Lanthanides and Actinides

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1 INTRODUCTION

The application of quantum chemistry to systems containing atoms of the lanthanide ($_{57}$La–$_{71}$Lu) and/or actinide ($_{90}$Th–$_{103}$Lr) series is a considerable challenge and has been attempted only by a comparatively small number of researchers. Several complications, some of which will be described in the following, prevent standard quantum chemical approaches from being successful in this field in all respects. However, although no entirely satisfactory calculations on these systems can be performed at present, the rapid development of computer technology as well as quantum chemistry methodology and software made considerable progress possible in the 1990s and will certainly permit accurate investigations of compounds containing lanthanides and actinides to be made in the near future.

The available relativistic electronic structure calculations for lanthanide- and actinide-containing molecules were briefly reviewed by Pyykkö[1] in 1987. Extensive reviews for lanthanide and actinide compounds have been published more recently by Dolg and Stoll[2] and Pepper and Bursten,[3] respectively. Calculations for lanthanide- and actinide-containing molecules as well as some related transition metal systems have been summarized by Balasubramanian.[4] Some information is also available from several reviews of relativistic quantum chemistry, e.g., by Pyykkö[5] or Malli.[6] A bibliography of relativistic quantum chemical studies collected by Pyykkö[7] is available on the Internet.

The remainder of this article discusses some general points important for quantum chemical studies of systems containing lanthanides and actinides, then briefly summarizes the quantum chemical methods applied so far to study f element systems, and finally focusses on a few characteristic examples. Owing to the limited space available here many interesting investigations have been omitted and only a broad overview can be given. The reader is referred to the above-mentioned reviews for a more complete set of citations.

2 GENERAL

2.1 Superconfiguration Model

In the lanthanide and actinides series the 4f and the 5f shell, respectively, are filled with electrons. Owing to the high degeneracy of the f shells (14 spin orbitals) a rather large number of possible electronic (micro)states may arise even for atoms; e.g., for n electrons in m spin orbitals, $m!/n!(m-n)!$ possible *Slater determinants* can be constructed. In the case of a half-filled s, p, d, and f shell one has 2, 20, 252, and 3432 possibilities. The situation is even more complicated since the open f shell is frequently accompanied by an open 5d, 6s, 6p and 6d, 7s shell for the lanthanides and actinides, respectively. Therefore, the valence shell to be considered in quantum chemical investigations comprises orbitals with three different main quantum numbers which are also located in three different spatial shells of the atoms, as shown in Figures 1 and 2 for Ce and Th, respectively. The valence f orbitals have their maximum density just outside an M^{30+} core (small core), the actinide 5f shell being more diffuse than the compact lanthanide 4f shell. The valence d orbitals are located outside an M^{12+} core (medium core), the actinide 6d orbitals again extending more than the lanthanide 5d orbitals. Finally, the lanthanide 6s (6p) and actinide 7s (7p) shells are rather similar with respect to their spatial characteristics and are located outside the chemically intuitive M^{4+} core (large core).

In molecules, several lanthanide or actinide centers may be present, resulting in a too large number of unpaired electrons to be treated rigorously by *ab initio* methods in many cases, especially when not merely the high-spin state described by a single Slater determinant is considered. A typical example is Gd_2, which is possibly the diatomic molecule with the highest experimentally observed spin-multiplicity (18 unpaired electrons, $^{19}\Sigma$ ground state).[8]

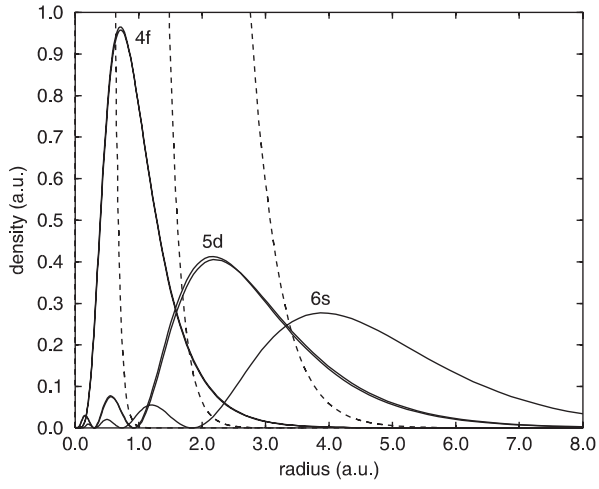

Figure 1 Radial densities of the 4f, 5d, and 6s valence spinors of Ce (solid lines) and total radial densities of the Ce^{30+}, Ce^{12+}, and Ce^{4+} cores (dashed lines, from left to right) from average-level Dirac–Hartree–Fock calculations for the $4f^15d^16s^2$ configuration

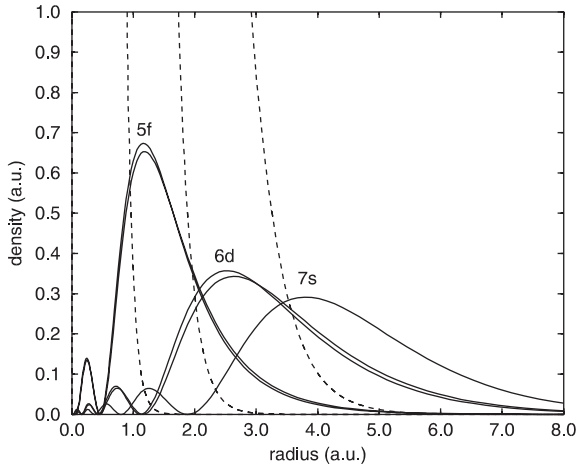

Figure 2 Radial densities of the 5f, 6d, and 7s valence spinors of Th (solid lines) and total radial densities of the Th^{30+}, Th^{12+}, and Th^{4+} cores (dashed lines, from left to right) from average-level Dirac–Hartree–Fock calculations for the $5f^16d^17s^2$ configuration

The large number of low-lying electronic states makes a rationalization of the electronic structure of lanthanide and actinide compounds rather difficult. The situation from a spectroscopist's point of view is even more complicated owing to the numerous isotopes occurring for some lanthanides and actinides, which cause a huge number of spectral lines. A simple model is needed to extract the basic features of the electronic structure and to enable a successful analysis of the experimentally determined data to be made. For an experimental chemist the exact quantum mechanical classification of the electronic ground state may in fact not be of particular interest and again a simple model to describe the main features is called for. In the case of the lanthanides a straightforward scheme, i.e., the so-called superconfiguration model,[9] exploiting (from a spatial (Figure 1), not an energetic (Figure 3) point of view) the core-like character of the 4f shell, is helpful in many cases for a simplified interpretation of the electronic structure. Although from an energetic point of view (orbital energies) the 4f shell is part of the valence space, judged by its spatial extension (radial expectation values) it has an atomic core-like character (Figure 1), even in a molecular environment. The coupling of the 4f shell to the spatially well-separated partially occupied valence shell is comparatively weak and may be neglected in a first approximation. The spectroscopic constants of a molecule, e.g., bond lengths, bond angles, and vibrational frequencies, are therefore mainly determined by the 4f subconfiguration as well as the subconfiguration and substate of the valence shell. The different couplings within the 4f shell and between the 4f shell and the valence shell just cause different constant shifts in energy; e.g., they affect the dissociation energy but not the shape of the *potential energy (hyper)surface* near the equilibrium structure. Electronic states with the same 4f subconfiguration and the same valence substate exhibit nearly identical spectroscopic constants independent of the total overall electronic state. Therefore it is convenient to assign all electronic states arising from the same 4f subconfiguration to belong to a common so-called superconfiguration. A typical theoretically[10] and experimentally[11] well-investigated example is the $4f^1\sigma^1_{6s,6p}$ superconfiguration of cerium monoxide (CeO); the 4f orbitals fall into the σ, π, δ, and ϕ symmetries in the C_{∞_v} point group, giving rise to eight $\Lambda\Sigma$-coupled electronic states, i.e., $^{1,3}\Sigma$, Π, Δ, Φ. After the inclusion of spin–orbit interaction a total of 16 electronic states in an energy interval of 4458 cm^{-1} arise in the $\omega\omega$ or the intermediate coupling scheme. All of these states have nearly identical spectroscopic constants: $R_e = 1.82 \pm 0.01$ Å, $\omega_e = 823 \pm 3 cm^{-1}$.

The superconfiguration model of course fails in all cases where the 4f orbitals explicitly participate in chemical bonding, i.e., in the sense that they contribute to molecular valence orbitals and partly lose their core-like character. This is the case, e.g., in formally tetravalent cerium compounds such as cerium dioxide, CeO_2. Similarly, for actinides the 5f orbitals are spatially more diffuse than the 4f orbitals of the lanthanides (Figure 1) and are energetically less well separated from the other valence orbitals (Figure 3). The actinide 5f shell therefore often actively participates in chemical bonding, as is reflected by the higher valences of the early actinide elements (e.g., UF_6 vs. NdF_3), and the superconfiguration model becomes inappropriate.

2.2 Relativistic Effects

Relativistic effects,[12] which become important for heavy elements, have a substantial influence on the electronic structure of lanthanides and especially actinides as well as their compounds and should not be neglected in accurate calculations (see ***Relativistic Theory and Applications***). The discussion of relativistic effects is usually based on a one-particle model, e.g., the comparison of relativistic Dirac–Hartree–Fock and nonrelativistic Hartree–Fock results for one-particle energies and wavefunctions. The so-called direct scalar-relativistic effects tend to stabilize and contract, especially for the s and p shells, whereas the indirect relativistic effects, also called relativistic self-consistent field effects, dominate for the d and f shells and result in a destabilization and expansion (Figure 3). As a consequence the ordering of the low-lying configurations in nonrelativistic and relativistic atomic calculations is often completely different (Figure 4). The differential relativistic effect on the term energies of the low-lying $4f^26s^2$

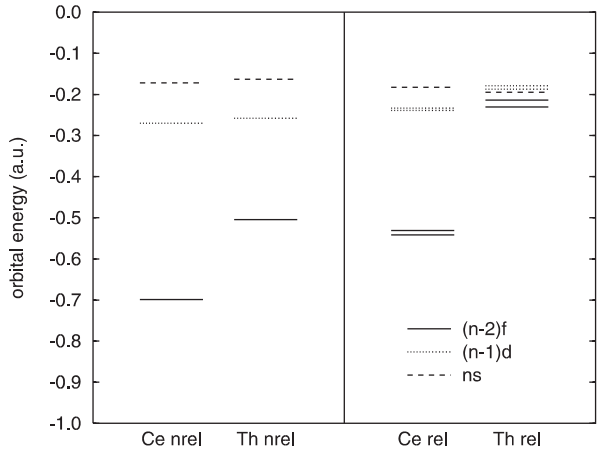

Figure 3 One-particle energies of orbitals and spinors of the $(n-2)f^1(n-1)d^1ns^2$ configuration of Ce ($n = 6$) and Th ($n = 7$) from average-level nonrelativistic (nrel) Hartree–Fock and relativistic (rel) Dirac–Hartree–Fock calculations

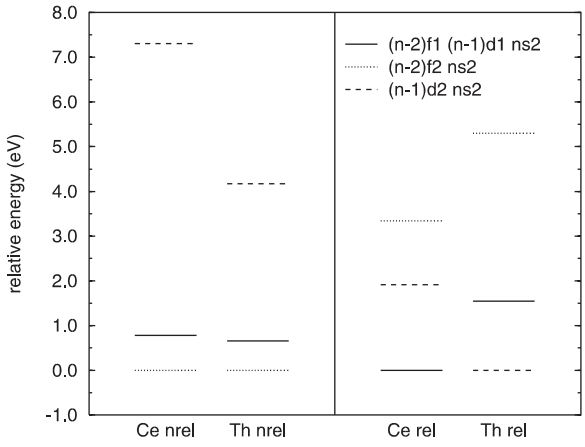

Figure 4 Relative energies of the $(n-2)\mathrm{f}^2 n\mathrm{s}^2$, $(n-2)\mathrm{f}^1(n-1)\mathrm{d}^1 n\mathrm{s}^2$, and $(n-1)\mathrm{d}^2 n\mathrm{s}^2$ configurations of Ce ($n = 6$) and Th ($n = 7$) from average-level nonrelativistic (nrel) Hartree–Fock and relativistic (rel) Dirac–Hartree–Fock calculations

(nonrelativistic ground state) and $4\mathrm{f}^1 5\mathrm{d}^1 6\mathrm{s}^2$ (relativistic ground state) configurations of Ce is 4.13 eV; in the case of the heavier homolog Th the contribution to the energetic separation of the $5\mathrm{f}^2 7\mathrm{s}^2$ (nonrelativistic ground state) and $6\mathrm{d}^2 7\mathrm{s}^2$ (relativistic ground state) configurations is 9.47 eV. These differential relativistic effects are among the largest observed for valence states in the entire periodic table.

Besides the scalar-relativistic effects, spin–orbit coupling has to be taken into account: the fine structure splitting of the one-particle energies of the 4f and 5d shells in the $4\mathrm{f}^1 5\mathrm{d}^1 6\mathrm{s}^2$ configuration of Ce is 2277 cm^{-1} and 1101 cm^{-1}, respectively. The corresponding results for the 5f and 6d shells in the $5\mathrm{f}^1 6\mathrm{d}^1 7\mathrm{s}^2$ configuration of Th are 3683 cm^{-1} and 1765 cm^{-1}. Spin–orbit coupling causes a breaking of the nonrelativistic symmetry; e.g., the nonrelativistic LS coupling scheme has to be replaced by the relativistic jj coupling scheme for atoms in principle. However, experiment shows that in many cases neither pure LS nor jj coupling, but rather an intermediate coupling scheme, has to be applied.[13] This may be achieved in general, starting from either coupling scheme, by the use of multi-configurational wavefunctions. In the case of molecules the wavefunction has to be adapted to the appropriate double-group symmetry. The double group arises as the natural extension of the usual spatial point group, according to which orbitals are usually classified, by also considering the symmetry properties of the spin functions.

The large relativistic effects cause different ground states for the atoms Ce and Th, i.e., $4\mathrm{f}^1 5\mathrm{d}^1 6\mathrm{s}^2\ {}^1G_4$ and $6\mathrm{d}^2 7\mathrm{s}^2\ {}^3F_2$, respectively. However, the substantial increase of relativistic effects when going from the lanthanide to the actinide series also has consequences for related molecules; e.g., the ground states of the monoxides CeO and ThO are $\phi^1_{4\mathrm{f}}\sigma^1_{6\mathrm{s,p}}\ {}^3\Phi_2$ and $\sigma^2_{7\mathrm{s,p}}\ {}^1\Sigma^+$, respectively (for *ab initio* calculations, cf. Refs. 10, 14, 15); for the sandwich compounds cerocene and thorocene, $\mathrm{M(C_8H_8)_2}$ (M = Ce, Th), the $e^1_{2u,4f}e^3_{2u,\pi}\ {}^1\mathrm{A}_{1g}$ and $e^4_{2u,\pi}\ {}^1A_{1g}$ ground states have the same overall symmetry (in D_{8h}), but have to be described by different leading configurations (see below). It should be noted that for the thorium compounds mentioned large f orbital participation in bonding was observed and although the 5f shell is not occupied as such in the ground states, thorium cannot be viewed as a d transition metal as is sometimes suggested. Lanthanides and actinides are in many respects quite similar, especially in a nonrelativistic treatment (Figures 3 and 4). However, quantitative and, as has just been demonstrated, qualitative differences result from the different impacts of relativistic effects in the two rows. Bonds formed by f elements sometimes show a relativistic bond length expansion, in contrast to the more often observed contraction in non-f elements.[5,12]

2.3 Correlation Effects

For a quantitative comparison of results from quantum chemical calculations with experimental data the one-particle picture has to be abandoned and the effects of electron correlation have to be taken into account. Nevertheless, electronic states may in most cases still be classified by the leading configuration in a multi-configurational wavefunction. Electron correlation effects often act opposite to relativistic effects; e.g., for atoms they tend to stabilize the electronic states with a higher f occupation number. A typical example are the $4\mathrm{f}^n 5\mathrm{d}^1 6\mathrm{s}^2 \rightarrow 4\mathrm{f}^{n+1} 6\mathrm{s}^2$ excitation energies of the lanthanide elements displayed in Figure 5. The correlation contributions may be estimated by a comparison of uncorrelated relativistic all-electron Wood–Boring results and experimental data. A similar picture is to be expected for the actinides; however, experimental data are less readily available. Since electron correlation is especially strong when electrons come close to each other, e.g., between electrons occupying orbitals located in the same region of space, it is mandatory for accurate work to include besides the (partially occupied) valence orbitals also a number of (fully occupied) semi-core orbitals in the correlation treatment. In the case of Ce, besides the 4f, 5d, and 6s orbitals (four valence electrons) at least the 5s and 5p semi-core orbitals (eight electrons) have to be considered; if electronic states with different 4f occupation numbers are to be investigated, the 4s, 4p, and 4d core orbitals (18 electrons), i.e., a total of 30 electrons, also have to be correlated. Correlation contributions are of course also important for molecules, especially for the determination of binding energies.

Although several approaches and corresponding program systems for correlated relativistic electronic structure

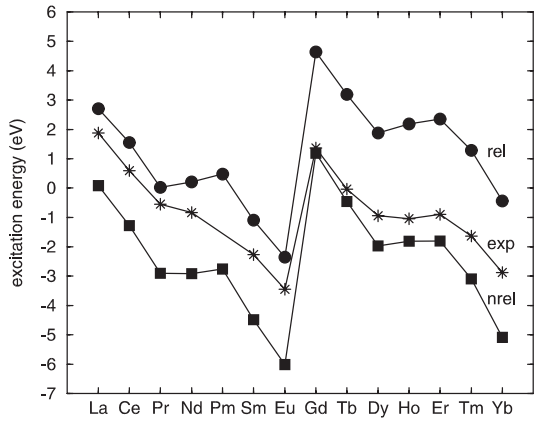

Figure 5 $4\mathrm{f}^n 5\mathrm{d}^1 6\mathrm{s}^2 \rightarrow 4\mathrm{f}^{n+1} 6\mathrm{s}^2$ excitation energies of the lanthanide elements from nonrelativistic Hartree–Fock (nrel) and scalar-relativistic Wood–Boring (rel) calculations in comparison with experimental data (exp)[2]

calculations have been developed, none of them currently appears to be able to cope at a pure *ab initio* level with molecules containing f elements. The main bottleneck is the required large-scale correlation treatment in the presence of a relativistic Hamiltonian including the symmetry-breaking effects of the spin–orbit term.

2.4 Lanthanide and Actinide Contraction

The lanthanide and actinide contraction may be defined as $\Delta_{\mathrm{Ln}} = d(\mathrm{La}) - d(\mathrm{Lu})$ and $\Delta_{\mathrm{An}} = d(\mathrm{Ac}) - d(\mathrm{Lr})$, respectively, were $d(\mathrm{M})$ denotes either a metal–ligand distance in a molecule or a crystal ($d(\mathrm{M}) = R_e(\mathrm{M-X})$) or a radial orbital expectation value ($d(\mathrm{M}) = \langle r \rangle$). For the lanthanide contraction a value of 0.18 Å is obtained from the experimentally determined radii of the eightfold-coordinated ions La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$). Early Dirac–Hartree–Fock one-center expansion calculations on the $^1\Sigma^+$ states of LaH and LuH yield a value of 0.21 Å, about 10% of this value being due to relativistic effects.[16] The corresponding result for the actinide contraction derived from calculations of AcH and LrH is 0.33 Å.[16] The values for the contractions, however, depend strongly on the compounds, as has been demonstrated, e.g., by Wang and Schwarz[17] using relativistic density functional calculations: compounds with rigid bonds, such as LnO (force constant 5 N cm^{-1}) undergo only a small contraction (0.06 Å), whereas those with soft bonds, such as LnH (force constant 1 N cm^{-1}), show a large contraction (0.19 Å). LnF (force constant 3 N cm^{-1}) has intermediate values. The lanthanide contraction may also be explained by a larger 4f orbital participation in bonding for the lanthanum compound in all cases, showing only a small contraction.[2] A new study by Küchle et al.[18] including relativistic as well as electron correlation effects finds smaller contractions for the actinides (Table 1). It is notable that the actinide contraction of the monoxides is entirely a relativistic effect, i.e., at the nonrelativistic level a slight actinide expansion is obtained.

The effects of the lanthanide/actinide contraction on the post-lanthanide/actinide main group elements have been investigated by Bagus et al. and Seth et al., respectively.[19] The latter show that the interpretation of the observed total effect in terms of shell-structure and relativistic effects is dependent on the order in which these contributions are taken into account, i.e., a nonadditive behavior is observed (Figure 6).

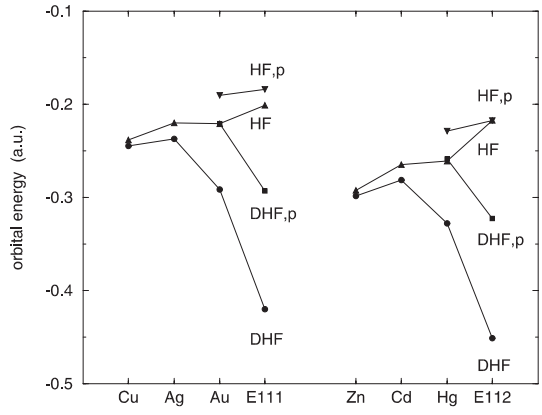

Figure 6 Orbital energies of valence s orbitals for group 11 and 12 metals. DHF and HF denote relativistic Dirac–Hartree–Fock and nonrelativistic Hartree–Fock results, respectively; p stands for a pseudoatom calculation, in which the 4f (Au, Hg) and 5f (E111, E112) shells were removed and the nuclear charge was decreased by 14 units[19]

3 METHODS

A brief overview of the methods applied so far for the study of f element systems[2,3,5] is provided in the following sections.

3.1 All-electron Methods

3.1.1 Dirac–Hartree–Fock Approach and Beyond

The most rigorous way for electronic structure calculations to be carried out is by means of correlated fully relativistic calculations based on the Dirac–Coulomb Hamiltonian, if possible including also higher-order corrections to the electron–electron interaction such as the Gaunt or Breit terms. The one-center expansion Dirac–Hartree–Fock technique was used in early studies of lanthanide and actinide hydrides and allowed insight into relativistic and shell structure effects.[16] After the problems due to the so-called finite basis set disease were overcome the algebraic Dirac–Hartree–Fock approach replaced the finite-difference-based one-center expansions. However, owing to the enormous computational effort only a few calculations with a modest basis set quality and no or very limited correlation treatments have been carried out for molecular f element systems so far.[6,20–22] Although the *Hamiltonian* used in these calculations is certainly quite accurate, the wavefunction is usually too poor to yield results in close agreement with experimental values. Further software development appears to be necessary before the approach can be applied routinely to f element systems.

3.1.2 Density Functional Approaches

A simpler treatment of the electron–electron interaction terms in the Hamiltonian is achieved by density functional

Table 1 Bond Lengths R_e (Å) of the Diatomics MX (M = La, Lu, Ac, Lr; X = H, O, F) and Resulting Values of the Lanthanide and Actinide Contraction ΔR_e (Å) from Relativistic (rel) and Nonrelativistic (nrel) All-electron Self-consistent Field Calculations[18]

		La	Lu	ΔR_e	Ac	Lr	ΔR_e
rel	H	2.053	1.956	0.097	2.187	2.030	0.157
nrel	H	2.042	1.933	0.109	2.104	1.986	0.118
rel	O	1.812	1.786	0.026	1.919	1.848	0.071
nrel	O	1.767	1.777	−0.010	1.803	1.830	−0.027
rel	F	2.050	1.942	0.108	2.139	2.015	0.124
nrel	F	2.040	1.948	0.092	2.095	2.029	0.066

methods, e.g., at the four-component fully relativistic[23] or the two- and one-component quasi-relativistic[24] level (see ***Density Functional Theory, HF and the Self-consistent Field*** and ***Density Functional Theory Applications to Transition Metal Problems***). Although these methods cannot provide detailed information on all electronic states, their performance for ground state properties of lanthanide and actinide systems is rather good when modern functionals going beyond the local density approximation are used.[17,25] Such modern methods are implemented in the Amsterdam or Beijing density functional codes (ADF, BDF) and indeed compete with pure *ab initio* approaches for many cases of chemical interest.

3.2 Valence-only Methods

3.2.1 Pseudopotential Approaches

Some simplifications, with only little loss of accuracy, are possible by restricting the explicitly treated electrons to the valence electron system. This is achieved in the so-called pseudopotential, effective core potential, or model potential approaches, which include the major relativistic effects only implicitly via parametrization of a valence model Hamiltonian in formally nonrelativistic calculations (see ***Relativistic Effective Core Potential Techniques for Molecules containing Very Heavy Atoms***). The extension of the actual valence shell over three different main quantum numbers affords the use of a small core for accurate calculations. The most complete set of such small-core pseudopotentials for lanthanides and actinides, for both a nonrelativistic and a relativistic parametrization including spin–orbit coupling, is available from the Stuttgart group.[15] In the case of the lanthanides it is also possible to include the 4f shell into the pseudopotential core and to perform calculations within the superconfiguration model.[26] Relativistically parametrized effective core potentials for lanthanides and actinides using a larger core are available from various other groups.[27,28] Care has to be taken when selecting a medium-core or large-core pseudopotential or effective core potential, since frozen-core errors may dramatically affect energy differences between different states: in the case of Ce the errors for medium-core (12 valence electrons) and large-core (4 valence electrons) pseudopotentials amount to several tenths of an electronvolt or even several electronvolts, respectively, when the 4f occupation number is changed.[2]

3.2.2 Semiempirical Approaches

The intermediate neglect of differential overlap scheme developed by Rösch, Zerner, and co-workers[29,30] for the ground state (INDO/0) and the spectroscopy of excited states (INDO/S) allows an even larger reduction of the computational effort. The method appears to give rather accurate results for the lanthanide series; however, owing to missing experimental data for the parametrization the performance for the actinide series appears to be less satisfactory.

The semiempirical relativistically parametrized extended Hückel scheme developed by Pyykkö and Lohr[31] was one of the first methods at hand to investigate the electronic structure of polyatomic lanthanide and actinide molecules, albeit only in a rather approximate way. Since this is an effective one-particle model, it is possible to discuss quantities such as orbital energies and corresponding shapes of orbitals for configurations, but not the individual electronic states.

Information on individual electronic states for fixed geometries can be obtained from ligand field theory.[9]

4 SELECTED RESULTS

In the following sections a small selection of results from recent studies on lanthanide and actinide systems will be summarized.

4.1 Atoms

Computational methods which do not give good results for atomic calculations, i.e., for excitation energies, ionization potentials, and electron affinities, should be viewed with great care when applied to molecules. Test calculations on atoms should be performed in addition to molecular calculations in order to calibrate the treatment of relativistic and electron correlation effects.

4.1.1 Tables

Experimental data for the electronic spectra of lanthanides and actinides are available[13] and may serve to parametrize semiempirical approaches or to calibrate *ab initio* calculations. Total energies, orbital energies, radial orbital expectation values, and maxima from relativistic Dirac–Hartree–Fock as well as nonrelativistic Hartree–Fock calculations have been summarized by Desclaux[32] and form a useful starting point for (qualitative) discussions of the electronic structure of lanthanide and actinide compounds.

4.1.2 Individual Atoms

The most accurate treatment currently available for lanthanide and actinide atoms is a relativistic Fock-space coupled-cluster approach based on Dirac–Hartree–Fock solutions for the Dirac–Coulomb–Breit Hamiltonian. Huge one-particle basis sets up to *h* or *i* functions have to be applied to obtain the desired high accuracy. Calculations of this kind are only possible when the spherical symmetry of the atom is taken into account. The electronic states arising from an f^2 configuration in Pr^{3+} and U^{4+} are calculated with average errors of 313 cm^{-1} and 114 cm^{-1}, respectively,[33] when compared to experimental data.[13] The Breit interaction is found to contribute up to a few hundred wavenumbers. The average errors increase when different configurations are considered, e.g., to 595 cm^{-1} for Yb $6s^2$, $6s^16p^1$, and $6s^15d^1$.[33] It is to be expected that the quality of the results will be significantly worse when energy differences between electronic states arising from configurations with different f occupation are considered. Their accurate theoretical determination has rarely been dealt with and appears to be a real challenge for *ab initio* methods. It is noteworthy that because of relativistic effects Lr probably has a $7s^27p^1\ ^2P_{1/2}$ ground state, whereas the ground state of Lu is $6s^25d^1\ ^2D_{3/2}$.[33]

4.2 Diatomic Molecules

The theoretical study of diatomic molecules is interesting in comparison to results from experimental spectroscopic studies,

which can be carried out with high accuracy, but are often difficult to analyze. Useful theoretical information can also be obtained for the contribution of the valence f orbitals to chemical bonding or the causes and the magnitude of the lanthanide and actinide contraction.

4.2.1 Hydrides, Oxides, and Fluorides

The monoxides and monofluorides are experimentally (see Refs 34, 35 and references cited therein) and theoretically[17,26,30,36–38] the most extensively investigated diatomics of the lanthanides. The ground state superconfigurations of the monoxides are $4f^n\sigma^1$, except for EuO and YbO where $4f^{n+1}$ superconfigurations are expected owing to the stability of a half-filled or filled 4f shell.[9] The dissociation energies of the lanthanide monoxides show a characteristic sawtooth behavior (Figure 7). Within a superconfiguration the dissociation energies behave almost linearly with respect to the nuclear charge of the metal; the nonmonotonic trend results from the atomic $4f^{n+1}6s^2 \rightarrow 4f^n5d^16s^2$ excitation energies linking the two superconfigurations at large internuclear distance (Figure 5). The ground state assignment for YbO ($4f^{14}$ or $4f^{13}\sigma^1$ superconfiguration) is still under debate.[35,36] The theoretical work illustrates the problems of *ab initio* calculations in predicting accurately energy differences between states belonging to different 4f occupations when both electron correlation effects and relativistic effects including spin–orbit coupling have to be taken into account. The spectroscopic constants of low-lying electronic states of EuO, GdO, YbH, and YbF have been studied by *ab initio* pseudopotential calculations.[37] INDO/S results for excitation energies are available for LnO (Ln = La, Ce, Pr, Gd, Tm, Lu).[30] Density functional theory has been used to investigate the ground state properties of lanthanide monohydrides, monoxides, and monofluorides as well as the magnitude and origin of the lanthanide contraction.[17]

A study of the monohydrides, monoxides, and monofluorides of lanthanides and actinides using *ab initio* all-electron and pseudopotential techniques is also available.[18] The spectroscopic constants of low-lying electronic states of ThO[14,15] as well as UH and UF[39] have been investigated using the *ab initio* pseudopotential approach. No low-lying electronic states with occupied 5f orbitals have been found in ThO, but a significant contribution of the 5f orbitals to the *chemical bond* has been detected. The 5f orbitals as well as the 6d orbitals in UH and UF retain an atomic-like character and are only slightly influenced by chemical bonding. The electronic structure is largely determined by the highly polarizable U 7s orbital and the low U ionization potential. These findings explain the similarity of the spectroscopic constants of the alkaline earth systems SrH and SrF to those of UH and UF, respectively.

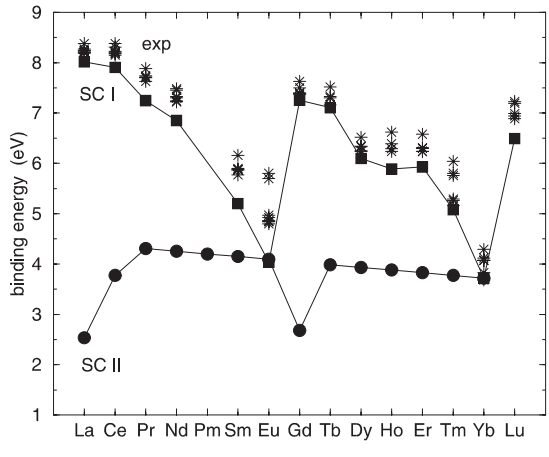

Figure 7 Dissociation energies of the lanthanide monoxides from quasi-relativistic pseudopotential calculations for the $4f^n\sigma^1$ (SC I) and $4f^{n+1}$ (SC II) superconfigurations in comparison to experimental data (exp)[2]

4.2.2 Dimers

The lanthanide dimers have only been treated with pseudopotentials attributing the 4f shell to the core;[38] e.g., the $4f^7\ 4f'\ 6s\sigma_g^2\ 6s\sigma_u^1\ 5d\sigma_g^1\ 5d\pi_u^2$ superconfiguration for the $^{19}\Sigma$ ground state of Gd_2 was predicted.[8] The explicit treatment of two partially occupied f shells appears to be a considerable challenge for *ab initio* approaches. Such an *ab initio* study using relativistic pseudopotentials was performed by Pepper and Bursten[40] on the uranium dimer U_2, which appears to have a $^{13}\Delta_g$ ground state with 12 unpaired electrons, corresponding to a leading $5f^3\ 5f'^3\ 7s\ \sigma_g^1\ 7s\ \sigma_u^1\ 6d\ \sigma_g^1\ 6d\ \pi_u^2\ 6d\ \delta_g^1$ superconfiguration.

4.3 Polyatomic Molecules

Several classes of polyatomic lanthanide and actinide systems have attracted the attention of theoreticians in the past. Typical issues addressed in these studies were the geometry of the uranyl cation UO_2^{2+} and the isoelectronic thorium dioxide ThO_2, the planar and/or pyramidal geometry of the lanthanide trihalides, the low-lying electronic states of uranium hexafluoride UF_6, the electronic ground state configuration of cerocene, $Ce(C_8H_8)_2$, the metal–ring bonding and the electronic states in uranocene, $U(C_8H_8)_2$, or the properties of endohedral fullerenes with lanthanides and actinides.

4.3.1 Cerium and Thorium Dioxide, Uranyl Cation

The question why the uranyl cation UO_2^{2+} has a linear geometry whereas the isoelectronic thorium dioxide ThO_2 ($\theta = 122 \pm 2^\circ$) is bent has been investigated by several workers, among them Tatsumi and Hoffmann, Wadt, DeKock et al., and Pyykkö et al.,[41] but still does not seem to be fully settled.[3] Tatsumi and Hoffmann explained the linearity of UO_2^{2+} through an activation of the 5f orbitals by the chemically accessible semi-core 6p shell. Wadt attributed a smaller importance to the role of the 6p shell and explained the difference in geometry in terms of the orbital energy ordering of the empty 5f and 6d orbitals, which are responsible for the back-bonding in the completely ionic model systems $Th^{4+}(O^{2-})_2$ and $U^{6+}(O^{2-})_2$. Whereas for thorium the 6d orbitals are slightly lower in energy than the 5f orbitals, the 5f orbitals of uranium are found significantly below the 6d orbitals. It is therefore expected that back-bonding occurs mainly to 6d in ThO_2 and to 5f in UO_2^{2+}, explaining the bent and linear geometries, respectively. It was pointed out by Pyykkö et al. that, in addition to the role of the 6p shell and the 5f and 6d orbital energies, also the bond length has to be taken into account: as is clear from Figure 2,

for large bond lengths only the 6d orbitals can contribute and lead to a bent molecule, whereas for a decreasing bond distance the linearizing effect of the 5f orbitals will get stronger. The relativistic bond lengthening observed in UO_2^{2+}, in contrast to the usually found relativistic bond length contraction, has been explained by Allen et al.[42] to be mainly due to the formation of a hole in the 6p orbital and the corresponding loss of mass–velocity stabilization for decreasing bond distances. It was pointed out by Schwarz, however, that different schemes exist to explain relativistic bond length changes.[12] From all studies on UO_2^{2+} and related compounds it became apparent that the 6p shell cannot be considered as a part of the core for quantitative investigations, although this is usually done when qualitative chemical arguments are used.

Cerium dioxide, CeO_2 ($\theta = 146 \pm 2^\circ$), is the lanthanide homolog of ThO_2 and is also found to be bent. Density functional as well as *ab initio* pseudopotential calculations have been performed by DeKock et al. and Heinemann et al.[43] Here, 6s5d hybridization appears to be the driving force for bending the molecule, whereas 6s6p and 6s4f hybridization favor a linear geometry. Although the cerium 4f orbitals are energetically much lower than the 5d orbitals (Figure 3) owing to their core-like character (Figure 1), they seem to have a weaker interaction with the ligands. Interestingly, CeO_2 is found to be linear in nonrelativistic calculations, whereas it is bent in relativistic calculations, in agreement with the experimental findings.

4.3.2 Lanthanide Trihalides

The lanthanide trihalides have been thoroughly investigated with a variety of methods ranging from semiempirical extended Hückel-type calculations to correlated *ab initio* pseudopotential studies.[23,26,29,44–48] The question whether a planar (D_{3h}) or pyramidal (C_{3v}) structure is more stable is still not settled since the energy differences involved are rather small. From pseudopotential studies including[44] and excluding[26] the 4f orbitals from the valence space one may conclude that at least for the bond lengths of these molecules the 4f orbital participation in bonding is very small.

4.3.3 Uranium Hexafluoride

Uranium hexafluoride UF_6, which plays a key role in the nuclear fuel cycle and is also important for uranium-using lasers, is one of the most frequently studied actinide systems. One-particle properties and chemical bonding have been investigated with density-functional-based approaches, e.g., relativistic one-component Hartree–Fock–Slater[24] and four-component Dirac–Fock–Slater[49] calculations. Single-point Dirac–Hartree–Fock calculations for UF_6 as well as ThF_4 have been performed and relativistic effects on the SCF binding energy have been determined.[20] The systems UF_6^+ and UF_6^- as well as the chemical bonding in the UF_6 ground state have been discussed by Hay et al.[50] on the basis of *ab initio* pseudopotential calculations. The relativistic pseudopotential study of Hay[50] on UF_6 is probably the first quantum chemical investigation of a polyatomic actinide compound where electron correlation effects and also relativistic effects including spin–orbit coupling have been taken into account. A simple method to include spin–orbit effects in correlated calculations has been used; e.g., the Hamiltonian matrix including terms arising from an effective one-particle spin–orbit operator was set up and diagonalized in the basis of correlated many-electron states derived without spin–orbit interaction. Hay gives a detailed analysis of the electronic states with and without spin–orbit interaction up to term energies of 10 eV.

4.3.4 Cerocene and Thorocene

Cerocene, $Ce(C_8H_8)_2$ (D_{8h} symmetry), was long believed to be a cerium(IV) complex, i.e., a Ce^{4+} closed shell ion η_8-complexed by two essentially planar aromatic $C_8H_8^{2-}$ rings.[51] Theoretical considerations and subsequent *ab initio* calculations,[52] however, led to a different picture: a Ce^{3+} ion with a $4f^1$ subconfiguration is complexed by two $C_8H_8^{1.5-}$ rings, where the hole is delocalized symmetrically over both rings. Owing to configuration interaction of this $4f^1\pi^3$ superconfiguration with the higher-lying $4f^0\pi^4$ configuration the $^1A_{1g}$ state falls below the lowest triplet state $^3E_{2g}$. Cerocene thus has to be viewed as a cerium(III) complex. This purely theoretically derived picture has recently been confirmed by experiment.[53] In contrast to cerocene the heavier homolog thorocene, $Th(C_8H_8)_2$, has the expected $5f^0\pi^{41}A_{1g}$ ground state,[52] most likely owing to the strong relativistic destabilization of the Th 5f orbitals (Figure 3).

4.3.5 Uranocene

The synthesis of uranocene, $U(C_8H_8)_2$ (D_{8h} symmetry), in 1968[54] brought about considerable interest among theoreticians in organoactinide sandwich compounds.[31,51,55,56] It is notable that the stability of uranocene was predicted five years before the actual synthesis and was assumed to be due to a strong bonding interaction between the U 5f and the ring π orbitals,[57] in close analogy to ferrocene, $Fe(C_5H_5)_2$. The compound is a uranium(IV) complex, i.e., a U^{4+} ion with a $5f^2$ subconfiguration η_8-complexed by two essentially planar aromatic $C_8H_8^{2-}$ rings. The e_{2u} HOMOs of the η_8-coordinated $C_8H_8^{2-}$ rings form group orbitals of e_{2u} and e_{2g} symmetry, which yield a stabilizing interaction with the U 5f and 6d orbitals of the same symmetry, respectively. Although originally the 5f bonding was assumed to be responsible for the stability of uranocene,[54] several molecular orbital studies revealed that the 6d bonding is of equal or even greater importance.[51,55,56] The E_{3g} ground state (D_{8h}^* double-group notation, formally corresponding to U^{4+} $5f^2{}^3H_4|M_J| = 3$) and the low-lying excited states have been studied with pseudopotential spin–orbit configuration interaction calculations by Chang and Pitzer.[56] The magnetic moment was predicted to be $2.30\mu_B$, in excellent agreement with the experimental value of $2.36\mu_B$.[58]

4.3.6 Endohedral Fullerenes

In the last few years several endohedral fullerenes, $M_m@C_n$, i.e., closed carbon cages C_n ($n = 28, 60, 80, 82$) with encapsulated metal atoms M or metal dimers M_2, have been investigated by pseudopotential[58,59] and density functional methods.[60–62] Scalar-relativistic density functional calculations by Rösch et al.[61] on $Ce@C_{28}$ yield a tetravalent cerium ion in the center of the cage. The C_{28} cage appears to

be sufficiently small that the 4f orbitals contribute significantly to covalent metal–cage bonding. The corresponding uranium complex $U@C_{28}$ was not found to have a tetravalent uranium central atom with a $5f^2$ configuration in *ab initio* pseudopotential spin–orbit configuration interaction calculations by Chang et al.[58] The lowest electronic state is rather $5f(a_1)^1\ \pi^*(e)^1\ E(^1E)$ in T_d^* (T_d) symmetry and is 0.5 eV below the lowest state with a U $5f^2$ subconfiguration. It is yet unclear if a better account for electron correlation effects would give the expected tetravalent uranium ground state. The ground and excited states of several $M@C_{60}$ and $M@C_{60}^+$ systems, including those with La, Eu, and U, have been investigated by Chang et al.[59] at the pseudopotential SCF level.

4.4 Solids

Quantum chemical schemes can also be used to treat local properties of solids, provided a reasonable orbital localization and embedding of the subsystem under study can be achieved. An example are impurities in crystals, e.g., a Eu^{3+} impurity in Ba_2GdNbO_6[22] or $Ce^{n+}(n = 2, 3, 4)$ in MF_2 (M = Ca, Sr, Ba),[21] for which studies at the all-electron Dirac–Hartree–Fock level are available.

5 CLOSING REMARKS

Quantum chemistry for lanthanides and actinides is an active area of current research. The applicable methods range from relativistically parametrized semiempirical extended Hückel-type approaches to fully relativistic all-electron Dirac–Hartree–Fock calculations with a subsequent correlation treatment. It is emphasized that electron correlation effects and relativistic effects including spin–orbit coupling have to be treated simultaneously in order to avoid errors arising from the nonadditivity of these effects. Considerable progress is expected, especially on the *ab initio* side of quantum chemical applications, for small lanthanide and actinide systems during the next few years.

6 RELATED ARTICLES

Applications to Transition Metals; Configuration Interaction; Density Functional Theory, HF and the Self-consistent Field; Density Functional Theory Applications to Transition Metal Problems; Metal Complexes; Relativistic Effective Core Potential Techniques for Molecules containing Very Heavy Atoms; Relativistic Effects of the Superheavy Elements; Relativistic Theory and Applications; Transition Metal Chemistry.

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