

Dirac-Fock one-centre expansion calculations on the molecular model systems ThH₄ and UH₆

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Résumé. — On présente certains résultats de calculs relativistes Dirac-Fock à un centre pour les systèmes modèles ThH₄ et UH₆. Les hybridations, les distributions radiales et l'influence des 5f : s sur la distance de liaison sont discutées. Une valeur de 30 pm est prédite pour la contraction actinidique.

Abstract. — Relativistic Dirac-Fock one-centre expansion calculations are presented for the molecular model systems ThH₄ and UH₆. The hybridizations, the radial distributions and the effect of the 5f : s on the bond length are discussed. A value of 30 pm is predicted for the actinoid contraction.

Relativistic effects influence strongly the chemical properties of the latter half of the periodic system (for a review, see e.g. Ref. [1]). We are studying these effects by Dirac-Fock one-centre expansion calculations on the covalent model hydrides MH_n. These seem to be sufficiently realistic so that e.g. the covalent radii of the central atom may be obtained [2]. For the MH_n systems (M = Ti, Zr, Hf, Th, Cr, Mo, W), the calculated M-H bond lengths differ in the average from the experimental

M-X by 16, 39, -3, 42, 55 and 75 pm (picometers) for X = H_{bridge}(BH₄), C(σ), F, Cl, Br and I, respectively. This suggests a *hydridic* hydrogen covalent radius of 58 pm. Then a comparison between UH₆(f⁰) and (106)H₆(f¹⁴) (see Fig. 1) may be used to get a value of 30 pm for the actinoid contraction of bond lengths. A comparison between ThH₄ and (104)H₄ (taken from Ref. [3]) leads to the same value. As seen from figure 1, adding the 5f : s shortens the U-H bond by 22 pm. For ThH₄ the corresponding value is only 8 pm.

The hybridizations of ThH₄ and UH₆ are shown in table I. The electron configurations mentioned in the table caption are the relativistic equivalents of the (a₁)² (t₂)⁶ and (t_{1u})⁶ (e_g)⁴ ground states of ThH₄(T_d) and UH₆(O_h), respectively. We emphasize that the ThH₄ 5f : s are centred on the hydrogens while the UH₆ 5f : s exhibit both an *inner* radial density maximum around 1.3 a.u. and an *outer* one at the ligands. Although all these orbitals s-f are partially a description of the hydrogens in the one-centre model used, they also are partially *true* 7s, 7p, 6d and 5f orbitals of the metal atom. It is thus quite appropriate to speak of s-p-d hybridization of Th and s-p-d-f hybridization of U in the present molecular model systems.

The 7p shells are more diffuse than the 6d shells.

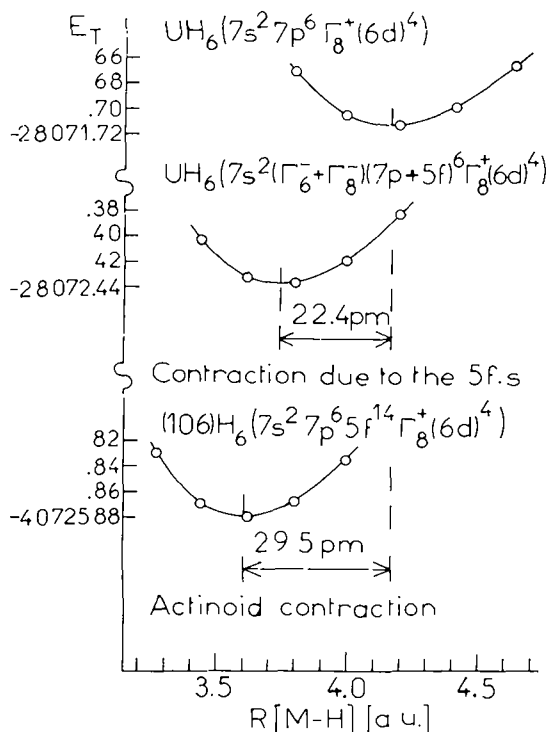


Fig. 1. — Dirac-Fock potential energy curves for UH₆ (without and with the 5f functions) and for (106)H₆. The total energy E_T(R) is given in atomic units.

Table I. — Hybridizations for ThH₄ at R = 3.868 a.u. assuming the electron configuration Γ₆(s + f)² (Γ₇ + Γ₈) (p + d + f)⁶ and for UH₆ at R = 3.8 a.u. assuming the electron configuration (7s)² (Γ₆⁻ + Γ₈⁻) (p + f)⁶ (Γ₈⁺(d))⁴.

System	Hybridization
ThH ₄	7s ^{0.81} 7p ^{0.87} 6d ^{1.92} 5f ^{0.40}
UH ₆	7s ¹ 7p ^{1.44} 6d ² 5f ^{1.56}

Therefore their norm, $N(7p)$, increases with increasing R . Adding the $7p : s$ to the basis increases very considerably the long-range force on the hydrogens. This suggests that a good hydrogenation catalyst should have, close to its ground state electron configuration other originally unoccupied but energetically accessible AO : s (here $7p$) that provide sufficient bonding at the various $R : s$ involved in the reaction. A more detailed discussion will appear shortly [2].

References

- [1] PYYKKÖ, P., *Adv. Quantum Chem.* **11** (in press).
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- [3] PYYKKÖ, P. and DESCLAUX, J. P., *Chem. Phys. Lett.* **50** (1977) 503.