-1} above the ground state.

The reaction between a uranium atom and a nitrogen molecule N_2 leading to the formation of the triatomic molecule NUN was also studied.[25] The system proceeds from a neutral uranium atom in its $(5f)^3$ $(6d)(7s)^2$, ^5L ground state to the linear molecule NUN, which has a $^1\Sigma_g^+$ ground state and uranium in a formal U(VI) oxidation state. The effect of spin–orbit coupling has been estimated at crucial points along the reaction. The system proceeds from a quintet state for U + N_2, *via* a triplet transition state to the final closed shell molecule. An eventual energy barrier for the insertion reaction is caused by the spin–orbit coupling energy.

The lowest electronic states of the CUO molecule were also studied.[26] The ground state of linear CUO was predicted to be a Φ_2 (a Φ state with the total angular momentum Ω equal to two). The calculated energy separation between the Σ_0^+ and Φ_2 states is −0.36 eV at the geometry of the Σ_0^+ state (R(C–U) = 1.77 Å and R(U–O) = 1.80 Å), and −0.55 eV at the geometry of the Φ_2 state (R(C–U) = 1.87 Å and R(U–O) = 1.82 Å). These results indicate that the Φ_2 state is the ground state of free CUO. Such a prediction does not confirm the experimental results presented by L. Andrews and coworkers,[27] supported also by some Density Functional Theory calculations. According to their results the ground state of the CUO molecule shifts from a closed shell ground state to a triplet ground state, when going from a Ne matrix (analogous to free CUO) to an Ar matrix. Other groups are also working on the topic,[28] which is still under debate.

4. Actinide chemistry in solution

The identification and characterization of actinide chemistry in solution is important for understanding actinide separation and predicting actinide transport in the environment, particularly with respect to the safety of nuclear waste disposal.[29] The uranyl $UO_2{}^{2+}$ ion, for example, has received considerable interest due to its importance for environmental chemistry of radioactive elements and its role as a benchmark system for higher actinides. A large amount of experimental and theoretical work has thus been published over the years. Direct structural information on the coordination of uranyl in aqueous solution has been mainly obtained by extended X-ray absorption fine structure (EXAFS) measurements,[30] while X-ray scattering studies of uranium and actinide solutions have been more rare.[31] Theoretically, various *ab initio* studies of uranyl and related molecules, with a polarizable continuum model to mimic the environment and/or a number of explicit water molecules, have been performed.[32–34] We have performed a structural investigation of the carbonate system of dioxouranyl (VI) and (V), $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$[35] in water. This study showed that only minor geometrical rearrangements occur in the one-electron reduction of $[UO_2(CO_3)_3]^{4-}$ to $[UO_2(CO_3)_3]^{5-}$ confirming the reversibility of this reduction.

We have also studied the coordination of the monocarbonate, bicarbonate and tricarbonate complexes of neptunyl in water, by using explicit water molecules and a continuum solvent model.[36] The monocarbonate complex was shown to have a pentacoordinated structure, with three water molecules in the first coordination shell, and the bicarbonate complex has a hexacoordinated structure, with two water molecules in the first coordination shell. Overall good agreement with experimental results was obtained.

It seems that in order to understand the structural and chemical behavior of uranyl and actinyls in general in solution, it is necessary to go beyond a quantum chemical model of the actinyl species in a polarizable continuum medium, eventually with the inclusion of a number of explicit water molecules. A dynamic description of these systems is important for the understanding of the solvent environment to the charged ions. It is thus necessary to combine quantum chemical results with molecular dynamics simulations. Empirical and/or semi-empirical potentials are commonly used in most of the existing molecular simulation packages and they are generated to reproduce information obtained by experiment or to some extent results obtained from theoretical modeling. Simulations using these potentials are therefore accurate only when they are performed on systems similar to those for which the potential parameters were fitted. If one wants to simulate actinide chemistry in solution, this approach is not adequate because there are very little experimental data available for actinides in solution, especially for actinides heavier than uranium.

An alternative way is to generate intermolecular potentials fully *ab initio* from molecular wave functions for the separate entities. We have recently studied the structure and dynamics of the water environment to a uranyl ion using such an approach (the non-empirical model potential, NEMO, method). This scheme has been developed during the last 15 years.[37] It has largely been used to study systems like liquid water and water clusters, liquid formaldehyde and acetonitrile and the solvation of organic molecules and inorganic ions in water. The interested reader is referred to a recent review article[37] by Engkvist *et al.* for references on the specific applications.

The interaction between uranyl and a water molecule has been studied using accurate quantum chemical methods.[38] The information gained has been used to fit a NEMO potential, which is then used also to determine other interesting structural and dynamical properties of the system. Multiconfigurational wave function calculations have been performed to generate pair potentials between uranyl and water. The quantum chemical energies have been used to fit parameters in a polarizable force field with an added charge transfer term. Molecular dynamics simulations have been performed for the uranyl ion and up to 400 water molecules. The results showed a uranyl ion with five water molecules coordinated in the equatorial plane. The U–water distance is 2.40 Å, which is close to the experimental estimates. A second coordination shell starts at about 4.7 Å from the uranium atom. Exchange of waters between the first and second solvation shell is found to occur through a path intermediate between association and interchange. This study is the first fully *ab initio* determination of the solvation of the uranyl ion in water.

5. The actinide–actinide chemical bond

Is it possible to form bonds between actinide atoms and, if so, what is the nature of these bonds? Experimentally, there has been some evidence of such bonds both in gas phase and in matrix studies. The uranium molecule was detected in gas phase already in 1974.[39] The dissociation energy was estimated to be 50 ± 5 kcal mol^{-1}. L. Andrews and co-workers have found both U_2 and Th_2 molecules using matrix isolation spectroscopy. Both molecules have also been found in gas phase using laser vaporization of a solid uranium or thorium target. Small molecules containing U_2 as a central unit have also been reported, for example, H_2U–UH_2 [40] and OUUO.[39]

5.1 The U_2 molecule

Theoretically, not much was known about the nature of the chemical bond between actinides before the study of U_2 by the present authors.[2] The same molecule was theoretically studied in 1990,[41] but the methods used were not advanced enough to allow a conclusive characterization of the chemical bond.

Is it possible to say something about the bonding pattern of a molecule like U_2 based on qualitative arguments? Before undertaking the study of the diuranium molecules, some systems containing a transition metal and a uranium atom were studied.[42–44] The ground level of the uranium atom is $(5f)^3$ $(6d)^1$ $(7s)^2$, $^5L_6$ with four unpaired electrons that could in principle form a quadruple bond. The double occupancy of the 7s orbital will, however, prevent the unpaired orbitals from coming in contact and being able to form the bonds. We find on the other hand a valence state with six unpaired electrons only 0.77 eV above the ground level: $(5f)^3(6d)^2(7s)^1$, $^7M_6$. An hextuple bond could thus in principle be formed if it were strong enough to overcome the needed atomic promotion energy of 1.54 eV. There is, however, one more obstacle. The 7s and 6d orbitals can be expected to overlap more strongly than the 5f orbitals. In particular the 5fϕ orbitals, which are occupied in the free atom, will have small overlap. Thus we also need to transfer electrons from 5f to 6d to form a strong bond. As we shall see, it is this competition between the atomic configuration and the ideal molecular state that determines the electronic structure of the uranium dimer. It is difficult to proceed further with the analysis without performing explicit calculations.

Such calculations were performed using an ANO-RCC basis set of the size: 9s8p6d5f2g1h.[2] As pointed out above there are potentially 13 active orbitals on each atom involved in the bonding (5f, 6d, 7s). This would yield an active space of 26 orbitals with 12 active electrons, an impossible calculation. A number of trial calculations were performed using different smaller active spaces. The results had one important feature in common. They all showed that a strong triple bond was formed involving the $7s\sigma_g$ and $6d\pi_u$ orbitals. The occupation numbers of these three orbitals were close to two with small occupation of the corresponding antibonding orbitals. It was therefore decided to leave these orbitals inactive and also remove the antibonding orbitals $7s\sigma_u$ and $6d\pi_g$. This approximation should work well around equilibrium but of course prevents the calculation of full potential curves.

With six electrons and six MOs removed from the active space one is left with 6 electrons in 20 orbitals, a calculation that could easily be performed. A number of calculations were performed with different space and spin symmetry of the wave function. The resulting ground state was found to be a septet state with all the six electrons having parallel spin. Also the orbital angular momentum was high with $\Lambda = 11$. The spin–orbit calculations showed that the spin and orbital angular momenta combined to form a $\Omega = 8$ state. The final label of the ground state is thus: $^7O_8$.

The main terms of the multiconfigurational wave function were found to be:

$$\psi(3,11) = 0.782(7s\sigma_g)^2(6d\pi_u)^4(6d\sigma_g)(6d\delta_g)(5f\delta_g)(5f\pi_u)(5f\phi_u)(5f\phi_g) + 0.596(7s\sigma_g)^2(6d\pi_u)^4(6d\sigma_g)(6d\delta_g)(5f\delta_u)(5f\pi_g)(5f\phi_u)(5f\phi_g)$$

This wave function reflects nicely the competition between the preferred atomic state and the most optimal binding

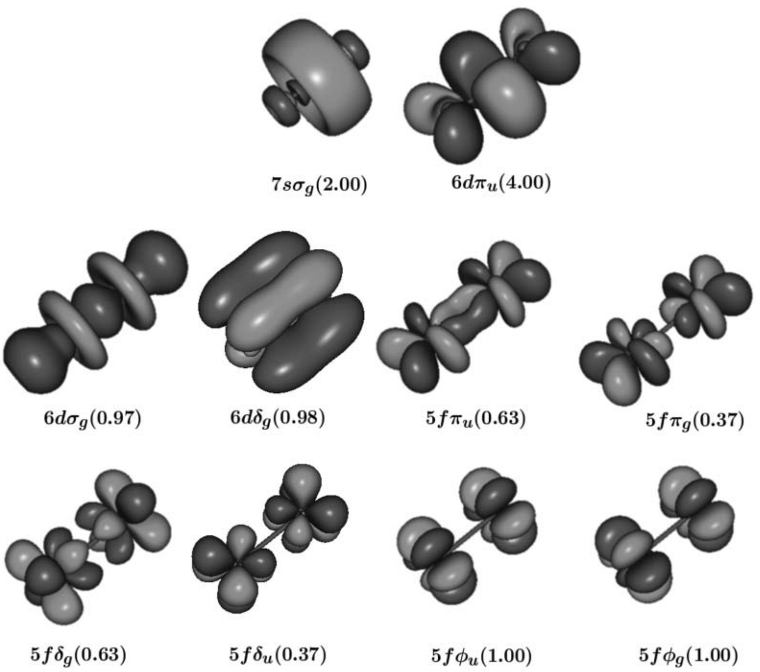

Fig. 1 The active molecular orbitals of the U_2 molecule. The occupation number is given below each orbital. (Reproduced with permission from ref. 2. Copyright 2005 Nature Publishing Group.)

situation. We have assumed that the triple bond is fully formed. There are also two electrons in 6d dominated sigma bonds, $6d\sigma_g$ and $6d\delta_g$. The rest of the MOs are dominated by 5f. Two weak bonds are formed using $(5f\delta_g)$ and $(5f\pi_u)$ orbitals. Note the large occupation of the corresponding antibonding orbitals. Finally the $5f\phi$ orbitals remain atomic and do not contribute to the bonding (equal occupation of the bonding and antibonding combinations). Formally, a quintuple bond is formed but the large occupation of some antibonding orbitals reduces the effective bond order below five. We show the orbitals and their occupation number in Fig. 1.

Due to the weak bonding of the 5f orbitals, the effective bond order is not five but closer to four. It is interesting to note the occupation of the different atomic valence orbitals on each uranium atom. They are 7s: 0.94, 6d, 2.59, and 5f: 2.44. Compare that to the population in the lowest atomic level with 7s singly occupied: 7s: 1.00, 6d: 2.00, and 5f: 3.00. We see a transfer of about 0.6 electrons from 5f to 6d. This is how much the molecule can utilize the better bonding power of the 6d orbitals compared to 5f.

The calculations gave a bond distance of 2.43 Å and a bond energy of about 35 kcal mol^{-1}, including the effects of spin–orbit coupling. An experimental value of 50 ± 5 kcal mol^{-1} was reported in 1974.[39]

5.2 Other di-actinides

Is it possible that other actinides can form dimers? We already mentioned that Th_2 has been detected in the gas phase and in a rare gas matrix. We have recently studied this dimer and also the dimers of Ac and Pa. Details of this study have been published elsewhere,[45] but some of the major findings are reported here.

We present in Table 2 the excitation energies needed to produce a valence state with all orbitals singly occupied. It is largest for Ac. The price to pay to be able to form a triple bond between two Ac atoms is 2.28 eV. For Th we need only 1.28 eV and can then in principle form a quadruple bond. Note that in these two cases only 7s and 6d orbitals are involved. For Pa, 1.67 eV is needed resulting in the possibility of forming a quintuple bond. The uranium case has already been described above and we saw that in spite of six unpaired atomic orbitals a quintuple bond is formed with an effective bond order that is actually closer to four than five.

It is the competition between the needed atomic promotion energy and the strength of the bond that will determine the electronic structure. In Table 3 we present the results of the calculations and in Table 4 the populations of the atomic orbitals in the dimer are given. The results illustrate nicely the trends in the series. A double bond is formed in the actinium dimer involving the $7s\sigma_g$ and the $6d\pi_u$ orbitals. But the σ_u orbital is also doubly occupied, which would reduce the bond order to one. The molecule uses the 7p orbital to reduce the antibonding power of this orbital resulting in a unique

Table 2 The energy needed to reduce the occupation number of the 7s orbital from two to one in the actinide atoms Ac–U (in eV)[a]

Ac:	$(7s)^2(6d)^1$, $^2D_{3/2} \rightarrow (7s)^1(6d)^2$, $^4F_{3/2}$	1.14
Th:	$(7s)^2(6d)^2$, $^3F_2 \rightarrow (7s)^1(6d)^3$, $^5F_1$	0.64
Pa:	$(7s)^2(6d)^1(5f)^2$, $^4K_{11/2} \rightarrow (7s)^1(6d)^2(5f)^2$, $^6L_{11/2}$	0.87
U:	$(7s)^2(6d)^1(5f)^3$, $^5L_6 \rightarrow (7s)^1(6d)^2(5f)^3$, $^7M_7$	1.01

[a] From the NIST tables.[53]

Table 3 The dominating electronic configuration for the lowest energy state of the actinide dimers Ac_2–U_2

Ac_2:	$(7s\sigma_g)^2(7s7p\sigma_u)^2(6d\pi_u)^2$	$^3\Sigma_g^-$
Th_2:	$(7s\sigma_g)^2(6d\pi_u)^4(6d\delta_g)(6d\sigma_g)$	$^3\Delta_g$
Pa_2:	$(7s\sigma_g)^2(6d\pi_u)^4(6d\delta_g)^2(6d\sigma_g)^2$	$^3\Sigma_g^-$
U_2:	$(7s\sigma_g)^2(6d\pi u)^4(6d\sigma_g)^1(6d\delta_g)^1(5f\delta_g)^1(5f\pi_u)^1(5f\phi_u)^1(5f\phi_g)^1$	^7O_g

Table 4 Mulliken populations (per atom), bond distances, bond energies (D_0), and Effective Bond Order (EBO) for the early di-actinides

	7s	7p	6d	5f	R_e/Å	D_0/eV	EBO
Ac_2:	1.49	0.49	0.96	0.04	3.63	1.2	2.5
Th_2:	0.93	0.01	2.83	0.21	2.76	3.3	3.7
Pa_2:	0.88	0.02	3.01	1.06	2.37	4.0	4.5
U_2:	0.94	0.00	2.59	2.44	2.43	1.2	4.2

population of the 7p orbital that we do not see for the other di-actinides. The populations are with this exception close to that of the free atom. The bond energy is also small and the bond length large.

Already in the thorium dimer we see another pattern. The 7s population is reduced to close to one. The electron is moved to 6d and a strong quadruple bond is formed, which is the result of three two-electron bonds and two 6d one-electron bonds. We also start to see some population of the 5f orbitals which hybridizes with 6d. The strongest bond is formed between two Pa atoms. Here the contribution of 6d is maximum and we see a complete promotion to the atomic state with five unpaired electrons. A quintuple bond is formed with a short bond distance and a bond energy close to 5 eV. Again the bond contains the $(7s\sigma_g)^2$ $(6d\pi_u)^4$ triple bond plus a $6d\sigma_g$ two-electron bond and two $6d\delta_g$ one-electron bonds. The 5f population is increased to one electron but we still do not see any orbital dominated by this atomic orbital. They are all used in combination with the 6d orbitals.

With the Pa_2 dimer we have reached the maximum bonding power among the actinide dimers. In U_2 the bond energy decreases and the bond length increases. This is due to the increased stabilization of the 5f orbitals and the corresponding destabilization of 6d. Large transfer of electrons from 5f to 6d is no longer possible and the bonds become weaker and more dominated by the atomic ground state, even if we still see a complete promotion from a $(7s)^2$ to a $(7s)^1$ state. This trend will most certainly continue for the heavier di-actinides and we can thus without further calculations conclude that Pa_2 is the most strongly bound dimer with its fully developed quintuple bond and an effective bond order not much smaller than five.

6. Diuranium inorganic chemistry

The natural tendency of a uranium atom to be preferentially complexed by a ligand, than to explicitly form a direct U–U bond, has precluded the isolation of stable uranium species exhibiting direct metal-to-metal bonding. From the experimental point of view, the synthesis of multiply bonded uranium compounds poses many challenges. Although the uranium ionic radius is not exceedingly large, the presence of many electrons combined with the preference for certain coordination modes with common ligands makes the task of stabilizing the hypothetical U–U bond difficult. The tendency for the higher oxidation states of uranium would suggest that if a multiple bond is to be formed between uranium atoms, such species will rather bear several ligands on each multivalent U center.

As previously discussed, the uranium atom has six valence electrons and the U–U bond in U_2 is composed of three normal two-electron bonds, four electrons in different bonding orbitals and two non-bonded electrons leading to a quintuple bond between the two uranium atoms. Multiple bonding is also found between transition metal atoms. The Cr, Mo, and W atoms have six valence electrons and a hextuple bond is formed in the corresponding dimers, even if the sixth bond is weak. The similarity between these dimers and the uranium dimer suggests the possibility of an inorganic chemistry based on the latter. A number of compounds with the M_2 (M = Cr, Mo, W, Re, *etc.*) unit are known. Among them are the chlorides, for example, Re_2Cl_6, $Re_2Cl_8^{2-}$ [46,47] and the carboxylates, for example Mo_2 $(O_2CCH_3)_4$.[48] The simplest of them are the tetraformates, which in the absence of axial ligands have a very short metal–metal bond length.[49]

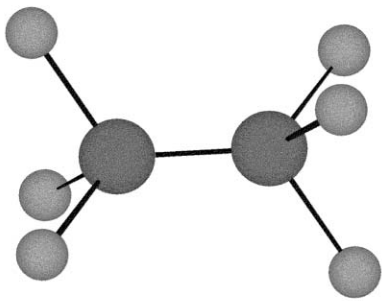

Fig. 2 The structure of U_2Cl_6.

We have recently shown that corresponding diuranium compounds are also stable with a multiple U–U bond and short bond distances.[50,51] We have studied two chlorides, U_2Cl_6 and $U_2Cl_8^{2-}$, both with U(III) as the oxidation state of uranium (See Fig. 2), and three different carboxylates (See Fig. 3), $U_2(OCHO)_4$, U_2 $(OCHO)_6$, and U_2 $(OCHO)_4Cl_2$. All species have been found to be stable with a multiply bonded U_2 unit.

In the diuranium chlorides, the formal charge of the uranium ion is +3. Thus six of the twelve valence electrons are available and a triple bond can in principle be formed. U_2Cl_6 can have either an eclipsed or a staggered conformation. Preliminary calculations have indicated that the staggered conformation is about 12 kcal mol^{-1} lower in energy than the eclipsed form. We have thus focus our analysis on the staggered structure.

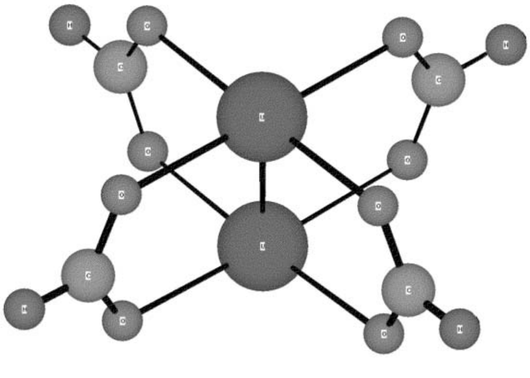

Fig. 3 The structure of $U_2(OCHO)_4$.

The U–U and U–Cl bond distances and the U–U–Cl angle have been optimized at the CASPT2 level of theory. The ground state of U_2Cl_6 is a singlet state with the electronic configuration $(\sigma_g)^2$ $(\pi_u)^4$. The U–U bond distance is 2.43 Å, the U–Cl distance 2.46 Å and the U–U–Cl angle 120.0 degrees. At the equilibrium bond distance, the lowest triplet lies within 2 kcal mol^{-1} from the singlet ground state. The two states are expected to interact *via* the spin–orbit coupling Hamiltonian. This will further lower the energy, but will have a negligible effect on the geometry of singlet electronic states. It is known from a number of earlier studies, for example, on the uranium dimer, that spin–orbit coupling effects vary only slowly in the region around the equilibrium geometry. (The reader should refer to the original papers[50,51] for a broader discussion on the topic.)

The dissociation of U_2Cl_6 to 2 UCl_3 has been studied. UCl_3, unlike U_2Cl_6, is known experimentally.[52] Single point CASPT2 energy calculations have been performed at the experimental geometry, as reported in ref. 52, namely a pyramidal structure with a U–Cl bond distance of 2.55 Å and a Cl–U–Cl angle of 95 degrees.

$U_2Cl_8^{2-}$ is the analogue of $Re_2Cl_8^{2-}$. We have optimized the structure for $U_2Cl_8^{2-}$ using an active space formed by six active electrons in thirteen active orbitals, assuming D_{4h} symmetry. As in the U_2Cl_6 case, the molecular orbitals are linear combinations of U 7s, 7p, 6d, and 5f orbitals with Cl 3p orbitals. The ground state of $U_2Cl_8^{2-}$ is a singlet state with an electronic configuration of $(5f\sigma_g)^2(5f\pi_u)^4$. The molecule presents a U–U triple bond. The U–U bond distance is 2.44 Å , the U–Cl bond distance is 2.59 Å and the U–U–Cl angle is 111.2 degrees. $U_2Cl_8^{2-}$ is different compared to $Re_2Cl_8^{2-}$ in terms of molecular bonding, in the sense that the bond in $Re_2Cl_8^{2-}$ is formally a quadruple bond, even though the δ_g bond is weak, because Re^{3+} has four electrons available to form the metal–metal bond. Only a triple bond can form in $U_2Cl_8^{2-}$ because only three electrons are available on each U^{3+} unit.

7. Conclusions

In 1998 quantum chemistry was recognized through the award of the Nobel Prize in Chemistry to W. A. Kohn and J. A. Pople jointly. This recognition was not only based on the ability to solve the quantum-mechanical equations to a good degree of approximation for molecules, but also on the fact that the field could perform theoretical simulations of real benefit to the community. *Ab initio* quantum chemistry has made so many advances in the last 40 years, that it now allows the study of molecular systems containing any of the atoms of the periodic system, provided that electron correlation and relativistic effects are properly taken into account. Such methods are available and they are especially useful when one wants to study systems which are not easy to handle in a laboratory, like actinide compounds. Examples have been here presented of how it is possible to characterize the structure and spectroscopy of actinide compounds both in the gas phase and in solution. Many challenges still remain open and the interplay between theoreticians and experimentalists will certainly enhance the possibilities for further progress in actinide chemistry.

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