Computational studies of new heavy-element species.

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Preface

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Helsinki, September 2001

Michal Straka
List of original publications

This thesis is based on the following publications. They are referred to by the corresponding Roman numerals.


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## Abbreviations

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<th>Description</th>
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<tr>
<td>B3LYP</td>
<td>Becke’s Three Parameter Hybrid Functional (B3) with the Lee-Yang-Parr correlation functional (LYP)</td>
</tr>
<tr>
<td>BO</td>
<td>Born-Oppenheimer approximation</td>
</tr>
<tr>
<td>BSSE</td>
<td>Basis set superposition error</td>
</tr>
<tr>
<td>CASSCF</td>
<td>Complete active space self consistent field</td>
</tr>
<tr>
<td>CASPT2</td>
<td>Complete active space perturbation theory through 2nd order</td>
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<tr>
<td>CC</td>
<td>Coupled cluster</td>
</tr>
<tr>
<td>CCSD</td>
<td>Coupled cluster with single and double excitations</td>
</tr>
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<td>CCSD(T)</td>
<td>CCSD augmented with perturbatively calculated triples</td>
</tr>
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<td>4-CCSD(T)</td>
<td>Four-component CCSD(T)</td>
</tr>
<tr>
<td>CI</td>
<td>Configuration interaction</td>
</tr>
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<td>CISD</td>
<td>CI with single and double excitations</td>
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<tr>
<td>Cp</td>
<td>Cyclopentadiene</td>
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<td>DC</td>
<td>Dirac-Coulomb Hamiltonian</td>
</tr>
<tr>
<td>DCB</td>
<td>Dirac-Coulomb-Breit Hamiltonian</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>ECG</td>
<td>Explicitly correlated Gaussian</td>
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<tr>
<td>ECP</td>
<td>Effective core potential</td>
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<tr>
<td>HF</td>
<td>Hartree-Fock</td>
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<tr>
<td>KS</td>
<td>Kohn-Sham</td>
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<tr>
<td>MO</td>
<td>Molecular orbital</td>
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<td>MP2</td>
<td>Møller-Plesset perturbation theory through second order</td>
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<td>MR-CI</td>
<td>Multireference CI</td>
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<td>Non-relativistic</td>
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<td>Potential energy surface</td>
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<td>QCI</td>
<td>Quadratic CI</td>
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<tr>
<td>R</td>
<td>Relativistic</td>
</tr>
<tr>
<td>R12</td>
<td>$r_{1,2}$, interelectronic wavefunction</td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
</tr>
<tr>
<td>SD</td>
<td>Slater determinant</td>
</tr>
<tr>
<td>SE</td>
<td>Schrödinger equation</td>
</tr>
<tr>
<td>SO</td>
<td>Spin-orbit</td>
</tr>
<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
<tr>
<td>VE</td>
<td>Valence electron</td>
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<tr>
<td>ZPE</td>
<td>Zero-Point Energy</td>
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</table>
1 Introduction

In the last few decades, computational tools based on quantum mechanics
have spread virtually over all sciences, from physics and astronomy to chem-
istry and even to fields like biology, pharmaceutical sciences, and medicine.

There are several good reasons for doing theoretical calculations: Using
the known principles of quantum mechanics and numerical mathematics
one can produce both new knowledge and new understanding in the fields
mentioned. This is particularly valuable when the experiment is expensive,
difficult, or dangerous. One can also predict new chemical species, drugs,
materials. Also their properties, such as the interaction mechanisms with
their surroundings, can be studied.

The relativistic quantum chemistry, necessary for the heavier elements
already at the qualitative level, has developed enormously since the mid-
1970ies. The particular tools used in the present work are the pseudopoten-
tial ab initio methods. Granted the existence of these well-calibrated
methods, all elements of the Periodic Table are roughly equally difficult.
Small molecules combining any elements can be treated, including both rel-
ativity and electron correlation. Quantum electrodynamics, "the last train
from physics to chemistry", will make only a small change, currently at the
limit of the observable.

A particular problem where both relativistic and electron correlation ef-
facts play a role is the metallophilic attraction, which is essentially a strong
van der Waals attraction. We here study it for previously less-known cases
like In(I), Tl(I) and Hg(II).

We also study the possible existence of new actinide compounds, both as
an immediate extension of already known actinide oxyfluoride systems, and
in one radically new proposed case of uranium(XII). Furthermore, unknown
properties of certain molecules, such as the thermochromatographically ob-
served NpO₂F, are now computationally determined.

The more detailed motivations of our work were:

1. To support the experimental evidence for In(I)-In(I) and Tl(I)-Tl(I)
   metallophilic attraction by theoretical calculations. To study the role
   of electronic correlation and relativistic effects in such calculations.

2. To study the Hg(II)-Hg(II) metallophilic attraction, its nature and
   strength. To calculate a theoretical van der Waals radius of Hg(II)
since the values found in the literature differ extensively.

3. There are a few F₈d⁰ actinide oxyfluoride species known. Based on
   the isoelectronic principle we predict a whole family of F₈d⁰ actinide
oxyfluoride species, their gas-state structures and vibrational spectra.

4. Experimentalists have so far failed with attempts to prepare Pu(VIII) compounds. Do they exist, and how endothermic would they be?

5. The uranium atom has a very diffuse semicore 6p shell. Could one oxidize the 6p electrons in a chemical reaction? This leads ultimately to the idea of a UO₆ molecule, which would be the first U(XII) species and the first species with an atom in a formal oxidation state higher than VIII.

2 Methodology

There is no universal black-box method to solve an arbitrary chemical problem with required accuracy. Approximations have to be made and the optimal theoretical tool has to be chosen for particular problems. A large number of quantum chemical methods from very accurate to very rough approximations are available nowadays. By proper reasoning and calibration many chemical problems can be solved with desired accuracy. Usually the rule “more accurate = more expensive” applies; therefore the computational cost and accuracy of approximation have to be balanced. The following section is a brief overview of the methods used in this thesis; the reader is referred to textbooks¹⁻⁵ for further details.

2.1 Ab initio methods

In theoretical ab initio methods, we start from the time-independent Schrödinger equation (SE)

\[ H \Psi = E \Psi, \]  

where \( \Psi \) is the wavefunction describing the system and \( H \) is the Hamiltonian of the system. The Hamiltonian (in non-relativistic approximation; for relativistic Hamiltonian see below) can be written in atomic units (a.u.) as

\[ H = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_i \sum_A \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}}. \]  

Two fundamental approximations are introduced in order to solve the SE. In the Born-Oppenheimer approximation (BO) we formally decouple the movement of nuclei and electrons, based on the fact that nuclei, being much heavier, move much slower than electrons. We keep the nuclei fixed and neglect
their kinetic energy. Then the nuclear repulsion will be constant and the electronic wavefunction will depend on nuclear coordinates only parametrically. Once the electronic problem is solved, we can solve (with similar assumption) the motion of nuclei by replacing the electronic coordinates with its values averaged over the electronic wavefunction. An exact solution of the SE in BO approximation is known only for one-electron systems. The Schrödinger equation for \( N \) electrons is a system of \( 3N \) differential equations coupled by the electron repulsion term, \( r_{1,2} \). In order to solve this system we approximate the wavefunction by a product of independent one-electron functions. This can be referred to as the one particle approximation. The introduced error can be treated by correlation methods.

Recently, the \( r_{1,2} \) (R12) and Explicitly correlated Gaussian (ECG) methods were introduced.\(^6\) In these methods, the wavefunction is a product of two (in R12) - or more (in ECG) - electron functions; the \( r_{1,2} \) interaction is included in the wavefunction. These methods are in stage of development and they are not ready for routine use yet.

### 2.1.1 Hartree-Fock approximation

In the Hartree-Fock method (HF) we approximate the electronic wavefunction by the Slater determinant (SD), which is an antisymmetrized product of one-electron functions, the spin orbitals

\[
\Psi_0 = SD = \left| \psi_1 \psi_2 ... \psi_n \right>.
\]  

(3)

Using the variational principle we optimize a trial SD in order to minimize the ground state energy of system \( E_0 \) given as

\[
E_0 = \frac{\langle \Psi_0 | H | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}.
\]  

(4)

This procedure leads to the set of one-electron equations, the Hartree-Fock equations

\[
f_1 \psi_1(1) = \epsilon_1 \psi_1(1)
\]  

(5)

\[
f_1 \psi_i(1) = \left[ -\frac{1}{2} \nabla_i^2 - \frac{Z_A}{r_{1i}} + \sum_j (J_{ij} - K_{ij}) \right] \psi_i(1)
\]  

(6)

\[
J_{j}(1) \psi_i(1) = \int \left[ \psi_j^*(2) \frac{1}{r_{1j}} \psi_j(2) dx_2 \right] \psi_i(1)
\]  

(7)

\[
K_{j}(1) \psi_i(1) = \int \left[ \psi_j^*(2) \frac{1}{r_{1j}} \psi_j(2) dx_2 \right] \psi_j(1).
\]  

(8)
Here \( f_1 \) is the one-electron Fock operator, \( J_i \) is the Coulomb operator, and \( K_j \) is the exchange operator. The \( \epsilon_i \) is the orbital energy of orbital \( i \). The HF equations are non-linear and can be solved iteratively by the self-consistent field method (SCF). The solution of the HF equations provides orbitals, orbital energies, and the ground state energy of the system. The 'exact' (numerical) HF solution is known only for atoms and diatomic molecules.\(^7\) In practical calculations we expand the spin orbitals as linear combinations of basis set functions. Basis sets furthermore approximate the HF wavefunction. The basis set error can be estimated by extrapolating the results obtained from basis sets of increasing size to infinity.

The limitation of HF approximation comes from the fact, that we substitute the wavefunction by the product of independent one-electron functions. From a physical point of view, the HF does not treat correctly situations where two electrons are close to each other. The missing interaction is referred to as the dynamic correlation. Furthermore, multireference systems (systems in mixed states) cannot be described by a single Slater determinant, as in HF, but rather by a linear combination of Slater determinants. This is referred to as the static correlation. The difference between the HF energy and the exact non-relativistic energy of a given system is called the correlation energy.

### 2.1.2 Configuration interaction

The Configuration interaction (CI) is conceptually the simplest method for calculating the correlation energy. In CI the HF wavefunction is expanded to linear combination of \( N \)-electron excited Slater determinants. This is called a CI expansion

\[
\Psi = c_0 \Phi_0 + \sum_{ra} c_r^a \Phi_r^a + \sum_{a<b<r<s} c_{rs}^{ab} \Phi_{rs}^{ab} + \ldots
\]  

(9)

Here the \( \Phi_{rs}^{ab} \) are \( n \)-tuple excited determinants, the coefficients \( c \) represent the weight coefficients. In CI we variationally minimize the energy given as in Eq. 4 in a CI expansion basis.

The Full CI includes all possible excitations. In a given basis set it is exact. It is computationally expensive and is used only for very small systems and benchmarking. Full CI method is size extensive. A method is said to be size extensive if it treats correlation energy with the same accuracy regardless of the system size. In the CISD (CI with Singles and Doubles) we include only single and double excitations into the wavefunction. The CISD is relatively cheap but it is not size-extensive and it has to be empirically corrected by the so-called Davidson correction for quadruples.\(^8\) The Quadratic CI (QCI) method was designed to be size extensive.
2.1.3 Perturbation theory.

Perturbation theory (PT) is a very general method used in many problems of quantum theory. In PT we formally split the exact Hamiltonian of the problem into

$$H = H_0 + \lambda V,$$  \hfill (10)

where $H_0$ is the zero-order or unperturbed Hamiltonian, $V$ is the perturbation, and $\lambda$ is a scaling factor. Then we can write the SE as

$$H \Psi_i = (H_0 + \lambda V) \Psi_i = E \Psi_i$$  \hfill (11)

Provided that we know the eigenvalues and eigenfunctions of $H_0$ and that $V$ is "weak", we can expand the energy $E$ and the wavefunction $\Psi_i$ in a Taylor series

$$E = E_i^0 + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \lambda^3 E_i^{(3)} + \cdots$$  \hfill (12)

$$\Psi_i = \Phi_i^{(0)} + \lambda \Phi_i^{(1)} + \lambda^2 \Phi_i^{(2)} + \lambda^3 \Phi_i^{(3)} + \cdots.$$  \hfill (13)

Inserting the energy and wavefunction expansion into Eq. 11 and comparing the terms with the same powers of $\lambda$, we obtain a series of equations for different order corrections to the wavefunction and energy. Perturbation theory is size extensive through all orders.

In *Møller-Plesset perturbation theory*, the $H_0$ is given as the sum of one-electron Fock operators. An example is the Møller-Plesset perturbation theory through second order (MP2) often used in quantum chemistry. The MP2 correction to the HF ground state energy of a molecule is

$$E_0^{(2)} = \frac{1}{4} \sum_{abrs} \frac{\left| \langle ab \parallel rs \rangle \right|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}.$$  \hfill (14)

Here $a$, $b$ and $r$, $s$ run over occupied and unoccupied HF orbitals, respectively. The $\epsilon$ quantities are the HF orbital energies. MP2 is the simplest well-established approximation to treat the correlation energy. It may be used in applications, where a single-determinant description works and the dynamic correlation is moderately important. MP2 fails for degenerate and multireference systems. The higher-order corrections are computationally demanding and do not give systematic accuracy; MP4 is sometimes used.

2.1.4 Coupled cluster theory

In the Coupled cluster (CC) theory we expand the wavefunction $\Psi_0$ in the *cluster expansion*:

$$\Psi_0 = (e^T) \Psi_0.$$  \hfill (15)
Here $\Phi_0$ is an unperturbed (usually Hartree-Fock) wavefunction and $T$ is the excitation operator given as sum of single, double... n-tuple excitation operators

$$T = T_1 + T_2 + T_3....$$

(16)

The $T$ is usually approximated by the first few members, as e.g. in the Coupled cluster with singles and doubles (CCSD), where $T = T_1 + T_2$. Further approximations can be made after expansion of $e^T$; a number of different CC approximations has been derived. From them the CCSD and CCSD(T) (CCSD augmented with perturbatively calculated triples) are the most well-established. They are computationally very demanding and concomitantly very accurate single-reference methods. Close to the minimum geometry, they can partially "heal" the lack of static correlation. The $T1$ diagnostic enables justification of using CC for particular problem. It can point to possible multireference problems in the system. The CC methods are size extensive.

2.1.5 Multireference methods

Molecules with low-lying excited states or near degeneracies, cannot be described correctly by a single reference state (Slater determinant). Such systems exist in mixed states and a combination of two or more Slater determinants has to be taken for their correct description. Such systems are referred to as multireference ones. Several multireference methods are used. In Multireference CI (MR-CI) the CI expansion is built from a chosen linear combination of SDs. In Complete active space self consistent field (CASSCF or CAS) we approximate the wavefunction by a short CI expansion designed from a chosen subspace of valence and virtual orbitals. We perform both orbital and CI coefficient optimization to minimize the energy of the system. The CASSCF problem is very demanding and calculations are limited to short CI expansions and small systems. In order to treat the dynamic correlation better, a second order perturbation theory formalism on the CAS wavefunction in the CASPT2 method was developed.

2.2 Relativistic effects

Close to heavy nuclei, the electrons move with speeds comparable to the speed of light, hence relativity will play an important role in the quantum mechanical description of heavy element systems. A quantitative theoretical description of relativistic systems is based on the 4-component Dirac-
Coulomb (DC) or Dirac-Coulomb-Breit (DCB) Hamiltonian

\[ H_{DC} = -\sum_i [\epsilon \alpha_i \cdot \hat{p}_i + \beta c^2] + \sum_A V_A(r_{iA}) + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} \]  

(17)

\[ H_{DCB} = H_{DC} - \sum_{i<j} \frac{1}{2r_{ij}} [\alpha_i \cdot \hat{\alpha}_j + \frac{(\alpha_i \cdot \hat{r}_{ij})(\alpha_j \cdot \hat{r}_{ij})}{r_{ij}^2}], \]  

(18)

where \( c \) is the speed of light, \( \alpha \) and \( \beta \) are the 4 x 4 Dirac matrices, and the \( \hat{p}_i \) is the momentum operator of electron \( i \). \( V_A \) describes the external potential due to nucleus \( A \) with charge \( Z_A \). This Hamiltonian leads to a four-component wavefunction, which describes both electronic and positronic states. PT and CC formalisms can be derived in the 4-component case to treat the electronic correlation, as in the 4-MP2 and 4-CCSD(T) approaches. The four-component treatment is computationally very elaborate and the calculations are currently restricted to one heavy atom with a few lighter ones. Elimination of the positronic states leads to two-component methods, such as n-ORA (n-th order regular Hamiltonian approximation; \( n = 0, 1, 2 \ldots \)) and Douglas-Kroll-Hess method (DKH). They can be reduced on spin-averaging to one-component methods.

**Pseudopotential methods.** A quite different way of treating the relativistic effects is the pseudopotential theory. It is based on the observation that the inner core electrons are unchanged in chemical reactions and only the outermost electrons of atoms are responsible for most of the chemical properties of molecules. Hence we can "freeze" the inner core electrons and model them by a pseudopotential (PP), also called effective core potential (ECP). As a result we get a model system of valence electrons interacting with frozen cores. The Hamiltonian of this model system can be written as

\[ H_{PP} = \sum_{i=1}^{n_v} \left[ -\frac{1}{2} \hat{p}_i^2 + \sum_A V_A^{PP}(r_{iA}) \right] + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Q_A Q_B}{R_{AB}}. \]  

(19)

Here the pseudopotential \( V_A^{PP} \) represents the influence of inner core of atom \( A \) on valence electrons. The mutual interaction of cores is often approximated as long distance point-charge interaction (\( Q_A = Z_A - n_{e,A} \)). In case of polarizable and/or overlapping cores, the core-core interaction has to be taken into account. Originally, the pseudopotentials were designed as one-center one-electron operators. It turned out that using different local potentials for different angular momentum quantum numbers in semi-local PPs and/or including the projection operators onto core orbitals in non-local PPs gives a much better performance. Modern PPs also include averaged spin-orbit effects or treat them using separate spin-orbit potentials. Pseudopotentials are usually generated from very accurate ab initio calculations.
2.3 Density functional theory

The *density functional theory* (DFT) is an alternative to the wavefunction based ab initio methods. Since it treats the dynamic correlation effects and is much less demanding than ab initio correlation methods such as MP2 or CI, it can be used for large systems and with larger basis sets far beyond the limit of ab initio methods. Especially with transition metals, it usually gives better results than HF or even MP2. The DFT is based on the idea that the exact ground-state electronic energy can be expressed in terms of the electron probability density $\rho$

\[
E[\rho] = -\frac{1}{2} \sum_i \int \psi_i^*(\mathbf{r}_1) \nabla_i^2 \psi_i(\mathbf{r}_1) d\mathbf{r}_1 - \sum_A \frac{Z_A}{r_{1A}} \rho(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{XC}[\rho],
\]

(20)

where $\psi_i$ are the *Kohn-Sham (KS) orbitals*. The exact ground state charge density $\rho$ at a given location $\mathbf{r}$ can be written as

\[
\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2.
\]

(21)

By applying the variational principle to the electronic energy with charge density $\rho$, we arrive at the *Kohn-Sham equations*

\[
\left\{-\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{1A}} + \frac{1}{2} \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1)\right\}\psi_i(\mathbf{r}_1) = \epsilon_i \psi_i(\mathbf{r}_1).
\]

(22)

They can be solved in SCF manner, if we know the exchange-correlation potential, $V_{XC}$, defined as a functional derivative of the exchange-correlation energy, $E_{XC}$. There is no unique way to define the $V_{XC}$ and hundreds of them have so far been proposed. In our work we use the hybrid B3LYP method where the exchange part of $V_{XC}$ is modeled by the *Becke’s three parameter functional*, and the correlation part is modeled by *Lee-Yang-Parr correlation functional*.

2.4 Intermolecular interactions

The chemical bond is a very complex phenomenon. Idealized concepts of ionic, covalent, and van der Waals bonding are very useful, but they never occur in pure form. We can relate different types of bonding to the changes which the interacting subsystems undergo. In ionic type of bonding, a large flow of electron density from one system to another causes different charge
populations on subsystems. In covalent bonding the electron density typically increases in the bonding region between the interacting nuclei. In the van der Waals bonding only small changes in the subsystems appear, the subsystems will interact due to their dipole, quadrapole ...n-pole moments and through induction and dispersion forces. It is clear that all these mechanisms will always act together but their importance in total interaction will strongly depend on the particular subsystems and the distances between them.

The interaction energy of weakly bound subsystems can be divided into several contributions

\[ V_{\text{INT}} = V_{\text{EL}} + V_{\text{IND}} + V_{\text{DISP}}. \]  

(23)

The \( V_{\text{EL}} \) corresponds to classical electrostatic interaction of multipole moments of subsystems and can be either attractive or repulsive. \( V_{\text{IND}} \) corresponds to classical induction and is always attractive. The dispersion term \( V_{\text{DISP}} \) is of quantum mechanical nature and can be seen as interaction of fluctuating charge distributions from a classical point of view. It is always attractive. At the van der Waals minimum these three terms are in equilibrium together with \( V_{\text{SHORT}} \), which represents short range forces originating from penetration of electron clouds of subsystems via resulting overlap and exchange effects.

There are different methods to treat weak intermolecular interactions. The Supermolecular approach is based on calculation of energy differences between the supersystem and its subsystems. This model is simple and treats short range effects automatically, but it suffers from the basis set superposition error (BSSE). BSSE appears due to the incompleteness of the basis set, where the calculated subsystems, when close to each other, "improve" mutually their energies by the basis set of their neighbor. This causes overestimations of calculated interaction energies and underestimations of calculated distances. It can be substantially reduced by using the counterpoise correction method\(^{20}\) but its use leads to an additional computational costs. Also high computational accuracy is needed, since the interaction energies are calculated as small differences of large numbers. Because we had access only to supermolecular method software, we used the supermolecular approach in our work, always counterpoise corrected.

Local correlation methods, such as L-MP2 or L-CCSD,\(^{21}\) use in fact the same procedure as supermolecular approach, however, due to exclusion of certain energy contributions from correlation, the BSSE is substantially reduced. The Symmetry adapted perturbation theory (SAPT)\(^{22}\) can be regarded as double perturbation theory, where the additional perturbation stands for the intermolecular interaction of the interacting systems.
2.5 Software

The presented calculations were done with several program packages, written elsewhere.

**Gaussian 98**\textsuperscript{23} was used for single point calculations, gradient geometry optimizations and frequency calculations at the HF, MP2 and CC levels.

**Molcas-4**\textsuperscript{24} was employed for HF, CASSCF and RASSCF gradient geometry optimizations, and also for CI and MR-CI calculations.

**Turbomole**\textsuperscript{25} was used for fast geometry optimizations at HF and MP2 levels. All these codes enable calculations with ECPs. Some of the geometry optimizations and frequencies were calculated numerically by internal numerical procedures built into the software, or by scan-coordinate technique followed by manual fit to appropriate potential. For visualization the Molden\textsuperscript{26} and Rasmol\textsuperscript{27} programs were employed. A number of simple subroutines in F77 and Python were written for routine work. The 4-component calculations were done by our coauthor Ken Dyall with his DREAMS\textsuperscript{28} program suite.
3 Results on metallophilic attraction

Substantial evidence for a weak metallophilic attraction between closed-shell metal atoms or ions has been accumulated.\textsuperscript{29} The origin of the interaction seem to be dispersion effects,\textsuperscript{30} influenced for heavy metals by relativistic effects.\textsuperscript{29} The most common cases involve d\textsuperscript{10}, d\textsuperscript{8}, and s\textsuperscript{2} systems, such as Pt(0) and Au(I), Ir(I), or Tl(I), respectively. A number of theoretical investigations was made, especially for Pt and Au, a few studies exist on Tl(I), and none were done on Hg(II). In papers I and II we studied some model systems for Tl(I)-Tl(I), In(I)-In(I), and Hg(II)-Hg(II) closed-shell interactions.

3.1 Modeling the Tl(I)-Tl(I) and the In(I)-In(I) interaction

Short distances between two Tl or two In atoms are known in certain compounds,\textsuperscript{29} among which one of the most notable examples would be the experimental solid state dimer structures of [C\textsubscript{5}(CH\textsubscript{2}Ph)\textsubscript{5}M]\textsubscript{2} (M=In, Tl).\textsuperscript{31} A few computational studies on the Tl-Tl interaction in such compounds have been published. Schwerdtfeger\textsuperscript{32} modeled cyclopentadienyl rings by hydrogens at QCI level and without BSSE correction, using the large-core 3-VE ECP on Tl. He found a global minimum of the Tl\textsubscript{2}H\textsubscript{2} system at a diamond-like $D_{2h}$ geometry, see Figure 1, system 2. A local $C_{2h}$ minimum corresponding to Tl-Tl interaction was also found, see Figure 1, system 1. The (MH)\textsubscript{2} (M=B-Tl) systems were also considered by Treboux and Barthelat in Ref. 33. Extended Hückel calculations on various models were reported\textsuperscript{34,35}

In paper I we studied the M-M interaction in [C\textsubscript{5}(CH\textsubscript{2}Ph)\textsubscript{5}M]\textsubscript{2} (M=In, Tl) systems, modeling it by the $C_{2h}$ (MH)\textsubscript{2} dimer systems (hydrogen models, Figure 1, system 1) and the C\textsubscript{s} (MCp)\textsubscript{2} dimer systems (cyclopentadienyl models, Figure 1, system 3). The method-dependence from MP2 to CCSD(T) was studied. Both 21-VE (small core) and 3-VE (large core) ECPs were used for In and Tl to study the possible differences between them. Scalar relativistic effects were compared by using relativistic (R) and non-relativistic (NR) 21-VE ECPs. For the quality of the basis sets and appropriate references we refer to Table 1 of paper I.
The spin-orbit effects were not studied. The monomer systems were optimized at the MP2 level using different ECPs and basis sets. With the optimized structures of monomers kept stiff, we optimized the secondary $C_{2h}$ minima for dimers. The optimizations of dimers were counterpoise corrected.

**Hydride models.** The results for the hydride models are listed in Table 1. The comparison of monomer distances for a 21-VE ECP with the experiment shows reasonable agreement for InH. The difference of 2.2 pm for TlH might be due to the missing spin-orbit effect in the calculation. It shortens the Tl-H bond by nearly 2 pm.$^{36,37}$ For the hydride monomers, the 3-VE ECPs seem to give similar results as the 21-VE ECPs. The influence of relativity is seen. While for the In system relativistic effects 'shorten' the
bond by 1 pm, for the Tl system the shortening is already 3 pm at the scalar relativistic level.

Table 1: The $C_{2h}$ minimum geometries and stabilization energies of (MH)$_2$ models; M=In, Tl.

<table>
<thead>
<tr>
<th>M</th>
<th>ECP</th>
<th>M-M (pm)</th>
<th>M-H$^a$ (pm)</th>
<th>M-M-H (degrees)</th>
<th>ΔE (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>3-VE</td>
<td>305.3</td>
<td>183.0</td>
<td>118.1</td>
<td>-32.6</td>
</tr>
<tr>
<td></td>
<td>21-VE</td>
<td>302.0</td>
<td>182.8 (183.8$^b$)</td>
<td>116.7</td>
<td>-29.8</td>
</tr>
<tr>
<td></td>
<td>21-VE-NR</td>
<td>300.0</td>
<td>183.7</td>
<td>117.4</td>
<td>-39.2</td>
</tr>
<tr>
<td>Tl</td>
<td>3-VE</td>
<td>342.5</td>
<td>187.6</td>
<td>117.7</td>
<td>-12.9</td>
</tr>
<tr>
<td></td>
<td>21-VE</td>
<td>321.7</td>
<td>189.2 (187.0$^b$)</td>
<td>119.5</td>
<td>-20.0</td>
</tr>
<tr>
<td></td>
<td>21-VE-NR</td>
<td>314.7</td>
<td>192.0</td>
<td>117.6</td>
<td>-37.5</td>
</tr>
</tbody>
</table>

$^a$ Optimized for monomers.

$^b$ Experimental values. Taken from Refs. 38, 39.

For a hydride dimer model the MP2 Tl-Tl distance is 321.7 pm compared to 362 pm in solid-state [C$_5$(CH$_2$Ph)$_5$M]$_2$.$^{31}$ Comparison of the 3-VE and 21-VE calculations on Tl-Tl systems shows large differences. In principle the 21-VE ECP should give better results. The difference between 21-VE and the 3-VE MP2 interaction energy can be understood from the data in Table 2.

Table 2: Calculated $C_{2h}$ dimerization energies (kJ mol$^{-1}$) of (MH)$_2$, M=In, Tl. Number of correlated electrons on a metal is given in parentheses. MP2 results, unless otherwise said.

<table>
<thead>
<tr>
<th>ECP</th>
<th>21-VE$^a$</th>
<th>21-VE$^b$</th>
<th>21-VE</th>
<th>3-VE</th>
<th>21-VE$^a$</th>
<th>3-VE$^a$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>-29.8</td>
<td>-29.8</td>
<td>-28.0</td>
<td>-32.6</td>
<td>-2.9</td>
<td>-7.0</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>-39.2</td>
<td>-39.2</td>
<td>-38.8</td>
<td>-10.6</td>
<td>-10.6</td>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>-20.0</td>
<td>-19.5</td>
<td>-10.0</td>
<td>-12.9</td>
<td>7.3</td>
<td>3.7</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>-37.5</td>
<td>-37.3</td>
<td>-34.8</td>
<td>-8.0</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ HF values.

If only the 6sp subspace of Tl is correlated at the 21-VE MP2 level, then about half of the interaction energy is lost. Thus the 5d orbitals of Tl seem to play an important role in the interaction. On the contrary, the 4d semicore orbitals of In seem to be less important.

The M-M distance for (TlH)$_2$ is substantially larger than for (InH)$_2$ and the interaction energy of (TlH)$_2$ is about 60% of the (InH)$_2$ one. This can be assigned to the role of relativity. Non-relativistic calculations give similar
dimerization energies for both In and Tl systems. At the non-relativistic level, the interaction would mainly originate from the 5s or 6s shells, and the 4d or 5d shells do not seem to be important, as seen from data in Table 2.

The effect of higher-level correlation is seen in Table 3. The contribution of the 5d Tl shell seems less important at the CCSD(T) level, now it is only about 20% of the interaction energy. The triple excitations play an important role in description of the interaction (compare CCSD and CCSD(T) results).

Table 3: The dimerization energy (kJ mol⁻¹) of (MH)₂ calculated at different levels of correlation. The number of correlated electrons of metal is given in parentheses.

<table>
<thead>
<tr>
<th>M, ECP</th>
<th>HF</th>
<th>MP2</th>
<th>MP3</th>
<th>MP4SDQ</th>
<th>CCSD</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In,3-VE(3)</td>
<td>-7.0</td>
<td>-32.6</td>
<td>-32.7</td>
<td>-29.8</td>
<td>-27.0</td>
<td>-34.2</td>
</tr>
<tr>
<td>In,21-VE(3)</td>
<td>-2.9</td>
<td>-28.0</td>
<td>-28.1</td>
<td>-25.4</td>
<td>-22.8</td>
<td>-29.5</td>
</tr>
<tr>
<td>Tl,3-VE(3)</td>
<td>+3.7</td>
<td>-12.9</td>
<td>-13.2</td>
<td>-11.6</td>
<td>-10.2</td>
<td>-14.0</td>
</tr>
<tr>
<td>Tl,21-VE(21)</td>
<td>+7.4</td>
<td>-20.1</td>
<td>-7.4</td>
<td>-12.1</td>
<td>-9.1</td>
<td>-14.7</td>
</tr>
<tr>
<td>Tl,21-VE(3)</td>
<td>+7.4</td>
<td>-10.0</td>
<td>-10.3</td>
<td>-8.8</td>
<td>-7.7</td>
<td>-11.6</td>
</tr>
</tbody>
</table>

**Cyclopentadienyl models.** The optimized gas-state InCp and TlCp structures are listed in Table 4. The calculated values are in reasonable agreement with the experimental gas-state electron diffraction measurements, except for the In 3-VE ECP calculation.

Table 4: Optimized distances (pm) and angles (degrees) of the MCp monomers and the Cp⁻ anion (M=In, Tl).

<table>
<thead>
<tr>
<th>M</th>
<th>ECP</th>
<th>M-Cp</th>
<th>C-C</th>
<th>C-H</th>
<th>X-C-Ha</th>
<th>M-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>3-VE</td>
<td>224.5</td>
<td>142.6</td>
<td>109.2</td>
<td>1.1</td>
<td>255.1</td>
</tr>
<tr>
<td></td>
<td>21-VE</td>
<td>228.2</td>
<td>142.7</td>
<td>109.2</td>
<td>1.0</td>
<td>258.5</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>231.4</td>
<td>142.6</td>
<td>110.0</td>
<td>4.5</td>
<td>261.3</td>
</tr>
<tr>
<td>Tl</td>
<td>3-VE</td>
<td>242.6</td>
<td>142.6</td>
<td>109.3</td>
<td>2.0</td>
<td>271.2</td>
</tr>
<tr>
<td></td>
<td>21-VE</td>
<td>238.0</td>
<td>142.7</td>
<td>109.3</td>
<td>2.0</td>
<td>267.1</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>241.3</td>
<td>142.1</td>
<td>109.2</td>
<td>0.9</td>
<td>269.9</td>
</tr>
</tbody>
</table>

Cp⁻   | 142.0 | 109.8 | 0.0 |

a Out of plane bending of the C-H bond.
The results for the cyclopentadienyl dimer models are listed in Table 5. The 21-VE calculations yield 396.0 and 381.9 pm for the Tl-Tl and In-In distances, respectively. These are too long compared to the experimental values for $[C_5(CH_2Ph)_5M]_2$ of 363 and 362 pm. The calculated angles are smaller than the experimental ones. In the experimental crystal structures of solid TlCp and InCp, the M-M distances between neighboring chains are 399 and 398.6 pm for Tl and In, respectively. These are comparable with our results.

Table 5: Optimized geometries (pm, degrees) and interaction energies (kJ mol$^{-1}$) of the (MCp)$_2$ (M=In, Tl) dimers. NR values of the energy for identical geometries are given in parentheses.

<table>
<thead>
<tr>
<th>M</th>
<th>ECP</th>
<th>M-M</th>
<th>M-M-Cp</th>
<th>$\Delta E$(HF)</th>
<th>$\Delta E$(MP2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>3-VE</td>
<td>425.1</td>
<td>104.8</td>
<td>+6.0</td>
<td>-8.5</td>
</tr>
<tr>
<td></td>
<td>21-VE</td>
<td>396.0</td>
<td>102.8</td>
<td>+14.0(+15.2)</td>
<td>-12.4(-12.4)</td>
</tr>
<tr>
<td>Tl</td>
<td>3-VE</td>
<td>437.8</td>
<td>97.4</td>
<td>+6.6</td>
<td>-6.8</td>
</tr>
<tr>
<td></td>
<td>21-VE</td>
<td>381.9</td>
<td>98.4</td>
<td>+19.7(+31.5)</td>
<td>-15.8(-12.0)</td>
</tr>
</tbody>
</table>

The MP2 interaction energy was calculated to be $-15.8$ kJ mol$^{-1}$ for the Tl-Tl system and $-12.4$ kJ mol$^{-1}$ for the In-In system, respectively. Now the relativity increases the interaction. This trend is opposite to the hydride model case. It may be the different intramolecular bonding in MCp and MH influencing the intermolecular interaction, but we have no definitive answer. We were not able to study the contributions from different shells, as the energy ordering of orbitals didn’t allow us to “freeze” them in an appropriate way. From Table 5 we see that the M-M interaction is repulsive at HF level, what suggest that EHT studies in Ref. 34,35 were based on incorrect physical model.

**Conclusion.** The existence of an M(I)-M(I) (M=In, Tl) interaction was supported by theoretical calculations. The model systems suggest the interaction energy to be about 10-20 kJ mol$^{-1}$, which may have an influence on the solid state structure of some M(I)-M(I) compounds. The similarity of the calculated dimer M-M distances with the experimental M-M distances in solid state MCp and disagreement with M-M distances in the $[C_5(CH_2Ph)_5M]_2$ systems suggest a significant influence of the benzyls in $[C_5(CH_2Ph)_5M]$ on its structure. The importance of scalar relativistic effects on the interaction was seen. The semi-core 5d shell of Tl plays a significant role in the interaction, in contrast to the In 4d shell of indium, which stays relatively untouched in interaction.
3.2 The Hg(II)-Hg(II) interaction

Hg(II) is isoelectronic to Au(I), for which many studies on closed-shell Au(I)-Au(I) contacts were reported.\textsuperscript{29} The existence of compounds with short Hg(II)-Hg(II) contacts leads to the question, how strong the Hg(II)-Hg(II) interaction is and what role it might play in the structural chemistry of the Hg(II) systems.

![Hg(II)-Hg(II) interactions](image)

Figure 2: The parallel, perpendicular, "T" shaped, and slipped structures of (HgR\textsubscript{2}) \textsubscript{2} (R=H, CH\textsubscript{3}) 1-4, respectively.

In Paper II we studied the Hg(II)-Hg(II) attraction (in following text, Hg-Hg), modeling it by dihydrogenmercury (HgH\textsubscript{2})\textsubscript{2} and dimethylmercury (HgMe\textsubscript{2})\textsubscript{2} dimers. We analyzed the interaction in the spirit of Eq. 23 using different mutual orientations of monomers, see Figure 2. Appropriate confor-
mations were used to deduce the theoretical van der Waals (vdW) radius of Hg(II). The geometries of monomers were pre-optimized and kept stiff in in counterpoise corrected dimer optimizations. We assumed a $D_{3d}$ symmetry for the dimethylmercury monomer to cancel the electrostatic octupole moment. Both CCSD(T) and MP2 methods were used for the hydride calculations.

**Optimized structures.** The optimized Hg-Hg distances for (HgH$_2$)$_2$ and (HgMe$_2$)$_2$ dimers at the various mutual orientations (see Figure 2) are listed in Table 6. The value of $-12.67$ kJ mol$^{-1}$ in Table 3 of paper II is a typographical error. The interaction energies in Table 6 show weak bonding of a few kJ mol$^{-1}$ for all calculated mutual orientations. The MP2 method underestimates the Hg-Hg distance and exaggerates the interaction energy as compared to the superior CCSD(T) results. The CCSD(T) energy nearly halves the MP2 one.

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Hg-Hg (pm)</th>
<th>$\Delta E$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HgH$_2$)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>MP2</td>
<td>377.4</td>
<td>$-3.10$</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>424.2</td>
<td>$-0.63$</td>
</tr>
<tr>
<td>2</td>
<td>MP2</td>
<td>336.3</td>
<td>$-7.80$</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>366.0</td>
<td>$-3.37$</td>
</tr>
<tr>
<td>3</td>
<td>MP2</td>
<td>454.1</td>
<td>$-4.72$</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>467.2</td>
<td>$-3.95$</td>
</tr>
<tr>
<td>4</td>
<td>MP2</td>
<td>370.8</td>
<td>$-7.40$</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>396.6</td>
<td>$-5.14$</td>
</tr>
<tr>
<td>(HgMe$_2$)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>MP2</td>
<td>404.4</td>
<td>$-7.79$</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>327.9$^a$</td>
<td>$-14.79^a$</td>
</tr>
<tr>
<td>2</td>
<td>MP2</td>
<td>340.8</td>
<td>$-12.67$</td>
</tr>
<tr>
<td>3</td>
<td>MP2</td>
<td>572.7</td>
<td>$-5.48$</td>
</tr>
<tr>
<td>4</td>
<td>MP2</td>
<td>511.6</td>
<td>$-6.00$</td>
</tr>
</tbody>
</table>

$^a$ After extraction of Me-Me repulsion, see text.

The parallel system 1 can be used to discuss the role of Hg-Hg attraction in the dinaphthalene system (C$_{10}$H$_6$)$_2$Hg$_2$, see Figure 3.
Figure 3: The structure of the \((\text{C}_{10}\text{H}_6)_2\text{Hg}_2\) system.

If we subtract the methyl-methyl repulsion which is estimated from an ethane dimer, we get a minimum distance of 328 pm with the interaction energy of \(-15\text{ kJ mol}^{-1}\). In the crystal structure of \((\text{C}_{10}\text{H}_6)_2\text{Hg}_2\) the Hg-Hg distance is 279.7 pm, clearly below 328 pm. Figure 4 shows that at the distance of 280 pm the interaction calculated at MP2 level is about zero. This explains the experimental outwards bending of 173.3(5) degrees of the C-Hg-C angle. We conclude that, in this molecule, the ligands determine the short Hg-Hg distance.
Figure 4: Interaction energies for the parallel (HgMe)₂ structure: (a) without subtraction, (b) after subtracting the repulsion between methyl groups.

The van der Waals radii of Hg(II). Two sources of the experimental van der Waals radii of Hg(II) were found in literature. Canty and Deacon¹⁴ obtained the value of 173 pm from a dataset contaminated by some intramolecular Hg-Hg contacts. The Bondi value of 155 pm¹² mixes Hg(II)...X contacts and gas viscosity measurements on mercury vapor. We can determine a theoretical vdW radius of Hg(II) from the Hg-Hg distances of systems 2 and 3 assuming an \( R_{vdw} \) of hydrogen of 120 pm. The average of our five values, which lie in interval 161-183 pm, gives

\[
R_{vdw}(\text{Hg(II)}) = 175(7)\text{pm}
\]  

(24)

This value supports the experimental value of Canty and Deacon. We are aware of our poor data set, obtaining of more accurate value would require a larger set of Hg(II)-Hg(II) systems.

Analysis of the Hg(II)...Hg(II) intermolecular interaction. Both studied monomers lack the odd multipole moments (dipole, octupole, ...) and the interaction will thus be dominated by the V(\( R^{-6} \)) dispersion (DISP) and the V(\( R^{-5} \)) electrostatic quadrupole-quadrupole (QQ) interaction. The
DISP part is always attractive. The QQ contribution is repulsive for parallel and perpendicular dimers, and attractive for the T-shaped and the slipped dimers. Other non-vanishing contributions as the $R^{-7}$ quadrupole-hexadecapole (QH), the $R^{-8}$ dispersion correction, the $R^{-8}$ quadrupole induction, and the $R^{-9}$ hexadecapole-hexadecapole (HH) terms should be negligible. In following three examples we compare the $R$ dependence of $V_{\text{INT}}$, calculated ab initio, with the $V_{\text{INT}}(R)$ obtained as a sum of contributions calculated from the monomer properties. For the calculated monomer properties and way of calculation of different contributions, see paper II.

The $(\text{HgH}_2)_2$ dimer. In Figure 5, we can see for the parallel orientation a cancellation of the electrostatic quadrupole-quadrupole (QQ) and dispersion (DISP) contributions at 1400 pm. The van der Waals minimum (in the figure, a maximum) appears at 366 pm, where the dispersion forces are balanced by the Pauli repulsion (fitted as $A \exp(\alpha R)$).

![Graph showing the interaction energies for a parallel $(\text{HgH}_2)_2$.](image)

Figure 5: Counterpoise corrected CCSD(T) interaction energies (points) and calculated individual contributions (lines) for a parallel $(\text{HgH}_2)_2$. Absolute values $|V(R)|$ are given.

For the T-shaped orientation (Figure 6), both QQ and DISP are attractive and no zero-crossing appears at large distances. The QH and IND(QQ) are
negligible.

![Graph showing V(R) vs R/pm](image)

Figure 6: Counterpoise corrected CCSD(T) interaction energies (points) and calculated individual contributions (lines) for the "T-shaped" (HgH₂)₂. Absolute values |V(R)| are given.

*The (HgMe₂)₂ dimer.* The calculated polarizability of dimethylmercury is nearly twice as large as that of the dihydride, while the quadrupole moments are comparable. Thus the dispersion attraction predominates. The QH and QQ contributions have different sign and they cancel each other at about 500 pm. They are anyway negligible.

**Conclusion.** Theoretical calculations support the existence of a weak attraction in Hg(II)-Hg(II) systems. The chosen models suggest its size to be about 5-10 kJ mol⁻¹. The calculated theoretical Hg(II) van der Waals radii of 175(7) pm supports the experimental value of Canty and Deacon.⁴¹ Both the interaction energy and the Hg-Hg distance depend on the geometry of the particular system, and it may vary with chemical environment. The interaction is mainly of the dispersion origin. (It may be quite different for polar systems.)

After paper II had appeared, Pickett et al.⁴³ published a dimeric solid-state structure with Hg-Hg contact of a 317 pm for bis(trimethylsilyl) mer-
cury, \([\text{Hg}(\text{C}_3\text{H}_9\text{Si})_2]_2\). The experimental structure is close to the 'perpen-
dicular', 2 one in Figure 2, where a Hg-Hg distance of 340.8 was calculated
at MP2 level for \([\text{Hg}(\text{Me})_2]_2\). The softer silyl group may give a stronger
interaction than the methyl.\(^{44}\)

![Figure 7: Counterpoise corrected CCSD(T) interaction energies (points) and
calculated individual contributions (lines) for the perpendicular \((\text{HgMe}_2)_2\),
Absolute values \(| V(R) |\) are given.](image)

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4 Results on new species

4.1 Indocene and Thallocene

The solid state structure of TlCp and InCp consists of infinite chains of alternating metal and cyclopentadienyl units. By "cutting" these, we arrive at the (CpM Cp)± species (Figure 1, system 5), of which the (CpM Cp)− is isoelectronic to known stannocene, Sn(Cp)2. One can also add one more Cp− group to the (CpM Cp)+ system obtaining the M Cp3 system, see Figure 1, system 5. From these, only (CpTlCp)− was experimentally observed and the results were supported by calculations.45 In paper I we looked for possible existence of such systems. In actual calculations, we optimized only the Cp-M distances and Cp-M-Cp angles keeping remaining internal coordinates frozen. The MCP3 systems were forced to C3v geometry.

The calculated systems are listed in Table 7. The (CpM Cp)± units were found to be linear except the (CpInCp)−, which had the Cp-In-Cp bond angle of 170 degrees. The experimental Tl-Cp distances to the ring center for (CpTlCp)− in different anion environments are 261, 285 and 273 pm (in the average 272 pm) with a Cp-Tl-Cp angle of about 155 degrees.45 Our (CpTl-Cp)− was calculated to be linear with a Tl-Cp distance of 267 pm. The minima were quite shallow with respect to bending of the Cp-M-Cp angle for all systems. For example, bending the Cp-Tl-Cp angle of the (CpTlCp)− from 180 to 150 degrees increases energy of this system by only 3 kJ mol−1. It is clear that the structure of the considered systems can be substantially influenced by the counterions. The Dsh-Dsd differences were small.

Table 7: The calculated geometries and spectroscopic constants for (CpM Cp)± and M(Cp)3 structures, with M=In, Tl. K correspond to symmetric stretch.

<table>
<thead>
<tr>
<th>System, symmetry</th>
<th>Tl-Cp (pm)</th>
<th>ωv (cm−1)</th>
<th>ωe χe (cm−1)</th>
<th>K (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CpInCp)+ , D5d</td>
<td>203.4</td>
<td>301.40</td>
<td>0.17</td>
<td>0.4475</td>
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<td>(CpInCp)− , D5h</td>
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<td>154.00</td>
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<td>(CpInCp)− , D5d</td>
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<td>153.93</td>
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<td>0.1167</td>
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<td>(CpInCp)− , Cs</td>
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<td></td>
<td>0.1166</td>
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<td>(CpTlCp)+ , D5d</td>
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<td>295.42</td>
<td>0.16</td>
<td>0.4300</td>
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<td>(CpTlCp)+ , D5d</td>
<td>267.0</td>
<td>156.05</td>
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<tr>
<td>InCp3 , C3v</td>
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<td>284.09</td>
<td>0.19</td>
<td>0.5965</td>
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<td>TlCp3 , C3v</td>
<td>237.4</td>
<td>276.00</td>
<td>0.19</td>
<td>0.5630</td>
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</table>

a Bent, optimized Cp-In-Cp angle was 170.1 degrees.
After this work had been published, the \((\text{Cp}^*\text{GaCp}^*)^+\) cation was observed\(^{10}\) (\(\text{Cp}^*\) = pentamethylcyclopentadienyl). The \(D_{5d}, \ D_{5h},\) or \(C_5\) geometries are not minima on the PES of the \((\text{Cp}^*\text{GaCp}^*)^+\) system. Instead, an \(\eta^1\text{-Cp}^*\text{Ga}^3\text{-Cp}^*\) system was found. In Ref.\(^{47}\) the zig-zag \([\text{TiCp}^1\text{TiCp}^1]^{+}\) system was observed. Possibly the inverted \(\text{MCpM}\) ions may exist.

At the stage of the work we were not able to perform full geometry optimizations and vibrational frequency calculations. The systems are not necessarily minima on the potential surface. The problem should be reconsidered and full optimization with frequency calculation should be performed to claim the existence of such systems.

### 4.2 Actinide oxy-fluoride species

Owing their complicated hybridization, actinides are a fascinating subject for theoretical studies. One purpose of such studies is to use complete maps of isoelectronic series to identify so far unknown chemical species. The trends of bond lengths or force constants along such isoelectronic series will then give an indication on the stability of the various species.

![Figure 8: A map of possible \(f^0 [\text{AnO}_2 \text{F}_n]^q\) species.](image)

In paper IV we studied the naked triatomic \(f^0d^0\) actinyls and their fluoride derivatives. A complete map of the possible \(f^0 [\text{AnO}_2 \text{F}_n]^q\) actinide oxyfluoride
species is shown in Figure 8 and examples of their general structures in Figure 9. Of the f^0d^0 actinyl species, the bent ThO_2\textsuperscript{48-51} and the linear uranyl UO_2\textsuperscript{2+}\textsuperscript{52,53} have been observed as matrix and/or gas-state species. PaO_2\textsuperscript{+}\textsuperscript{54} and green NpO_2\textsuperscript{3+}\textsuperscript{55} with a number of equatorial ligands are known in solution.

![Diagram of calculated species](image)

Figure 9: Structures of calculated species.

Of the f^0d^0 oxyfluoride species the UO_2F_2\textsuperscript{56} and UO_2F\textsuperscript{+}\textsuperscript{57} are known. The [UO_2F_n]\textsuperscript{2-n} series for n = 1-5 have been observed in aqueous solution.\textsuperscript{58}
The \( \text{UO}_2\text{F}_{3-} \) occurs in solids.\textsuperscript{59} Thermochromatographic evidence exist for gas-state \( \text{UOF}_4, \text{UO}_2\text{F}_2, \text{NpF}_7 \) and \( \text{NpO}_3\text{F} \) by Fargeas et al.\textsuperscript{50}

On the theoretical side, various members of the \( \text{OAnO}^{2+} \) series have recently been theoretically studied.\textsuperscript{61-63} For the tripositive \( \text{ONpO}^{3+} \), non-relativistic scattered-wave \( \text{X-}\alpha \) calculations at a fixed bond length exist.\textsuperscript{64} The \( [\text{UO}_2\text{N}]^{2-} \) series was recently considered by Schreckenbach et al.\textsuperscript{65}

Several studies on methodology for actinide species calculations found in literature\textsuperscript{65-70} suggest that using pseudopotentials with \( \text{DFT} \) for structure and frequency calculations gives reasonable results for closed-shell actinide systems. In our work we studied the method dependence (\( \text{HF}, \text{MP2}, \text{B3LYP}, \text{CCSD(T)} \)) on bare \( f^6 \) actinyls, using both large core and small core \( \text{ECPs} \),\textsuperscript{71} and the \( \text{aug-cc-PVDZ} \) basis sets for O and F. For calculation on oxyfluorides, the B3LYP and the MP2 methods were chosen for the production work. The deviation between these two should be a qualitative measure of the reliability of calculation. The \( \text{DF} \) calculations were done with basis sets of the \( \text{aug-cc-PVDZ} \) quality.

### 4.2.1 Actinyls

**Bonds and bond lengths.** The calculated An-O bond distances for \( f^6d^0 \) actinyls from \( \text{ThO}_2 \) through \( \text{PuO}_2^{4+} \) are shown in Figure 10. The \( \text{AmO}_2^{5+} \) disintegrates at QR-HF and DF levels. The \( \text{AcO}_7 \) is bent with the O-An-O angle of 112.8 degrees, An-O distance of 207.1 pm and frequencies 636\( (a_1) \), 559\( (b_2) \), 170\( (a_1) \) cm\(^{-1} \) at B3LYP level. This system was not studied in detail. The calculated \( \text{ThO}_2 \) is bent to about 120 degrees, the \( \text{PaO}_2^+ \) and \( \text{UO}_2^{4+} \) are linear at all levels. B3LYP calculations gave a slight bending of about 10 degrees for the \( \text{NpO}_2^{3+} \) and \( \text{PuO}_2^{4+} \). As we move from Th to Pu the An-O distance becomes shorter with a minimum at Pu on DF and QR-HF levels, or at Np on correlated level. The influence of correlation effects on \( R \) increases from \( \text{ThO}_2 \) to \( \text{PuO}_2^{4+} \). Large deviations of MP2 results and bending at B3LYP level suggested a more detailed study. We reoptimized both neptunyl and plutonyl using the CASSCF approach, correlating all 12 valence electrons in 16 orbitals (CAS12/16). It was found that while \( \text{NpO}_2^{3+} \) remains linear, with CASSCF geometry similar to the CCSD(T) one, the \( \text{PuO}_2^{4+} \) becomes unstable and decomposes on bending. The contribution of the \( f \) orbitals to the CASSCF wavefunction was about 10% for \( \text{NpO}_2^{3+} \) and 30% for \( \text{PuO}_2^{4+} \) at HF minimum geometry.
It is due to the virtual f orbitals, which go down in energy for heavier actinides and may become too low in energy for PuO$_2^{3+}$ to exist. Additional equatorial ligands may push the unoccupied f orbitals up and save plutonyl, see next chapter. A T1 diagnostic of 0.035 for PuO$_2^{3+}$ suggests that the CCSD(T) result may be irrelevant for this case (For NpO$_2^{3+}$ T1=0.022). For these reasons the MP2 method probably does not give reliable results beyond uranyl for the triatomic species. This may also explain the bending tendencies observed in B3LYP calculations.

**Nature of bonding.** A perennial question is that of the An hybridization, in particular concerning the 6pσ hole. From Figure 11 we see that this hole increases along the An series and reaches a maximum of about -0.5 around Np and Pu, using a Mulliken population analysis at the B3LYP energy minimum. The 5f character in the covalent bonds increases steadily from Th to Pu, while the 6d character remains almost constant. The bending of the molecules increases the 6d population, which is favorable for ThO$_2$ (and AcO$_2^-$) but not for the higher members of the series.
Figure 11: The orbital occupations and Mulliken charge $Q$ on An for the $f^0$ actinyls. For "p" curve, all 6$p^6$ electrons subtracted.

The participation of the lower lying $f$ orbitals in bonding of heavier actinides favors linear geometry. The highest four occupied molecular orbitals of NpO$_2^+$ are shown in Figure 12. They also show the shape of the doubly degenerate 5$f\delta_u$ LUMO and the LUMO+1 5$f\phi_u$ orbitals, respectively.

**Frequencies.** The trends in the antisymmetric and symmetric O-An-O stretching vibrations are plotted in Figures 13 and 14, respectively. The calculated antisymmetric frequency for ThO$_2$ agrees well with experiment, the symmetric one less so. The calculated $\sigma_u$ frequency of UO$_2^{2+}$ is considerably different from 952 cm$^{-1}$ tentatively assigned to UO$_2^{2+}$ in argon matrices by Hunt et al.$^{53}$ It was indeed reassigned to be the $\sigma_u$ of UO$_2^+$ by Zhou et al.$^{72}$ The symmetric stretch frequencies in Figure 14 exhibit similar trends as the antisymmetric ones.
The agreement between HF and DF results suggests that spin-orbit effects are not essential at HF level. We stress that the DF calculations are helpful as calibration of ECP calculations, but because of the importance of correlation in these systems, the DF does not give realistic comparisons with experiment. The correlation methods show similar trends for frequencies as for the distances, suggesting that also here the MP2 may not be reliable for bare plutonyl or neptunyl groups.
Figure 13: Trends in calculated antisymmetric stretching vibrational modes for the $f^0$ actinyls.

Figure 14: Trends in calculated symmetric stretching vibrational modes for the $f^0$ actinyls.
4.2.2 Oxyfluorides

All results presented in this section are the B3LYP ones; MP2 gives similar answers. The trends of bond lengths for actinyl fluorides are plotted in Figures 15 and 16. The lowest curve in Figure 15 corresponds to the actinyls, with a minimum at Np. The successive addition of 1 to 5 more equatorial fluorines, maintaining $f^0$ electronic structure, leads to a relatively moderate increase of the An-O distance. The An-F distances for $[\text{AnO}_2\text{F}_n]^q$, $n = 1-5$, as functions of $n$ are shown in Figure 16. Again, the heavier An have shorter distances for the same $n$. Increasing the $n$ will slightly lengthen the An-F distance.

![Graph showing trends in calculated An-O distances for the $[\text{AnO}_2\text{F}_n]^q$ species.](image)

Figure 15: The trends in calculated An-O distances for the $[\text{AnO}_2\text{F}_n]^q$ species.

The vibrational frequencies show similar behavior and do not bring any new insight. The trends are very systematic and neither encourage nor discourage the search for further species, which should be rather based on energies.
Figure 16: The trends in calculated An-F distances for the $[\text{AnO}_2\text{F}_n]^9$ species
**Equatorial bonding.** Coulson and Lester\(^{73}\) suggested that the equatorial bonding of UO\(_2\)(NO\(_3\))\(_3\)\(^-\) would take place between the U 5f\(\phi\) orbital and the nitrate oxygens. No evidence for this was found at HF ab initio level by Pyykkö et al.\(^{74}\) The total 5f\(\phi\)\(\rightarrow\)2p\(p\) overlap populations were about 0.03 only. We now find examples of 5f\(\phi\) involvement in equatorial bonding. For UO\(_2\)F\(_5\), UO\(_2\)F\(_3\)\(^-\), NpO\(_2\)F\(_3\), NpO\(_2\)F\(_5\)\(^-\), and NpO\(_2\)F\(_5\)\(^{2-}\) the Mulliken overlap populations are 0.11, 0.03, 0.16, 0.24, and 0.21, respectively. A closer look at the specific molecular orbitals in Figure 17 makes this covalent involvement quite evident. This suggests a rehabilitation of Coulson’s idea but in different systems than the uranyl trinitrate originally considered in 1956\(^ {73}\) and in 1994.\(^ {74}\)

![Figure 17: Selected molecular orbitals of UO\(_2\)F\(_5\)\(^-\) (a) and NpO\(_2\)F\(_5\)\(^{2-}\) (b): HOMO-7 and HOMO-10, respectively.](image)

**4.3 Does Pu(VIII) exist?**

Among the known actinide species those with the highest oxidation state appear to be the f\(^6\) Np(VII) and the f\(^{1}\) Pu(VII) compounds as for example the gas-state NpO\(_2\)F\(^{60}\) or PuO\(_2\)\(^{2+}\) reported in alkaline solutions.\(^ {64}\) Missing experimental and theoretical evidence for Pu(VIII) systems led us to the study of simple Pu(VIII) oxyfluoride species. We chose PuO\(_4\), PuO\(_2\)F\(_4\), and PuF\(_8\) species as a representative samples of hypothetical Pu(VIII) systems and
searched for minima on their hypersurfaces. To estimate the thermochemical stability of such compounds we also studied some Pu(VI) oxyfluoride systems. It turned out that though many Pu(VI) systems are known from experiment, \textsuperscript{60,75} their structures and vibrational spectra are, except for PuF\textsubscript{6}, still unknown.

The calculated structures of Pu(VIII) species and selected vibrational modes are listed in Table 8. The PuO\textsubscript{4} molecule has the \textit{D\textsubscript{4h}} symmetry, slightly distorted to \textit{D\textsubscript{2d}} at B3LYP level. The corresponding \textit{T\textsubscript{d}} systems were found to be saddle points at the HF and B3LYP levels. In Ref. \textsuperscript{76}, the isoelectronic UO\textsubscript{4}\textsuperscript{2–} was found to be a \textit{T\textsubscript{d}} system at minimum and the calculated NpO\textsubscript{4}\textsuperscript{2–} was found to be a \textit{D\textsubscript{4h}} system at the minimum. The \textit{D\textsubscript{4h}} PuO\textsubscript{4} system follows this trend. The PuF\textsubscript{8} system was found to be cubic, with the Pu-F distance only 2 pm longer than in PuF\textsubscript{6}. This suggests a sturdy structure.

**Thermochemistry.** In order to have a reference thermochemical point we studied several Pu(VI) species at B3LYP level, see Table 9. If we start from the experimentally known PuF\textsubscript{6} we can calculate B3LYP enthalpies for following hypothetical reactions

\[
\begin{align*}
\text{PuF}_6 + F_2 &\rightarrow \text{PuF}_8 & \Delta H = +284 \text{ kJ mol}^{-1} & \text{(25)} \\
\text{PuF}_6 - F_2 + O_2 &\rightarrow \text{PuO}_2\text{F}_4 & \Delta H = +515 \text{ kJ mol}^{-1} & \text{(26)} \\
\text{PuF}_6 - 3F_2 + 2O_2 &\rightarrow \text{PuO}_4 & \Delta H = +1239 \text{ kJ mol}^{-1} & \text{(27)}
\end{align*}
\]

Similar reactions with PuO\textsubscript{2}F\textsubscript{2} give -413, -182, and +544 kJ mol\textsuperscript{-1}. These numbers, though very qualitative, may encourage the search for Pu(VIII).

**Cubic versus antiprism structure.** Hwang and Seppelt\textsuperscript{77} found that the isoelectronic UF\textsubscript{8}\textsuperscript{2–} in crystalline (NO)\textsubscript{2}(UF\textsubscript{8}) has a square antiprism, \textit{D\textsubscript{4d}} structure with U-F(\text{av}) = 210.2 pm. Our calculated B3LYP value is 213 pm for the \textit{D\textsubscript{4h}} structure. All frequencies are positive. The \textit{O\textsubscript{h}} structure is a transition state with one imaginary double degenerate frequency (\textit{e\textsubscript{a}}), which corresponds to the rotation from cube to antiprism. The NpF\textsubscript{8}\textsuperscript{2–} was found to be cubic, like PuF\textsubscript{8}. The antiprism NpF\textsubscript{8}\textsuperscript{–} and PuF\textsubscript{8} have one imaginary frequency (\textit{b\textsubscript{1}}) corresponding to rotation of the antiprism to cube. The energy differences E(\textit{O\textsubscript{h}}) - E(\textit{D\textsubscript{4h}}) are +19, -7, and -26 kJ mol\textsuperscript{-1} for UF\textsubscript{8}\textsuperscript{2–}, NpF\textsubscript{8}\textsuperscript{2–}, and PuF\textsubscript{8}, respectively. Note the shortening of the An-F distance along the series U-Pu, Table 8.

**Conclusion.** The PuF\textsubscript{8}(\textit{O\textsubscript{h}}), PuO\textsubscript{2}F\textsubscript{4}(\textit{D\textsubscript{4h}}), and eventually PuO\textsubscript{4}(\textit{D\textsubscript{4h}}) are proposed to be possible new Pu(VIII) species. All of them would contain the so far unknown Pu(VIII). PuF\textsubscript{8} is an interesting molecule because it could be the first Pu(VIII) species and the first neutral cubic (\textit{O\textsubscript{h}}) X\textsubscript{Y\textsubscript{8}} molecule at the same time.
Table 8: Bond lengths (pm) and selected harmonic frequencies (cm⁻¹) for Pu(VIII) and AnF₈ systems for An=U,Np,Pu.

<table>
<thead>
<tr>
<th>System</th>
<th>Symm</th>
<th>Method</th>
<th>An-O</th>
<th>An-F</th>
<th>An-O stretch</th>
<th>An-F stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuO₄</td>
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</tr>
<tr>
<td>D₄h</td>
<td>DF</td>
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<td>974(a₁g)</td>
<td>733(b₁g)</td>
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<tr>
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<tr>
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Table 9: Calculated bond lengths (pm) and frequencies (cm$^{-1}$) for Pu(VI) systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Symmetry</th>
<th>State</th>
<th>Method</th>
<th>Pu-O</th>
<th>Pu-F</th>
<th>Pu-O stretching</th>
<th>Pu-F stretching</th>
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<td>PuF$_6$</td>
<td>$O_h$</td>
<td>$^1A_{1g}$</td>
<td>B3LYP</td>
<td>197.4</td>
<td>640($a_{1g}$)</td>
<td>612($t_{1u}$)</td>
<td>523($e_g$)</td>
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<td>$O_h$</td>
<td>$^1A_{1g}$</td>
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<td>912($b_2$)</td>
<td>880($a_1$)</td>
<td>776($a_1$)</td>
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$^a$ Ref. 75
4.4 A symmetry trend

One can notice the systematic trend in geometries of actinide oxyfluoride species. In Table 10 on each row the calculated symmetry of the molecule changes. Left of the vertical line the inversion symmetry is missing. Right of the vertical line it exists. A possible mechanism could be the constant 6d orbital energies as contrasted to the increasingly stabilized 5f orbital energies along the actinide series (Th-Am), see Ref. 78. Due to their stabilization, f orbitals participate in covalent bonding and thus influence more the resulting structure of the heavier actinide systems.

**Remark.** A careful check of Table 4 in paper IV reveals that ThO$_2$F$^-$ has $C_s$ geometry in contrast to the Pa and U analogues which are $C_{2v}$ systems. Furthermore the PaO$_2$F$_2$ and UO$_2$F$_2$ are $C_{2v}$ systems while the hypothetical NpO$_2$F$_2$ is a $D_{2d}$ system with inversion symmetry. However there is a large discrepancy between MP2 and B3LYP for this particular system and we didn’t include this result to Table 10. This phenomenon deserves a closer analysis; it was postponed to future investigations.

<table>
<thead>
<tr>
<th>Class</th>
<th>$\leftarrow$ No Inversion</th>
<th>Inversion $\Rightarrow$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AnO$_2^+$</td>
<td>ThO$<em>2$ $C</em>{2v}$</td>
<td>PaO$_2^{2+}$ UO$_2^{2+}$ NpO$_2^{2+}$</td>
</tr>
<tr>
<td>AnO$_6^-$</td>
<td>UO$_6^{4-}$ $T_d$</td>
<td>NpO$_6^{-}$ PuO$<em>4$ $D</em>{4h}$</td>
</tr>
<tr>
<td>AnF$_8^{2-}$</td>
<td>UF$<em>8^{2-}$ $D</em>{4d}$</td>
<td>NpF$_8^{-}$ PuF$_8$ $O_h$</td>
</tr>
</tbody>
</table>

Table 10: Examples on symmetry change.
4.5 A bold proposal: The UO$_6$ molecule

Though the uranium semicore 6p shell lies energetically below the 5f and 6d valence ones, it is radially outside the main maximum of the 5f shell and at shorter distances strongly participates in bonding, as known in uranyl. Would it be possible, in a chemical sense, to oxidize the 6p electrons away? This would ultimately lead to uranium in oxidation state XII as in octahedral UO$_6$, for instance. In covalent bonding the ligand electrons would come back to U, so the real charge on U could still be only moderately positive. Moreover, if the covalent bonds have enough of $f$ character, the nearly pure 5f states will be pushed up by $f$-f Coulomb repulsion and will not rob electrons from the ligands.

We studied the UO$_6$ molecule at several theoretical levels including fully relativistic DF and pseudopotential quasi-relativistic multireference methods, see Table 11. The oxygen basis sets were of the augmented-double-zeta quality for both DF and quasirelativistic calculations. The 32-VE ECP with corresponding basis set of triple-zeta quality was used for uranium. The very first question was that of orbital occupation in the hypothetical octahedral UO$_6$. From the U$^{12+}$O$^{2-}$ extreme limit the valence electron occupation would become

$$3a_{1g} + 2e_g + 3t_{1u} + t_{1g} + t_{2u} + t_{2g}$$ \hspace{1cm} (28)

which is the lowest energy quasi-relativistic closed-shell alternative. The HOMO here is the $a_{1g}$ spanned by p orbitals of the oxygen. Above it, there is an alternative, where the $a_{2u}$ orbital spanned by 5f$_{xy}$ orbital of U is occupied instead of the HOMO $a_{1g}$. Thus we get the valence electron configuration

$$2a_{1g} + 2e_g + 3t_{1u} + t_{1g} + t_{2u} + t_{2g} + a_{2u}$$ \hspace{1cm} (29)

These two alternatives, and their relativistic equivalents $(36g)^2(34u)^2$ or $(35g)^2(35u)^2$ were considered. The CASSCF reference for MR-CISD was obtained by correlating of two electrons in the $3a_{1g} + 1a_{2u}$ space. The reference was state-averaged for two lowest roots of $A_{1g}$ symmetry. The calculated bond lengths and vibrational frequencies are given in Table 11. At all single-determinant QR levels, we obtained local minimum with positive vibrational frequencies. The B3LYP distance of about 180 pm is decreased to 174 pm in the multireference case, and it is about 10 pm larger than de Jong's 4-CCSD(T) value for UO$_2^{2+}$ of 172 pm.$^{79}$ The symmetric vibration stretch in UO$_2^{2+}$ of 974 cm$^{-1}$ $^{79}$ corresponds to our $a_{1g}$ of 792 cm$^{-1}$. Our quasi-relativistic B3LYP values for UO$_2^{2+}$ were 170 pm and 1042 cm$^{-1}$, see paper IV.
Table 11: Calculated U-O bond lengths (pm) and vibrational frequencies (cm\(^{-1}\)) for UO\(_6\). The electron configuration \((36g)^2\)(34u)\(^2\) is assumed unless otherwise mentioned.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis (U)</th>
<th>U-O</th>
<th>(t_{2u})</th>
<th>(t_{2g})</th>
<th>(e_g)</th>
<th>(t_{1u})</th>
<th>(a_{1g})</th>
<th>(t_{1u})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>RSC+2g</td>
<td>172.1</td>
<td>117.8</td>
<td>479.0</td>
<td>893.4</td>
<td>931.9</td>
<td>949.8</td>
<td>1642.2</td>
</tr>
<tr>
<td>HF</td>
<td>RSC+2g+1h</td>
<td>172.0</td>
<td>103.4</td>
<td>479.6</td>
<td>897.3</td>
<td>937.3</td>
<td>956.2</td>
<td>1696.2</td>
</tr>
<tr>
<td>B3LYP</td>
<td>RSC+2g</td>
<td>179.5</td>
<td>221.8</td>
<td>373.8</td>
<td>755.3</td>
<td>331.5</td>
<td>785.9</td>
<td>838.2</td>
</tr>
<tr>
<td>B3LYP</td>
<td>RSC+2g+1h</td>
<td>179.4</td>
<td>219.2</td>
<td>374.4</td>
<td>760.5</td>
<td>329.4</td>
<td>792.5</td>
<td>842.5</td>
</tr>
<tr>
<td>MP2</td>
<td>RSC+2g</td>
<td>181.8</td>
<td>826.8</td>
<td>308.0</td>
<td>823.1</td>
<td>757.9</td>
<td>981.0</td>
<td>1234.4</td>
</tr>
<tr>
<td>CAS</td>
<td>RSC+2g</td>
<td>170.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAS(^a)</td>
<td>RSC+2g</td>
<td>170.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MR-CI+Q(^b)</td>
<td>RSC+2g</td>
<td>174.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MR-CI+Q(^a) (^b)</td>
<td>RSC+2g</td>
<td>172.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DF</td>
<td></td>
<td>173.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DF(^a)</td>
<td></td>
<td>181.8</td>
<td>265</td>
<td>312</td>
<td>614i</td>
<td>131</td>
<td>619</td>
<td>448</td>
</tr>
</tbody>
</table>

\(^a\) Electron configuration \((35g)^2\)(35u)\(^2\). \(^b\) Davidson-corrected for quadruple excitations.
At all QR levels, the \((35g)^2(35u)^2\) was clearly higher than the \((36g)^2(34u)^2\) state. Including an h function in the uranium basis set has only a marginal influence on the calculated parameters. The inclusion of the spin-orbit effect via the DF method changes the lowest closed shell state to \((35g)^2(35u)^2\) state. Now the \(e_g\) mode, which pulls off either two axial or four equatorial O atoms, is imaginary, see Table 11. It can be regarded as due to spin-orbit induced Jahn-Teller distortion, in which the \(a_{2u}\) mixes with the \(t_{1u}\) LUMO. Such a mixing is not possible for configuration \((36g)^2(34u)^2\) since there are no closely-lying orbitals of g-parity to mix with \(a_{1g}\) HOMO. In Table 12 the Mulliken populations at various levels are shown. The uranium Mulliken charge of about +3 is not very different from the value of +3.3 for \(\text{UO}_2^+\). There is a large 6p hole of 1.3 electron on U, compared to the \(\text{UO}_2^+\) one, which is about 0.5.

<table>
<thead>
<tr>
<th>Method</th>
<th>(R_e/\text{pm})</th>
<th>(Q(\text{U}))</th>
<th>6p</th>
<th>6d</th>
<th>5f</th>
<th>5g</th>
</tr>
</thead>
<tbody>
<tr>
<td>QR-HF</td>
<td>172.0</td>
<td>+3.43</td>
<td>3.84</td>
<td>2.04</td>
<td>2.10</td>
<td>0.50</td>
</tr>
<tr>
<td>B3LYP</td>
<td>179.5</td>
<td>+2.74</td>
<td>4.42</td>
<td>1.77</td>
<td>2.76</td>
<td>0.32</td>
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<tr>
<td>MP2</td>
<td>181.8</td>
<td>+1.94</td>
<td>4.56</td>
<td>1.7</td>
<td>3.5</td>
<td>0.30</td>
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<tr>
<td>MR-CI(^a)</td>
<td>170.0</td>
<td>+3.47</td>
<td>3.81</td>
<td>2.04</td>
<td>2.01</td>
<td>0.54</td>
</tr>
<tr>
<td>MR-CI(^b)</td>
<td>170.0</td>
<td>+2.38</td>
<td>3.69</td>
<td>1.92</td>
<td>3.72</td>
<td>0.48</td>
</tr>
<tr>
<td>DF(^a)</td>
<td>173.3</td>
<td>+2.84</td>
<td>3.76</td>
<td>1.90</td>
<td>2.87</td>
<td>0.50</td>
</tr>
<tr>
<td>DF(^b)</td>
<td>181.8</td>
<td>+2.92</td>
<td>4.38</td>
<td>1.73</td>
<td>2.63</td>
<td>0.31</td>
</tr>
</tbody>
</table>

For a qualitative thermochemical estimate we considered the reactions

\[
\text{UF}_6(g) + 3\text{O}_2(g) \rightarrow \text{UO}_6(g) + 3\text{F}_2(g)
\]  \(30\)

\[
\text{U(\text{metal})} + 3\text{O}_2(g) \rightarrow \text{UO}_6(g)
\]  \(31\)

\[
\text{U(g)} + 3\text{O}_2(g) \rightarrow \text{UO}_6(g)
\]  \(32\)

\[
\text{U(g)} + 6\text{O}(g) \rightarrow \text{UO}_6(g)
\]  \(33\)

Reaction 30 is endothermic by roughly +2000 kJ mol\(^{-1}\) at QR B3LYP level, and by roughly +2700 kJ mol\(^{-1}\) at DF level, respectively. The energies for the reactions 31, 32, and 33 are \(-150\) kJ mol\(^{-1}\), \(-680\) kJ mol\(^{-1}\), and \(-2100\) kJ mol\(^{-1}\), respectively. They were calculated by combining the experimental and B3LYP values. The ZPE corrections were small and are not included in these rather qualitative estimates.
Figure 18: The calculated CCSD(T) potential energy, and the corresponding value for the T1 diagnostic, along the a_{1g} U-O stretching coordinate.

In Figure 18 the QR CCSD(T) potential energy is plotted for the (36g)^2(34u)^2 state along the U-O a_{1g} stretching, together with the T1 diagnostic. The large value of T1 suggests a multireference nature of the UO_6 system. A proper configurational space would consist of 33 orbitals (18 of 2p of O + 15 of 6s5f5d of U) which is hardly possible even at QR level. Either experiment or a fully-relativistic multireference calculation can solve the question of the existence of UO_6. Finally, there may exist also other minima analogous to low-symmetry structures like WH_6 or peroxidic structures like (UO_2)^+(O_2^-)(O_2), which were not studied. Putting two extra electrons to UO_6 leads to UO_6^{2-} in (36g)^2(35u)^2 configuration, which at DF level is an octahedral minimum with all frequencies positive.

**Conclusion.** The UO_6 system seems to be a high energy minimum on the potential-energy surface at many but not all approximations. If it exists it would be the first system where the actinide 6p shell is formally oxidized, leading to U in a formal oxidation state XII. So far the highest known oxidation state of any element appears to be VIII, occurring for Ru, Os and Xe.
5 Conclusions

In the present work we supported the experimental evidence for closed shell metallophilic attraction in In(I)-In(I), Tl(I)-Tl(I) and Hg(II)-Hg(II) systems. The M-M interaction between these formally positively charged metals is of the order of 10-20 kJ mol$^{-1}$ for In and Tl and less than 10 kJ mol$^{-1}$ for Hg, and may be structure-driving in some solid-state structures. The origin of the metallophilic attraction for Hg(II) systems was found to be dispersion, influenced by relativistic effects. The van der Waals radius of Hg(II) was calculated to be 175(7) pm.

Theoretical predictions of novel heavy element compounds were presented. The calculations of isoelectronic series of actinide oxyfluoride systems suggest some directions for experimental search of novel actinide species and provide missing experimental data for some experimentally known systems. The role of f orbitals in equatorial bonding of actinides was reestablished. The structure and bonding trends in the isoelectronic series of actinide oxyfluoride species suggest non-negligible participation of f orbitals in covalent bonding and its resulting structure-driving importance. A symmetry-breaking along the An series, found for the AnF$_6^-$ series in addition to the AnO$_4^-$ and the AnO$_2^-$ ones, which were known before, is consistent with this observation. A few predicted novel systems of experimentally never observed Pu(VIII) compounds are likely to be possible gas-state species.

An exotic UO$_6$ system, the first example of uranium (and any element) in the oxidation state XII, was studied and neither entirely ruled out nor completely confirmed by calculations. The question of existence of this new system is a challenge for both experimental and theoretical chemistry.
References


43


[54] Ref. 51, p. 1511.


[57] Ref. 51, p. 352.

[59] Ref. 51, p. 1428.


[76] H. Bolvin, U. Wahlgren, O. Gropen, C. Marsden To be published.
