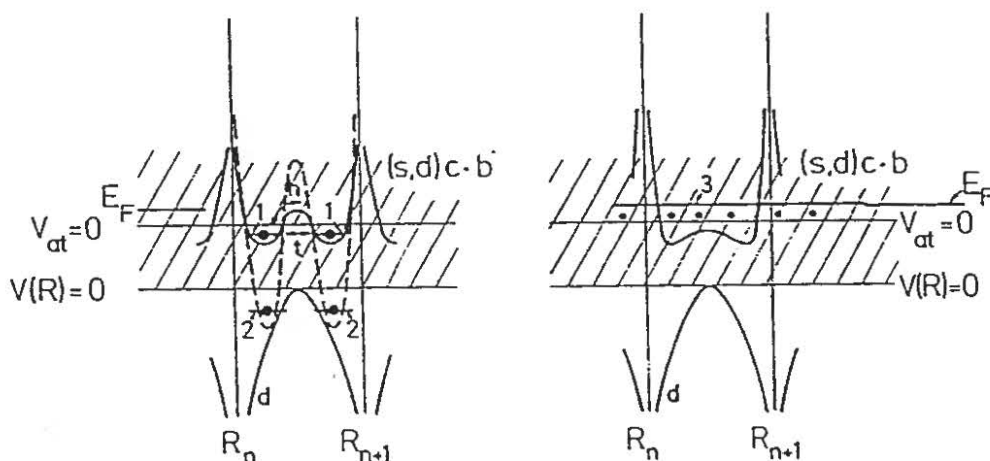


Many chemists have for years harbored the notion that f-orbitals (*i.e.*, orbitals with $l=3$) do not become involved in chemical bonding since they possess limited radial extension and/or are energetically "buried" in the atom compared with the d-orbitals. While these arguments are generally true for the 4f orbitals of the lanthanides,¹ the same cannot be said for all of the elements making up the 5f actinide group. In fact, whereas the reactivity of the lanthanides are all very similar, the actinides are best divided into two groups: the "light" actinides, which include the elements Th through Pu; and the "heavy" actinides, which encompass the remaining elements. While the heavy actinides are "lanthanide-like" in many respects, the light actinides more closely resemble the transition metals, and hence comprise a "5f transition series" rather than a "5f lanthanide" group.

A major problem associated with studying the actinides is the necessity for a relativistic treatment of these systems, since spin-orbit and other effects become very large ($\hat{H}_{s-o} \approx 10^3 - 10^4 \text{ cm}^{-1}$). Theoretical work in this area has been difficult, and band theoretical calculations of actinide solids and intermetallic compounds are currently on the forefront of solid-state research.^{2,3} A simplified picture of the band structure of an actinide solid is given below.⁴

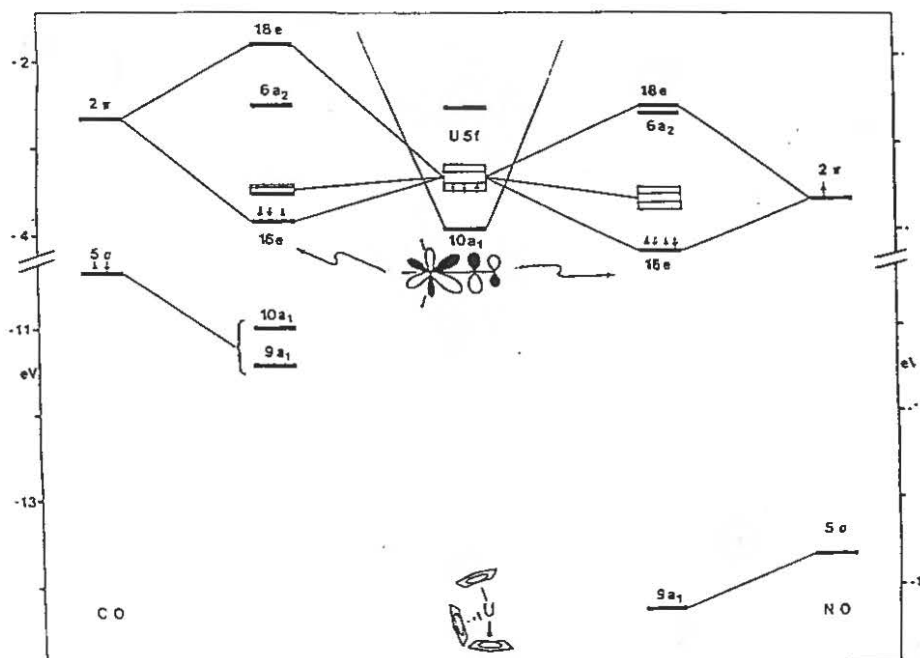


Determining whether the f-electrons are localized (state 2 in the above) or itinerant (*i.e.*, delocalized, state 3) directly addresses the question of f-f overlap in the solid. Experimentally, it is found that light actinide solids generally exhibit itinerant behavior, while the heavy actinides can best be described as localized systems.⁵

Although Moffitt originally proposed in 1956 that there was f-orbital involvement in $(\pi-C_5H_5)_3UCl$, this suggestion received little attention at the time.⁶ However, the synthesis and characterization of uranocene⁷ has led to a resurgence of actinide research in the past fifteen years.⁸ There is now convincing experimental and theoretical evidence of f-orbital participation in the bonding of the bis(cyclooctatetraenyl)actinides, $M(COT)_2$.^{7b,d,e} Much effort over the past decade has been directed toward elucidating the nature of the σ - and π -bonding in various actinide complexes.

Although the f-orbital interaction in the $M(COT)_2$ complexes is strictly π -bonding in nature, Tatsumi and Hoffmann's successful extended Hückel calculations⁹ analyzing of the linearity of the uranyl ion, UO_2^{+2} , prompted further work in the area of f-orbital σ -bonding. Recent synthetic^{10,2} and theoretical studies¹¹ have indicated that although f-orbitals do participate to some extent in the formation of σ bonds, the majority of the metal-ligand interaction involves the 6d orbitals.¹²

The recent synthesis of the first molecular carbonyl compound of uranium by Andersen,¹³ $(Me_3SiC_5H_4)_3UCO$, prompted Bursten to study the bonding of a series of tris(cyclopentadienyl)actinide complexes.¹⁴ X α -SW calculations indicate that the experimentally observed 170 cm^{-1} reduction in ν_{C-O^*} for $(Cp')_3UCO$ is due to π back-bonding from the metal f-orbitals into the π^* orbital of CO.^{14a}



Bursten's studies have further indicated that, although σ -bonding in Cp_3UL complexes primarily involves the 6d orbitals of the actinide, f-orbital π back-bonding is a major factor contributing to the stability of these compounds.^{14c}

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