Inorganica Chimica Acta, 94 (1984) 297–299

Comparison of Non-Relativistic and Quasi-Relativistic SCF-Xα Scattered-Wave Calculations of Uranocene, Thorocene and Cerocene

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Received October 10, 1983

The results of non-relativistic and quasi-relativistic SCF-Xα-SW calculations of uranocene, thorocene and cerocene are analyzed on the basis of selected orbital energies and charge distributions. The character of the ring–metal bonding is discussed. The f-orbital expansion found in previous non-relativistic molecular calculations is interpreted as a consequence of the Xα approximation by comparison of Xα model ground states of the corresponding metal atoms.

Introduction

Non-relativistic SCF-Xα Scattered-Wave (SW) calculations of uranocene and thorocene have shown [1] that $5f_{\pm 2}$ orbitals of the central atom contribute to ring–metal bonding, just as proposed at the time of the preparation of these compounds [2], but that 6d orbitals are also important. The agreement with photo-electron spectra was very satisfactory, even for the first ionization potential of uranocene. To clarify this success and to investigate the influence of relativistic effects on the bonding description of these compounds, quasi-relativistic Xα-SW calculations on $M(C_8H_8)_2$, M = U, Th, Ce have been performed [3]. It is the purpose of this paper to elaborate on these topics.

The quasi-relativistic Xα-SW method [4] allows for a fully relativistic treatment of the core electrons. Relativistic effects in the intersphere region are neglected even for valence electrons, resulting in a satisfactory approximation. The mass-velocity correction and the Darwin shift are taken into account, however, when calculating the logarithmic derivative of the radial wave-functions at the sphere boundaries. All calculations have been performed with the same idealized geometry and the same model parameters employed previously [1, 3].

Results and Discussion

The following discussion will be based on the energy and charge distribution of some characteristic molecular orbitals: the two highest filled orbitals with ligand π-character, $e_{2g}(\pi)$ and $e_{2u}(\pi)$, and the lowest and highest lying orbitals of metal f-character, $e_{3u}(f)$ and $e_{2u}(f)$. The resulting orbital energies and charge fractions in the metal sphere, both for non-relativistic and quasi-relativistic Xα-SW calculations, are collected in Tables I and II, respectively. The $e_{2u}(\pi)$ orbital is the HOMO in the closed-shell systems cerocene and thorocene, whereas two electrons occupy the $e_{3u}(f)$ level in uranocene.

As a general result one finds, not unexpectedly, relativistic effects larger for thorocene and uranocene than for cerocene. Very striking, however, is the rather small upward shift of the 5f(4f) manifold due to relativistic corrections. This fact may best be appreciated by comparing the corresponding shifts of atomic Xα eigenvalues. As an example, consider the 5f eigenvalue(s) of uranium in the configuration $5f^3\,6d^1\,7s^2$ which shift from −0.673 Ry to −0.198 and −0.138 Ry in a relativistic atomic Xα calculation (*cf.* Fig. 1, x = 0 and y = 0). This shift is caused by the well-known relativistic core contraction, mainly of the s and p electrons. The concomitant expansion of the 5f wavefunction renders these orbitals suitable for interaction with ligand π-orbitals. In the non-relativistic calculations of the molecules under study there is a comparable metal–ligand interaction as may be concluded, for example, from the energy of the $e_{3u}(f)$ orbital and the metal charge fraction in the $e_{2u}(\pi)$ orbital. What effect then is responsible for the f orbital expansion in the non-relativistic description?

A peculiarity of the Xα formalism may provide an answer to this question. The large differences in the atomic valence orbital energies between non-relativistic and relativistic calculations disappear when one compares Xα ground states instead of states with the experimental configuration. In the Xα model ground state [5] Fermi statistics is fulfilled, *i.e.* the levels must be filled strictly from below. To avoid partially filled levels below occupied other levels (*e.g.* as found for the uranium atom in the configuration $5f^3\,6d^1\,7s^2$, see Fig. 1) and to reach the Xα ground state, one has to redistribute electrons

0020-1693/84/$3.00

TABLE I. Comparison of Non-relativistic and Quasi-relativistic Xα-SW Molecular Orbital Energies for Cerocene, Thorocene and Uranocene (Energies in Ry).

Molecular orbital	Ce		Th		U	
	non-rel.	qu.-rel.	non-rel.	qu.-rel.	non-rel.	qu.-rel.
$e_{2u}(f)$	−0.200	−0.187	−0.143	−0.069	−0.186	−0.149
$e_{3u}(f)$	−0.257	−0.243	−0.243	−0.181	−0.280	−0.242
$e_{2u}(\pi)$	−0.313	−0.312	−0.333	−0.330	−0.335	−0.330
$e_{2g}(\pi)$	−0.373	−0.381	−0.385	−0.404	−0.367	−0.387

TABLE II. Orbital Charge Fractions in the Metal Sphere for Non-relativistic and Quasi-relativistic Xα-SW Calculations of Cerocene, Thorocene and Uranocene.

Molecular orbital	Ce		Th		U	
	non-rel.	qu.-rel.	non-rel.	qu.-rel.	non-rel.	qu.-rel.
$e_{2u}(f)$	0.628	0.690	0.670	0.786	0.544	0.674
$e_{3u}(f)$	0.963	0.955	0.899	0.780	0.944	0.907
$e_{2u}(\pi)$	0.392	0.330	0.329	0.203	0.462	0.327
$e_{2g}(\pi)$	0.190	0.206	0.190	0.211	0.165	0.198

or fractions thereof such that all partially filled orbitals have the same energy, all lower ones being completely filled.

Slater [5] has traced this property of the Xα ground state to the fact that the Xα orbital eigenvalue ϵ_k equals the derivative of the total energy E with respect to the orbital occupation number n_k:

$$\frac{\partial E}{\partial n_k} = \epsilon_k .$$

If one redistributes electrons from orbital 1 to orbital 2, keeping their total number constant,

$$n_1 + n_2 = n_1^o + n_2^o = n,$$

one obtains the change ΔE in total energy to first order as

$$\Delta E(n_1, n_2) = (\epsilon_1 - \epsilon_2)(n_1 - n_1^o).$$

For the ground state one concludes $\epsilon_1 = \epsilon_2$.

The resulting procedure to find an atomic Xα ground state is illustrated for uranium in Fig. 1, both for the non-relativistic and the relativistic treatment. The non-relativistic ground state of uranium (non-spin-polarized description) has the configuration $5f^{4.66}$ $6d^0$ $7s^{1.34}$ with the highest occupied levels at −0.151 Ry for 5f and 7s. The relativistic Xα ground state with its configuration $5f^{3.41}$ $6d^{0.59}$ $7s^2$ is close to the experimental findings. The highest occupied levels at −0.117 Ry are now $5f_{5/2}$ and $6d_{3/2}$. However, while the high position of the relativistic 5f levels is due to genuine shielding effects of contracted core orbitals, the almost comparable energy of the 5f level in the non-relativistic case is a consequence of enhanced electron–electron repulsion in a level carrying an augmented occupation. A comparison of non-relativistic and relativistic Xα atomic ground state configurations for cerium, thorium and uranium is given in Table III. The relativistic Xα ground state configurations for thorium and uranium show a strong improvement over the non-relativistic results. Again, relativistic effects for cerium are smaller.

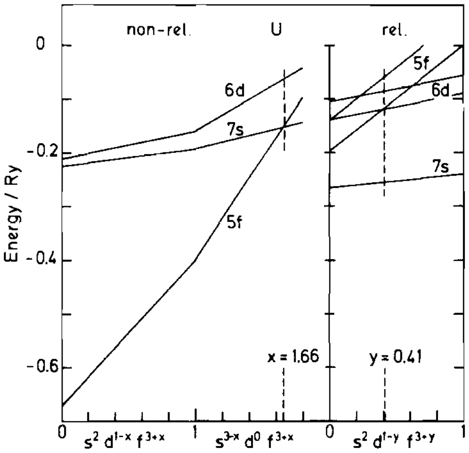

Fig. 1. Comparison of non-relativistic and relativistic Xα atomic eigenvalues of 5f, 6d, and 7s orbitals of uranium as a function of occupation numbers.

The differences between the non-relativistic and relativistic atomic Xα ground states are reflected to some extent in the corresponding molecular results. This is especially clear when one considers the upward shift of the metal f orbitals (*e.g.* $e_{2u}(f)$ and $e_{3u}(f)$; see Table I). Even the $e_{2u}(\pi)$ orbitals rise in energy, though to a much smaller degree, due to the metal f contribution. All other molecular orbitals

TABLE III. Comparison of Non-relativistic[a] and Relativistic Xα Atomic Ground State Configurations for Cerium, Thorium, and Uranium.

	Ce		Th		U	
	non-rel.[b]	qu.-rel.[c]	non-rel.[d]	qu.-rel.[e]	non-rel.[d]	qu.-rel.[e]
s	2	2	1.86	2	1.34	2
d	0	0.41	0	1.72	0	0.59
f	2	1.59	2.14	0.28	4.66	3.41

[a] Non-spin-polarized calculation; [b] 4f 5d 6s; [c] $4f_{5/2}$ $5d_{3/2}$ $6s_{1/2}$; [d] 5f 6d 7s; [e] $5f_{5/2}$ $6d_{3/2}$ $7s_{1/2}$.

TABLE IV. Partial Wave Analysis for the Valence Electrons of the Metal Atom Based on Non-relativistic and Quasi-relativistic Xα-SW Calculations for Cerocene, Thorocene and Uranocene.

	Ce		Th		U	
	non-rel.	qu.-rel.	non-rel.	qu.-rel.	non-rel.	qu.-rel.
s	0.187	0.228	0.152	0.265	0.159	0.281
p	0.263	0.294	0.140	0.206	0.167	0.247
d	1.519	1.617	1.554	1.692	1.384	1.593
f	1.864	1.619	1.741	1.205	4.136	3.504
Total	3.833	3.758	3.587	3.389	5.846	5.625

undergo a downward shift in the quasi-relativistic calculation (see $e_{2g}(\pi)$ in Table I), much as atomic s and d orbitals in the Xα ground state. Correlated with these energy shifts one observes changes in the localization of the molecular orbitals. The f orbital contribution to the $e_{2u}(\pi)$ orbital decreases in the quasi-relativistic calculations whereas a slight increase is found for the metal d contribution of the $3_{2g}(\pi)$ orbital (see Table II). The reduced localization of the non-bonding $e_{3u}(f)$ orbital in the quasi-relativistic case reflects the relativistic f orbital expansion. The increased localization of the antibonding $e_{2u}(f)$ correlates perfectly with the smaller f orbital character of the $e_{2u}(\pi)$ orbital.

These trends in changes of the metal contribution to the various molecular orbitals are amplified when summed over all orbitals in the valence region. The results of such a partial wave analysis in the metal sphere are collected in Table IV. The quasi-relativistic description shows a weaker population of the metal f orbitals for all three compounds and a stronger population of d, s, and p orbitals (changes in this order). All relativistic effects discussed above conform to the ordering Ce < Th < U.

The electronic structure of the compounds $M(C_8H_8)_2$, M = Ce, Th, U, and especially the ring–metal bonding, has been compared in detail elsewhere [2]. The material presented here may be used to add some comments on the relative covalent/ionic character of the ring–metal bonding in this series.

A rather straightforward case seems to be the amount of f-orbital covalency. As possible criteria one may take the charge fraction of the metal sphere in the $e_{2u}(\pi)$ orbital (Ce: 0.33; Th: 0.20; U: 0.33), the total f-wave population in the metal sphere (Ce: 1.62; Th: 1.12; U: 1.69, excluding the contribution from the $e_{3u}(f)$ orbital), and, because of the roughly constant d-orbital covalency in the $e_{2g}(\pi)$ orbital, the $e_{2u}(\pi)$–$e_{2g}(\pi)$ splitting (Ce: 0.069; Th: 0.074; U: 0.057 Ry). Stronger covalency in the latter case is indicated by a smaller splitting. Therefore one deduces from all three criteria increasing f-covalency in the order Th < Ce < U. The splitting of the metal f-orbitals in the ligand field, on the other hand, increases in the order Ce < U < Th.

If we were to derive an atomic charge from the total population of the metal sphere (Ce: 0.24; Th: 0.61; U: 0.38; see Table IV) we deduce increasing ionicity in the order Ce < U < Th. For the two actinide compounds these findings seem to agree with experiment [6]. Unfortunately, the present discussion does not provide a completely satisfactory picture for the relative strength of ring–metal covalency. A caveat may be in order here, concerning the uniform model geometry employed in all calculations of this work [1, 3]. Although a comparative study such as the present one becomes meaningful only under the assumption of uniform muffin-tin errors, there will certainly be limitations to such a model. This has to be kept in mind, especially while comparing any results for cerium with those for the two actinide atoms based on the same muffin-tin sphere size.

Acknowledgements

The author thanks A. Streitwieser for his encouraging interest and for many stimulating discussions. This work was supported in part by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie, Frankfurt, by the Bund der Freunde der TU München, and by NATO grant No. 1237.

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