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Total Energy Calculations of $RfCl_4$ and Homologues in the Framework of Relativistic Density Functional Theory

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Calculations of total and binding energies of group IV tetrachlorides MCl_4 (M = Ti, Zr, Hf, and element 104, Rf) were performed using the four-component fully relativistic density functional method. The calculations show the binding energies to be in good agreement with thermochemical dissociation energies obtained via the Born−Haber cycle. The method therefore demonstrates a predictive power which is important for further applications in the area of the heavy element compounds.

I. Introduction

Since almost a decade, interest in the chemical behavior of the transactinide elements has been revived. A number of isotopes has been found with considerable lifetimes which actually allow for chemical processing and studying the chemical behavior of these elements. The chemical experiments have been performed during the last years for the elements 104−107. Test experiments are presently under way to study the chemical properties of element 108. A complete summary of the experiments can be found in ref 1.

Because of the fact that the generation of few atoms of these elements is very expensive, theoretical considerations should be of great and indispensable help. In this context, our groups have tried to study the chemical behavior of transactinides theoretically on the basis of three approaches. (A summary of this field can be found in two reviews.[2,3])

The first approach includes predictions of chemical properties on the basis of atomic multiconfiguration-Dirac−Fock (MCDF) calculations[4,5] similar to the very first predictions of the chemistry for all elements with nuclear charges above $Z = 100$ on the basis of Dirac−Slater calculations.[6,7] Here, one gets first information on the valence electron structure, atomic and ionic radii or energies of the first excited states, ionization potentials, etc. There are nowadays also state of the art atomic coupled cluster (CC) calculations[8] including dynamic correlation.[9]

A second approach includes relativistic molecular calculations using the discrete variational method (DVM) for the molecules containing transactinide elements.[10−12]

The third approach uses various models connecting molecular calculations with real processes taking place in the experiments. The physicochemical quantities, for example, formation enthalpies or volatilities which can be estimated by chromatographic experiments, are usually derived indirectly from the calculations by relating overlap populations or effective charges with thermodynamical considerations. The papers by Pershina et al. are good references for these procedures and methods.[2,3]

Presently, we have moved further in the development of the DV method so that calculations of the total and, hence, the binding energy (D_e) are now possible. Therefore, in the present publication we report on our results of the D_e calculations for the tetrachloride compounds MCl_4 (M = Ti, Zr, Hf, Rf).

This paper is organized as follows: in section II, the methods which have been applied so far to the calculations of the electronic structure of the MCl_4 molecules are summarized followed by a description of the DV method and computational details in section III. Section IV contains the discussion of the results and a comparison with other calculations. Finally, in section V, a summary and conclusions are given.

II. Earlier Calculations of the Group IV Tetrachlorides

First calculations of the electronic structure of the group IV tetrachloride compounds were performed by Ziegler et al.[13] who used an early version of the Amsterdam density functional (ADF) method.[14] Their results for the binding energies came out to be about 5−10% below the experimental values.[15] In addition, they found out that relativistic effects contributed only of the order of a few percent to the total binding energies and that the nonrelativistic results showed better agreement with the experiment. These facts may be not too astonishing because one deals here with a d^2 configuration of the heavy metal atom. Nevertheless, one has to be aware that for the element Rutherfordium relativistic effects become somewhat stronger, so that a full relativistic calculation is indispensable.

Next, we mention the calculations of $RfCl_4$ using the quasi-relativistic multiple scattering method,[16] the Dirac−Slater multiple scattering[17] and the relativistic DV methods.[18] In all of the methods, the exchange as well as the correlation potentials

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are treated in the framework of the density functional theory (DFT). The treatment of the exchange-correlation part via the Slater-X_α approximation and the inability to get numerically accurate total energies still was the drawback of all these methods. On this level of sophistication only quantities like energy eigenvalues, overlap populations or effective charges could be calculated and used to interpret the chemical behavior.

Recently, Malli[19,20] reported on Dirac−Fock calculations for these molecules. However, his results for the binding energy of the lighter tetrachlorides were too low in comparison with the experimental values because correlation is totally missing in this method. In contrast to his calculations, good correlation calculations for halides and oxides of the elements Rf, Db, and Sg on the level of Møller−Plesset perturbation (MP2) and coupled cluster approaches were presented by Han et al.[21] who, on the other hand, approximated the relativistic effects on the level of one- and two-component relativistic effective core potentials (REP). Their calculated bond energies for most of the compounds were very close to the values determined by Pershina with quite different physicochemical evaluations.[3]

In view of the recent development of the DV method, it is a great challenge to apply it now to calculations of the electronic structure and binding energies of larger molecules as well as heavier transactinides. Even for atoms, accurate values for the total energies are difficult to achieve. Thus, one can even be less expectant with respect to the accuracy of the molecular calculations. Nevertheless, every kind of improved molecular calculation is most welcomed and needed for better understanding of the physics and chemistry of heavy molecules concerning their chemical behavior.

III. Method and Computational Details

The rapidly increasing power of computational resources and further developments of the DV program made it now possible to improve the DVM scheme to a new quality. We have a numerical four-component code taking relativistic effects fully into account and being able to perform total energy calculations with a numerical accuracy up to few meV. A recent study using this new version of the method for the ground states of 5d and 6p element diatomic molecules showed agreement with experiments of the order of 0.1−0.2 eV for the binding energies,[22] which demonstrates its predictive power. Here, the main features of the method are briefly summarized. More details about the molecular calculations may also be found in refs 23 and 24.

Starting from the no-pair approximation and neglecting the minor important contributions from the spatial components of the four-current $j^\nu(\vec{r}) = (j^0,\vec{j})$, the total energy (we use atomic units throughout) may be written as

$$E[n] = T_s + E_{\text{ext}}[n] + E_{\text{H}}[n] + E_{\text{xc}}[n] \tag{1}$$

with the density

$$j^0(\vec{r}) = n(\vec{r}) = \sum_{-mc^2<\epsilon_k\leq\epsilon_F} \psi_k^\dagger(\vec{r})\psi_k(\vec{r}) \tag{2}$$

constructed of N auxiliary one-particle Dirac spinors. This leads to the corresponding relativistic Kohn−Sham equations

$$([-ic\vec{\alpha}\cdot\vec{\nabla} + (\beta - 1)mc^2] + v_{\text{ext}}(\vec{r}) + v_{\text{H}}(\vec{r}) + v_{\text{xc}}(\vec{r}))\psi_k = \epsilon_k\psi_k \tag{3}$$

Here, the first term represents the kinetic energy and the second is the interaction of the electrons with the potential induced by the nuclear charges Z_α

$$v_{\text{ext}}(\vec{r}) = -\sum_\alpha \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}|} \tag{4}$$

The third term is the electrostatic interaction which is represented by the Hartree potential

$$v_{\text{H}}(\vec{r}) = e^2\int \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}d\vec{r}\,' \tag{5}$$

In the practical calculations, this term is evaluated by a multipolar expansion of an auxiliary charge density.[22,25] Finally, the last term denotes the exchange-correlation energy from which the exchange-correlation potential is derived as

$$v_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})} \tag{6}$$

For the selfconsistent solution of eq 3, the relativistic local density approximation (RLDA)[26] is applied (using the Vosko−Wilk−Nusair parametrization for correlation[27]), whereas the relativistic forms of the generalized gradient approximation (RGGA)[28] originally proposed by Becke for exchange[29] and Perdew for correlation[30] are added perturbatively in order to account for nonlocal schemes (post-LDA method). It should be emphazised that the relativistic treatment of the exchange-correlation functionals, denoted as RLDA and RGGA, respectively, has a negligible impact on the binding properties.[24,31] All matrix elements are evaluated by the highly accurate numerical three-dimensional multicenter integration scheme of te Velde and Baerends.[32] The molecular wave functions are obtained by a linear combination of numerical four-component atomic Dirac−Spinors. The corresponding relativistic Kohn−Sham equations are solved self-consistently thus enabling calculations of the total energy according to eq 1.

The molecular calculations were done in T_d symmetry which was found to be the most optimal for the MCl_4 (M = Ti, Zr, Hf, Rf) species. An optimized basis set was constructed in the following way: in a first step, molecular calculations were done with a minimal basis set which is taken from numerical atomic wave functions of neutral Cl and the central atoms (Ti, Zr, Hf, or Rf). As a result of these calculations, the total energy as a function of the internuclear metal−ligand distance was obtained. Because of the large electronegativity of the chlorine atoms there is a polarization of the electronic charge distribution (a slightly positively charged central atom and negatively charged chlorine atoms) leading to fractional occupation numbers of the valence orbitals. The atomic basis functions were recalculated with these new atomic occupations in order to include polarization effects in a consistent way. To be more complete, in a second step, further unoccupied *n*p and *n*d atomic wave functions were added to the basis sets of the central atoms Ti, Zr, Hf, and Rf. Additionally, wave functions with a 3d and 4s character obtained from slightly (≈2.0) ionized atoms were included for the chlorine basis. These wave functions were shifted toward the binding region. The inclusion of the additional basis sets led to changes in the total energy by approximately 3 eV (compared to the minimal basis sets), reflecting the importance of careful adjusting the basis sets. The addition of further basis functions did not change the energies anymore. Finally, the total energies were recalculated for all internuclear arrangements around the equilibrium geometry (in the assumed T_d symmetry) with the optimized basis.

TABLE 1: Binding Energies for the Tetrachlorides $TiCl_4$, $ZrCl_4$, $HfCl_4$ and $RfCl_4$

	RLDA(eV)	RGGA(eV)	atom corr (eV)	theor (eV)	exp (eV)[a]
$TiCl_4$	22.75	20.81	−0.58	20.23	17.81
$ZrCl_4$	23.80	21.98	−0.30	21.68	20.35
$HfCl_4$	23.30	21.46	−0.32	21.14	20.61
$RfCl_4$	21.65	19.75	−0.25	19.50	

[a] Reference 15.

The binding energy of the molecules under consideration would have been obtained simply by subtracting the total energy of the atoms from the total energy of the molecule. This would be no problem in case the atomic ground-state calculations were correctly defined. However, due to our density functional approach, this cannot in general be done for a specific total angular momentum for the single atoms. Instead of the ground-state energy, a weighted average value of the multiplet according to the partially occupied electronic levels is obtained. The procedure to correct for this difference has been discussed in some length in the publication of van Lenthe et al.[33] There is no such problem, however, for Cl because relativistically there is one $2p_{3/2}$ hole, giving a single state with $J = {}^3/_2$. But in the case of Ti, Zr, Hf, and Rf with the d^2 outer shell, one would have nonrelativistically the fully developed multiplets ^3F, ^1D, ^3P, ^1G, and ^1S with the atomic corrections being the difference between the average of the multiplet (calculated within DFT) and the true groundstate. Fortunately, in the relativistic calculation the "ground state" develops from the configuration $(d_{3/2})^2$ only. This *jj*-coupled configuration splits into the $J = 2$ ground state and the first excited $J = 0$ state. Thus, we have performed atomic MCDF calculations for these states and come up with corrections for the average of the *jj* multiplet and the $J = 2$ ground state of −0.58 eV for Ti, −0.30 eV for Zr, −0.32 eV for Hf, and −0.25 eV for Rf.

IV. Results and Discussion

Table 1 shows the results of our calculations for the binding energies of the four tetrachlorides $TiCl_4$, $ZrCl_4$, $HfCl_4$, and $RfCl_4$. In the first column, the values for the binding energies within the RLDA are listed. Nonlocal corrections, introduced by the RGGA, are given in column 2. All the values were calculated by subtracting the total energies of the atoms from total energy of the molecule after the atomic density functional calculations in the same approximation had been performed. The last part of the discussion in section III makes it clear that the atomic values had to be corrected due to the multiplet splitting corrections. The atomic corrections are given in the third column of Table 1. The final theoretical values are presented in the second last column which can be compared with the experimental binding energies for the tetrachlorides[15] (last column of Table 1). The latter ones were calculated via the Born−Haber cycle for the formation enthalpies and, therefore, have a definite inaccuracy of the experimental measurements, in average, of the order of 10%. Surprisingly, looking at the data of Table 1, a larger difference between experimental and theoretical values for the low-*Z* compound $TiCl_4$ can be observed. To check our results, the binding energy and the geometry of this molecule were calculated with the relativistic Amsterdam density functional method[32] including spin−orbit coupling and using the same exchange-correlation potential GGA (post-LDA) approach. Relativistic extensions to the exchange-correlation potentials are not available in this method, so that the ADF energies are denoted by LDA and GGA, respectively. However, as pointed out in section III, the relativistic forms of the LDA (RLDA) and GGA (RGGA) have only marginal influence on the binding properties. After the geometry optimization, the calculated binding energies (from spin-unpolarized calculations) for the LDA as well as the GGA turned out to be quite close to our results. For this low-*Z* system relativistic effects are very small and have no significant contribution to the binding behavior. In particular, the ADF-LDA binding energy of 22.81 eV can be compared with our value of 22.75 eV obtained in our four-component calculations at the same internuclear geometry (listed in Table 3). A slightly larger but marginal difference was observed for the GGA energies. The ADF post-LDA calculation gives $D_e = 20.89$ eV whereas our value is 20.81 eV for the binding energy. For this molecule the difference in the energy on the local as well as the nonlocal level obtained by the two-component compared with the four-component approach is less than 0.1 eV. The same analysis for the somewhat heavier $ZrCl_4$ molecule gives $D_e = 23.80$ eV for our RLDA binding energy compared with the ADF-LDA result of 23.94 eV. Our calculated RGGA binding energy is $D_e = 21.98$ eV, whereas the ADF-GGA result is 22.15 eV. This small but significant difference (0.14 and 0.17 eV for the LDA and GGA, respectively) can be attributed to the influence of the relativistic effects. Taking into account the good agreement between our and the ADF result for the lightest tetrachloride $TiCl_4$, we can conclude that our values are consistent within the density functional approach.

TABLE 2: Optimized Bond Distances for the Tetrachlorides $TiCl_4$, $ZrCl_4$, $HfCl_4$, and $RfCl_4$

	RLDA (au)	RGGA (au)	exp (au)
$TiCl_4$	4.08	4.16	4.10[a]
$ZrCl_4$	4.39	4.43	4.38[b]
$HfCl_4$	4.36	4.43	4.376[b]
$RfCl_4$	4.46	4.54	

[a] Reference 34. [b] Reference 35.

TABLE 3: Comparison of the Final Results for the Bond Distances and Bond Energies for $RfCl_4$ from the Various Publications

method	r_e (au)	D_e (eV)	ref
REP-KRHF[a]	4.51	16.9	21
AREP-MP2	4.42	20.4	21
REP-CCSD(T)	4.50	18.8	21
DFB[b]	4.51	15.5	20
4-comp RLDA	4.46	21.4	this work
4-comp RGGA	4.54	19.5	this work

[a] Relativistic effective core potential with Kramers' restricted Hartree−Fock. [b] Dirac−Fock−Breit. All other abbreviations are explained in the text.

Table 2 presents the values for the bond distances. A shift toward the larger values can be observed in going from the RLDA to RGGA. The same general trend was observed in a former investigation on diatomic molecules.[24] Additionally, it was found out that in the high-*Z* regime the RLDA binding distances are in better agreement with the experimental data than the RGGA values, which can also be observed in the present investigation for the MCl_4 molecules.

In Table 3, the values for the binding energy of $RfCl_4$ are compared with those of Han et al.[21] The averaged-spin REP-MP2 (AREP-MP2) calculation gives $D_e = 20.4$ eV while their REC−CCSD(T) method with correlation leads to 18.8 eV. Our value for the binding energy of 19.5 eV is just between their estimated values.

V. Summary and Conclusion

In this work we have applied the improved version of the DVM to compounds of the very heavy relativistic 6d element

Rf and its lighter homologues. As was shown in the earlier publications for diatomic molecules,[22,24] the consistent inclusion of the gradient corrections for the exchange-correlation potential as well as the correct calculation of the Hartree potential v_H (5) is mandatory. We also conclude that the energetics of the compounds are improved by the RGGA as compared to the RLDA, while the bond lengths are slightly overestimated by the RGGA which make them less accurate in comparison with the experiment. The atomic corrections for the ground state slightly improve the binding energies.

The rather good agreement between the calculated and experimental results, as well as the similarity between our binding energy for $RfCl_4$ and that obtained using the REP-CCSD(T) method shows that our RDFT method has a predictive power. The experimental trends in the D_e and R_e values (except of D_e for $HfCl_4$ in relation to $ZrCl_4$) are well reproduced, which demonstrates that the method is accurate enough and can be used to study the chemical properties of very heavy elements. Especially important is the application of the method for predictions of the heavy-element behavior in gas-phase chromatography experiments. There, at very high temperatures, a decomposition of studied species (e.g., $SgCl_6$, where Sg is element 106) could occur, so that the knowledge of their thermal stability is indispensable.

Besides, in the case of some other heavy element compounds, like for example volatile acid of Sg, the adsorption of molecules on the surface of the chromatography column takes place simultaneously with their decomposition. Thus, calculations of the energies of the decomposition reactions or the energies of formation of new species are very important for prediction of their chromatographic behavior.

In line with the current experimental research, our further theoretical investigations will be devoted to calculations of the electronic structure and bonding of other heavy-element systems, simultaneously giving an additional information about the reliability of our approach.

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