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# Recent progress in theoretical investigations of the electronic structure of the transactinides

V. Pershina[a,*], T. Bastug[b], B. Fricke[c]

[a]*Gesellschaft für Schwerionenforschung, D-64291 Darmstadt, Germany*
[b]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan*
[c]*Fachbereich Physik, Universität Kassel, D-34132 Kassel, Germany*

## Abstract

An overview is given of the recent development in the theory of molecular codes focusing on a newly developed version of the Dirac–Slater discrete-variational (DS-DV) method for complex multiatomic systems. Emphasis is put on the calculations of the chemical bonding in heavy element compounds. A new model to predict complex formation and extraction of the transactinides on the basis of the DS-DV molecular-orbital calculations is presented. © 1998 Elsevier Science S.A.

*Keywords:* Transactinides; Relativistic molecular calculations; Complex formation

## 1. Introduction

During the last several years investigations of the electronic structure of the transactinides have led to a new level of understanding of their physics and chemistry. The questions about bonding interactions, stability and influence of relativistic effects on these properties have become more clear after having performed molecular relativistic calculations. Among molecular codes, the local density functional (LDF) methods were mostly used [1]. Within the last 3–4 years a further development of the LDF and ab initio Dirac–Fock (DF) molecular theory [2] has offered new possibilities in their application to heavy systems. In the present publication an overview is given of the very recent progress in this area.

## 2. Methods used to calculate the electronic structure of heavy molecules

Available relativistic quantum–chemical methods for molecules and their application to transactinide systems are described in [1]. LDF methods, such as the DS discrete variational (DV) [3,4] or multiple scattering (MS) [6–8] ones, offer the possibility to treat chemically interesting and complex systems fully relativistically with sufficient accuracy. Calculations by using these methods for a large number of gas-phase molecules and complexes in aqueous solutions permitted to establish trends within the transition-element groups and along the transactinide row for molecular properties such as ionicity, covalence, stability towards oxidation or reduction, crystal-field and spin–orbit effects and the influence of relativistic effects on them. The results are described in [1].

During the last few years, the DS-DV method has experienced further improvements [9–11]. A weighted fitting procedure has been used for the molecular potential to minimize the error in the total energy and to give a variationally consistent functional. A more accurate numerical integration scheme [13], which allows for the calculation of highly accurate matrix elements has been introduced. As a result, considerably improved total energies during the SCF iterations are obtained reducing the error by a factor of $10^2$ to $10^4$. To achieve even a better accuracy attempts are in progress to improve the exchange-correlation functional [14].

Calculations using this method have shown good agreement with experiment. For $Au_2$, equilibrium bond length and dissociation energy are $R_e = 4.75$ Å and $D_e = 3.16$ eV [10], respectively, which can be compared with experimental values $R_e = 4.67$ Å and $D_e = 2.30$ eV. For $Hg_3^+$, the calculated $D_e$ is 2.87 eV [11], and the experimental value is 2.4 eV [12]. The latest version of the DS-DV method has been used to calculate dissociation energies of $RfCl_4$ and $SgCl_6$ (Rf – element 104; Sg – element 106) [15].

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*Corresponding author. Fax: 49 611 59712903; e-mail: v.pershina@gsi.de

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Another pronounced development has been observed in the methodology of ab initio DF methods [2]. A serious methodical problem for the many-electron systems is a treatment of the instantaneous electron–electron interaction (electron correlation). For heavy elements, correlation effects are known to be as large as relativistic effects [2]. Calculations using an uncorrelated version of the DF method have been performed for quite a number of transactinide molecules [19,20]. Correlated DF methods are still in the stage of development [17,18] to be applied to the very heavy systems.

Calculations using relativistic core potentials (RCP) [21] are also very promising, and such potentials have been recently developed for the elements Am through 112 [22]. Calculations of $Sg(CO)_6$ are in progress [22]. Less sophisticated quasirelativistic pseudopotentials (QRPP) have been applied to a larger extent to calculations of relatively small transactinide systems like HaO (Ha – element 105), 111H, $112F_2$ and $112F_4$ [23–25].

## 3. Recent results of the calculations of transactinide molecules using the DS-DV method and their discussion

### *3.1. Gas-phase compounds*

Calculations of dissociation energies and other spectroscopic constants of $MCl_4$ (M=Zr, Hf and Rf) and $SgCl_6$ (Sg=Mo, W and Sg) have been performed [15] using the new version of the DS-DV method [9]. As an example, a characteristic potential energy curve for $RfCl_4$ is shown in Fig. 1. Calculations of $D_e$ for $ZrCl_4$, $HfCl_4$ and $MoCl_6$, $WCl_6$ are in good agreement with experimental values, though the agreement for the bond lengths is less satisfactory. Table 1 shows a comparison of the DS-DV results for $MCl_6$ [15] with those obtained using the uncorrelated DF method [19,20]. The large discrepancy of the DF results with the experiment is accounted for by the lack of correlation. The new DS-DV results have confirmed the earlier made conclusion [16] about possible decomposition of $SgCl_6$ at high temperatures.

Table 1
Results of the calculations of $D_e$ and $R_e$ for $MCl_6$ (M=Mo, W and Sg)

| Method | $MoCl_6$ | $WCl_6$ | $SgCl_6$ | Refs. |
|---|---|---|---|---|
| $D_e$ (eV) | | | | |
| DS-DV | 20.97 | 22.18 | 20.05 | [15] |
| DF | 6.73 | 11.49 | 12.71 | [19,20] |
| Exp.[a] | 19.29 | 21.65 | (20.11)[b] | (See [16]) |
| $R_e$ (Å) | | | | |
| DS-DV | 2.33 | 2.36 | 2.45 | [15] |
| DF | 2.25 | 2.31 | 2.38 | [19,20] |
| Exp.[a] | 2.254 | 2.26 | (2.39)[b] | (See [16]) |

[a] Obtained via the Born–Haber cycle.

[b] Earlier estimates on the basis of the DS-DV results [16].

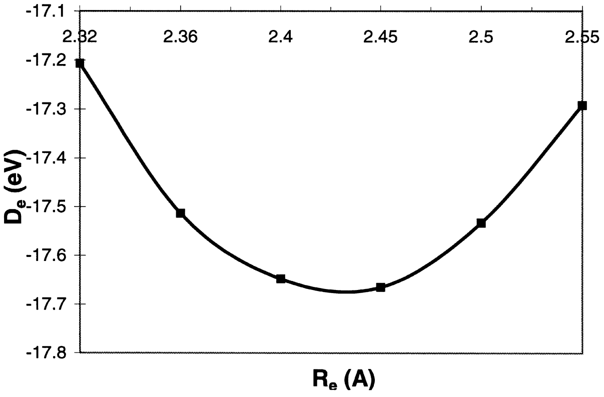

Fig. 1. Potential energy curve for $RfCl_4$ obtained as a result of the DS-DV calculations [15].

### *3.2. Transactinide complexes in aqueous solutions*

A particular progression has been recently achieved in predicting the stability of products of reactions such as hydrolysis or complex formation using the DS-DV method [26,27]. Since the total energies of large negative complexes cannot be calculated directly, a way was found to express a change in the free energy of a reaction via changes in both the electrostatic and covalent contributions to the metal–ligand bonding. This technique has been applied to predict hydrolysis and the complex formation of group 5 elements Nb, Ta, Ha and Pa. The former is expressed by the following equilibrium:

$$M(H_2O)_6^{5+} \Leftrightarrow M(OH)_6^- + 6H^+ \tag{1}$$

and the latter is given in a general form as

$$M(OH)_y^{(z-y)-} + aH^+ + aL^- \Leftrightarrow M(OH)_{y-a}L_a^{(z-y)-} + aH_2O. \tag{2}$$

For these reactions, $\log K = -\Delta G^r/2.3RT$, where $\Delta G^r$ is a free energy change, which can be calculated as a difference in the free formation energies $\Delta G^f$ of the components of the reactions. For a compound in a general form $M_xO_u(OH)_v(H_2O)_w^{(z-2u-v)+}$, the following expression for $\Delta G^f$ can be used [28]:

$$\begin{aligned} -\Delta G^f(u,v,w)/2.3RT = \sum a_i + \sum a_{ij} + \log Q \\ - \log(u!v!w!2^w) + (2u+v \\ + 1)\log 55.5. \end{aligned} \tag{3}$$

The second term on the right hand side, $\Sigma a_{ij}$, is a sum of each pairwise electrostatic interactions. It can be calculated using effective charges on atoms ($Q_i$) in a complex obtained as a result of the Mulliken population analysis [5] adopted in the DS-DV method:

$$2.3RT \sum a_{ij} = E^C = -B'Q_iQ_j/d_{ij}\varepsilon, \tag{4}$$

where $B'$ transforms the energy in eV; $d_{ij}$ is the metal–

ligand distance and $\varepsilon$ is an effective dielectric constant. The first term of Eq. (3), $\Sigma a_i$, is a covalent part of the binding energy and for any reaction its change, $\Delta E^{\mathrm{OP}}$, can be expressed as:

$$\Delta \sum a_i = \Delta E_{\mathrm{OP}} = K' \Delta \mathrm{OP}, \qquad (5)$$

where $K'$ is a coefficient, which can be estimated [26], and OP is the overlap population calculated using the same Mulliken numbers. The other terms are statistical. Thus, by defining the $\Delta E^{\mathrm{C}}$, $\Delta E^{\mathrm{OP}}$ and other terms of Eq. (3) for various complexes of interest, the free energy change of Eq. (1) or Eq. (2), and their equilibrium constants can be determined.

As an example, results of such calculations are presented in Table 2 for hydrolysis reaction (1). They show that a predominant factor in the total energy change $\Delta E^{\mathrm{t}}$, or $\Delta G^{\mathrm{r}}$, is a Coulomb energy difference $\Delta E^{\mathrm{C}}$. It means that as for the lighter elements of the periodic table, the electrostatic interaction defines the hydrolysis also for the heavier elements so that it decreases in the following order:

$$-\Delta G^{\mathrm{r}}, \text{ or } -\Delta E^{\mathrm{C}}: \mathrm{Nb} > \mathrm{Ta} > \mathrm{Ha} \gg \mathrm{Pa}. \qquad (6)$$

This electrostatic interaction has, however, been calculated on the basis of the real distribution of the relativistic electronic charge density. The simple electrostatic model, predicting hydrolysis constants to change linearly with the ratio of the cation charge to the ionic radius, is no more reliable since it does not reproduce even the difference between $\mathrm{Nb}^{5+}$ and $\mathrm{Ta}^{5+}$ (found experimentally [28]) having the same IR and formal charges.

Thus, a weaker hydrolysis of Ha in comparison with that of Nb and Ta has been predicted with the hydrolysis constant:

$$\log K_{16} = -5.25k - 3.29 + 14.51,$$

where $k$ can be defined if the $K$ for any lighter homolog of Ha is known [26].

For the formation of various complexes of these elements in HCl solutions, Eq. (2), the trend in the free energy change turned out to be also identical with the trend in $\Delta E^{\mathrm{C}}$:

$$-\Delta G^{\mathrm{r}}, \text{ or } -\Delta E^{\mathrm{C}}: \mathrm{Pa} \gg \mathrm{Nb} > \mathrm{Ha} > \mathrm{Ta}. \qquad (7)$$

This means that the complexes of Pa are formed at lower acid molarities, while for those of Ta higher $\mathrm{Cl}^-$ concentrations should be reached.

Table 2
$\Delta E^{\mathrm{C}}$, $\Delta$OP and $\Delta E^{\mathrm{t}}$ (eV) for hydrolysis reaction $\mathrm{M(H_2O)_6^{5+}} \Leftrightarrow \mathrm{M(OH)_6^-}$ (from [26])

| Parameter | Nb | Ta | Ha | Pa |
|---|---|---|---|---|
| $\Delta E^{\mathrm{C}}$ | 0.18 | 2.05 | 3.89 | 9.18 |
| $\Delta$OP | −0.89 | −0.89 | −0.85 | −0.51 |
| $\Delta E^{\mathrm{OP}}$ | 0.32 | 0.32 | 0.31 | 0.19 |
| $\Delta E^{\mathrm{t}}$ | 0.50 | 2.37 | 4.20 | 9.37 |

Applying the theory of the metal extraction by the anion exchange (which takes into account the complex formation) [29], the following trend in the $K_{\mathrm{D}}$ (distribution coefficient) values at the acid concentrations above 4–6 M HCl has been predicted [27]

$$K_{\mathrm{D}}: \mathrm{Pa} \gg \mathrm{Nb} \geq \mathrm{Ha} > \mathrm{Ta}.$$

Agreement of the theoretical results with the experiment on hydrolysis [28] and extraction of Nb, Ta, Ha and Pa [29–31] from HCl solutions by various amines is indicative of the reliability of the proposed model.

## 4. Conclusions

In summary, the improvements in the DS-DV method allow presently for calculating bonding in the very heavy systems with sufficient accuracy, though further developments are in progress. Particularly successful was the application of the DS-DV method to predict the equilibria of reactions. The ab initio DF methods are also under steady development. A combination of both the LDF and ab initio methods will be the best approach to study in future the electronic structure of the very heavy systems.

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