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The Quasi-relativistic Xα-SW Molecular Orbital Method in Organo-f-element Chemistry: Applications to UCl_4, $(\eta^5\text{-}C_5H_5)_4U$ and $(\eta^5\text{-}C_5H_5)_2UCl_2$*

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Abstract

The advantages and disadvantages of using the Xα scattered-wave molecular orbital method with quasi-relativistic corrections for the calculation of the electronic structure of organo-f-element compounds is discussed. Application of the method in organouranium chemistry is discussed via comparative calculations on UCl_4, $(\eta^5\text{-}C_5H_5)_4U$, and $(\eta^5\text{-}C_5H_5)_2UCl_2$. It is found that the $\eta^5\text{-}C_5H_5^-$ ligand is a better donor to U than is Cl^- and that the valence orbitals of $(\eta^5\text{-}C_5H_5)_2UCl_2$ are energetically closer to those of $(\eta^5\text{-}C_5H_5)_4U$ than UCl_4. The calculational results are in excellent accord with experimental photoelectron spectroscopic studies.

Introduction

The recent rapid growth in the organometallic chemistry of the lanthanide and actinide elements poses several interesting challenges to electronic structural chemists [1–5]. Foremost among these is providing an accurate description of the interaction of organic ligands with metal f-orbitals, and investigating how these are similar to or different from those with the d-orbitals of transition elements. The earliest attempts to provide such descriptions were undertaken on the highly symmetric molecules $(\eta^8\text{-}C_8H_8)_2U$ [6] and $(\eta^6\text{-}C_6H_6)_4U^{4+}$ [7], where the latter unknown complex was treated as an analogue of the pseudo-tetrahedral complex $(\eta^5\text{-}C_5H_5)_4U$. In each of the above examples, the high symmetry (D_{8h} or T_d) of the system dictates to a large extent which interactions between metal and ligand will dominate, and hence quantitatively accurate calculations serve only to 'fine-tune' the symmetry-driven bonding description. It is also notable that the $(\eta^8\text{-}C_8H_8)_2M$ and $(\eta^n\text{-}C_nH_n)_4M$ ($n = 5, 6$) structural frameworks are unique to the f-elements and have no analogues among the transition metal elements.

It is becoming clear that one of the most important classes of organo-f-element complexes is that of formulation $Cp^*_2MX_n$, where $Cp^* = \eta^5\text{-}C_5Me_5$ and n is generally equal to 1 or 2. These systems, in contrast to the ones mentioned earlier, have a very diverse parallel chemistry in the early transition metals [8] wherein there is a preponderance of compounds of formulation Cp_2MX_n where $Cp = \eta^5\text{-}C_5H_5$. These complexes usually have local C_{2v} symmetry about the metal center, a symmetry too low to allow the important metal–ligand interactions to be completely determined by group theoretical considerations. In this instance, it is also necessary to provide some measure of correction for the relativistic effects which are so important for the heavy elements (particularly the actinide elements) since these can greatly change the orbital energetics which emerge [9, 10].

In an effort to provide quantitative electronic structure calculations on organo-f-element systems, we have investigated the use of the Xα-SW molecular orbital method with quasi-relativistic corrections. We are finding this method to be a very satisfactory one for describing the bonding and energetics of these systems [11, 12]. The purpose of this paper will be twofold: first, to briefly review the Xα-SW method and its advantages and disadvantages with regard to organo-f-element electronic structure, and second to present an application of the method to the C_{2v} model molecule Cp_2UCl_2, the electronic structure of which we will compare to the related higher symmetry complexes UCl_4 and Cp_4U.

Computational Details

The Xα-SW calculations on UCl_4, Cp_4U, and Cp_2UCl_2 were undertaken using existing codes which incorporate the quasi-relativistic corrections of Wood and Boring [13]. Structural parameters were taken from the available structural data on UCl_4 [14], Cp_4U [15], and $Cp^*_2UCl_2$ [16] and were

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idealized to T_d, D_{2d}, and C_{2v} symmetry respectively. The initial molecular potential for each was constructed from a superposition of neutral atom charge densities. The bond lengths, sphere radii, and α values are summarized in Table I. Each calculation was performed with two different partial wave basis sets: A 'minimal' basis consisting of spherical harmonics through $l = 4$, $l = 3$, $l = 1$, $l = 1$, and $l = 0$ on the outer sphere, U, Cl, C, and H centers respectively, and an 'extended' basis in which the outer sphere, U, and Cl bases were extended through $l = 6$, $l = 4$ and $l = 2$ respectively. This comparison allowed the investigation of an increased basis set size on the results, and all results reported here are from the extended basis calculations. The calculations were converged in a fashion analogous to those of third-row transition metal systems in which relativistic corrections have been included [17]. Ionization potentials were calculated using Slater's transition state formalism [18].

TABLE I. Structural Parameters, Sphere Radii and α Values Used in the Xα-SW Calculations on UCl_4, $(\eta^5\text{-}C_5H_5)_4U$, and $(\eta^5\text{-}C_5H_5)_2UCl_2$.

Molecule	Bond length or angle	Value
$UCl_4(T\alpha)$	U–Cl	2.53 Å
	Cl–U–Cl	109.5°
$(\eta^5\text{-}C_5H_5)_4U(D_{2d})$	U–C	2.81 Å
	C–H	1.09 Å
	Cp–U–Cp[a]	109.5°
$(\eta^5\text{-}C_5H_5)_2UCl_2(C_{2v})$	U–C	2.80 Å
	U–Cl	2.68 Å
	C–H	1.09 Å
	Cp–U–Cp[a]	1.24°
	Cl–U–Cl	93.7°

Molecule	Atom	Sphere radius (Å)	α Value
UCl_4	Outer sphere	3.95	0.71283
	U	1.65	0.69200
	Cl	1.42	0.72325
$(\eta^5\text{-}C_5H_5)_4U$	Outer sphere	4.10	0.75417
	U	1.65	0.69200
	H	0.90	0.75928
	H	0.68	0.77725
$(\eta^5\text{-}C_5H_5)_2UCl_2$	Outer sphere	4.15	0.74304
	U	1.69	0.69200
	Cl	1.47	0.72325
	C	0.90	0.75928
	H	0.68	0.77725

[a] Cp denotes centroid of C_5H_5 ligand.

The Xα-SW Method for Organo-f-element Complexes

The Xα scattered-wave (Xα-SW) method has been the subject of several review articles [18–20] and hence we shall not detail all aspects of the method. It is pertinent, however, to briefly discuss the history of the method as this does have some impact on the current applications of the method [21]. All of the Xα formalisms, of which Xα-SW is but one, are derived from a suggestion made in 1965 by Slater that some theoretical concepts used in solid-state physics could be extended to molecular calculations [22]. The major suggestion made was the replacement of the non-local exchange operator $\hat{K}$ by the statistically averaged exchange for the free-electron gas model. This averaging leads to a local exchange operator which at any point in space r is proportional to the cube-root of the electron density at that point, $\rho(r)^{1/3}$. Gaspar, Kohn, and Sham [23, 24] showed that two steps of Slater's derivation did not commute, and that reversing the order of these led to the same functional dependence on $\rho(r)^{1/3}$ but that the actual value of the exchange potential was only 2/3 as great. The parameter α was introduced where $2/3 \leqslant \alpha \leqslant 1$ and form of the exchange potential used is:

$$\hat{V}_{X\alpha}(r) = -3\alpha\left(\frac{3}{8\pi}\right)^{1/3}\rho(r)^{1/3} \qquad (1)$$

In practice, α is generally closer to 2/3 and is chosen to give agreement between the total energy of atomic Xα calculations and atomic Hartree–Fock calculations [25, 26]. The name 'Xα' has its origin in eqn. (1) which is an exchange α times that originally proposed by Slater.

The $p^{1/3}$ dependence of the Xα local exchange operator renders impossible an analytical solution of the one-electron eigenvalue equations, and a number of approaches have been used to numerically solve these, including the scattered-wave (or multiple-scattering) method proposed by Slater and Johnson [27, 28]. In the scattered-wave solution, each atom of a molecule is enclosed in a sphere, and this cluster of atomic spheres is enclosed in an 'outer' sphere. The potential is assumed to be spherically symmetric within each of the atomic spheres and outside of the outer sphere, affording a separation of radial and angular functions for these regions. In the regions between the atomic spheres, the potential is volume-averaged to a constant, leading to a solution which can be obtained in a straightforward way from multi-center scattering theory, the details of which we shall not go through here. Consideration of the boundary conditions at the sphere boundaries leads to a secular determinant, the value of which depends parametrically on the one-electron energy ϵ. At true orbital energies of the molecule, the determinant vanishes, and in practice orbital energies are obtained by evaluating the determinant for a grid of ϵ values and searching for roots of the determinant. A separate determinant can be constructed for each irreducible representation of a point group, and hence the ease of numerically determining the orbital energies is dependent on the symmetry of the molecule.

It is clear that there are many differences, both in formalism and in solution, between the Xα-SW method and either *ab initio* or approximate LCAO–MO methodologies. There are several disadvantages to the Xα-SW method, all of which are due to either the introduction of the local statistically averaged exchange or to the scattered-wave method of solution. Most notable of these is that the introduction of a modified Hamiltonian leads to a total energy which is not governed by the variation principle, a problem common to all non- *ab initio* methods. As such, the total energy obtained from the method is unreliable, and the method is not generally used to calculate geometries or reaction pathways. Efforts are underway to remedy this problem [29].

The most pervasive problem in application of the Xα-SW method is the means by which the radii of the atomic spheres are chosen. Most often the radii are determined using a nonempirical procedure established by Norman [30, 31], a procedure based on satisfaction of the virial theorem. However, the radii which result from application of Norman's method are dependent upon the initial choice of atomic charges used in constructing the initial molecular potential. Thus, by way of example, the sphere radii obtained for UCl_4 would be different for a calculation started with neutral U and Cl atoms as compared to one in which U^{4+} and Cl^- were used as a starting point. In general, the absolute orbital energies are rather sensitive to the choice of sphere radii, but the relative energies of the orbitals with respect to one another are fairly insensitive.

Another problem involving the atomic spheres is due to an important study by Herman, Williams and Johnson [32]. In this study, they found that the results obtained from Xα-SW could be vastly improved by allowing the sphere radii to overlap. The formalism does not change at all for overlapping atomic spheres, but the guarantee of wavefunction continuity is lost in the overlapping regions; in these, there are actually two solutions, one from each of the atoms contributing a sphere to the overlap region. In practice, these discontinuities are small, especially since the sum of the radii is generally less than 1.2 times the bond length, but they do run counter to one of the basic tenets of quantum mechanics.

As has been mentioned above, finding the roots of the secular determinant is greatly facilitated by symmetry-adapting the partial-wave basis sets used in Xα-SW calculations. In the case of applying the method to low-symmetry molecules, especially those containing fragments of high local symmetry, a good amount of caution and care must be exercised. If a given irreducible representation of the point group has two roots which are sufficiently close in energy, it is possible to 'miss' the two roots unless an extremely fine grid of energy values is searched, a process which necessarily adds to the expense and convergence time of the calculation. We have devised a means of minimizing the possibility of problems with this by using a converged high-symmetry fragment as the starting point of a low-symmetry calculation [33]. With regard to the C_{2v} molecules Cp_2MX and Cp_2MX_2 we have not encountered any particular difficulties when M is an actinide metal [11] and similar success has been achieved for transition metal systems [34].

The final major disadvantage of the Xα-SW method results from the numerical, as opposed to analytical, nature of the orbitals. This necessitates the use of contour diagrams for display of the orbitals, in contrast to conventional LCAO–MO methods wherein population analysis of eigenvectors is generally used to facilitate interpretation. It is possible to partition an Xα-SW orbital into its contributions from the various atomic spheres, but this analysis does not indicate the bonding, nonbonding, or antibonding character of the orbital, nor does it indicate the degree of interaction between the atoms. We have developed a method, the projected Xα (PXα) formalism, for projecting numerical Xα-SW MO's onto an AO basis set [35], yielding LCAO–MO's, but at present the PXα method cannot be applied to f-element metals.

Despite the above problems with and difficulties of the Xα-SW method, the many advantages of it make it an excellent electronic structural tool for inorganic and organometallic chemists. It is computationally much faster than *ab initio* methods and requires significantly less mass storage. More important, in a comparison with *ab initio* methodology, the Xα-SW method has consistently yielded results superior to those of single-configuration *ab inito* (Hartree–Fock) calculations on transition metal systems; it has become clear that the inclusion of correlation, through either configuration interaction or a multi-configuration SCF approach, is essential to yield reasonable results for *ab inito* calculations on metal-containing systems [36–38]. These corrections to a single-configuration description not only add tremendously to the cost and complexity of a calculation, but adding them can only be done at the expense of losing an orbital description of the molecule, a description which inorganic chemists find indispensible in correlating reactivity with electronic structure. We have found that, for transition-metal systems, the charge distributions yielded by the Xα-SW method (as well as by other approximate methods which employ spherical averaging, such as extended Hückel or Fenske–Hall) more closely resemble those from a correlated *ab initio* calculation than do those of a Hartree–Fock single configuration calculation [38]. It is our belief, albeit unproven, that this result is general and that the Xα-SW method will yield charge distributions similar to those of a correlated wavefunction while retaining an orbital description.

An important adjunct of the Xα-SW method is Slater's transition state formalism [18], which allows for the easy calculation of ionization potentials and electronic transition energies. The details of the formalism have been nicely explained by Slater and will not be reiterated here. The formalism as applied to inorganic and organometallic systems has been largely successful in the correlation of photoelectron spectra; although the absolute ionization potentials yielded are often in error by more than one eV, the relative spacing of the ionization potentials is generally in excellent agreement with experiment. The application of the transition state formalism to electronic transitions, a more difficult problem, has not been as successful and there have been far fewer such applications. A means of providing correction terms for electronic transitions between weakly interacting orbitals has been proposed by Noodleman and Norman [39, 40].

With respect to the electronic structure of organo-f-element complexes, there are several specific advantages of the Xα-SW method. First, the method can accommodate f orbitals on atoms, a non-trivial consideration since most existing LCAO–MO codes cannot calculate molecular integrals over f orbitals. Closely related to this is the freedom the method provides from radial basis set choice. While the numerical nature of the orbitals has the disadvantage of necessarily requiring contour plots, it has the distinct advantage of allowing the atomic radial functions to change as the chemical environment changes. As will be discussed below, this feature can be used to investigate the influence of various ligands (*e.g.* Cl^- *vs.* Cp^-) on the radial distribution about an actinide center.

A major advantage of the Xα-SW method for heavy elements is the ease with which relativistic corrections can be included [41]. This is essential for an accurate description of the energetics of actinide complexes in particular, wherein the inclusion of relativistic effects can change valence orbital energies by more than one eV (*vide infra*). The incorporation of relativistic effects in a scattered-wave formalism has taken two forms. The first are the so-called 'quasirelativistic' methods, in which the major relativistic effects upon electrons are considered within the construct of single-group orbitals. These approaches, due largely to Wood and Boring [13], and to Rösch [42], include the mass-velocity correction and the Darwin shift of orbital energies within a one-electron framework. The major advantage of these approaches is the inclusion of the dominant relativistic effects on orbital energies with the preservation of 'normal' single group descriptors (a, b, t, *etc.*), which facilitates the comparison to non-relativistic calculations. The primary disadvantage is the neglect of spin-orbit interactions which, while not as important as the above two corrections, can significantly perturb the molecular energetics. The calculational results presented here employ the formalism of Wood and Boring and will be referred to as relativistic Xα (RXα) calculations.

A more correct, albeit more complex, treatment of relativistic effects within a scattered-wave formalism is the Dirac-scattered-wave (DSW) method developed by Yang and Case [43–45]. In this approach, the scattered-wave equations are developed using the Dirac equation rather than the Schrödinger equation and, hence, *all* relativistic effects are included at the one-electron level. This elegant approach has led to excellent results and has the important advantage that spin-orbit splittings are immediately available from the calculations. The principal disadvantage of the DSW approach is its complexity, in both implementation and interpretation; the DSW method is computationally more expensive than RXα approaches and the resulting description of the molecule involves four-component spinors over double-groups. While this latter point is not a serious disadvantage, it must be acknowledged that most inorganic chemists are somewhat uncomfortable with double-group descriptions of orbitals.

Results and Discussion

In this section, Xα-SW calculations with quasirelativistic corrections will be presented for three related uranium complexes. First, the tetrahedral complex UCl_4 will be examined. The high symmetry and small size of this molecule make it an ideal starting point for discussing the influence of ligands upon the uranium center. Next, the results for UCl_4 will be compared to those of Cp_4U, in which the coordination geometry about the uranium atom is tetrahedral with respect to the centroids of the C_5H_5 ligands. This direct comparison of two tetrahedral systems will facilitate a determination of the differences between Cl^- and Cp^- as ligands and will allow us to examine how flexible the U 5f radial distribution is. Additionally, the highly symmetric Cp_4U system will give an indication of the donor/acceptor properties of the Cp ligands. Finally, we will examine the electronic structure of the low-symmetry molecule Cp_2UCl_2 in light of the calculations on the higher symmetry homoleptic molecules.

Cp_2UCl_2 is a model of the well-characterized $Cp_2^*UCl_2$ molecule which is prototypical of the plethora of $Cp_2^*UMX_2$ systems in organo-f-element chemistry.

UCl_4

The uranium tetrachloride molecule provides an excellent test of the ability of ligands to split the f orbitals of a uranium center. Under T_d symmetry, the f orbitals will span the $a_1 + t_1 + t_2$ representations, the Cl σ lone pairs span $a_1 + t_2$, and the π lone pairs span $e + t_1 + t_2$. The converged nonrelativistic and quasirelativistic upper valence energy levels for UCl_4 are shown in Fig. 1. These results are in good accord with a previous nonrelativistic Xα-SW calculation on UCl_4 [46]. It is seen that the inclusion of relativistic corrections induces a >1 eV shift in the $5t_2$, $2t_1$, and $4a_1$ orbitals, all of which are >85% U 5f in character. The $3a_1$ and $3t_2$ orbitals represent the U–Cl σ bonds, each of which is roughly 75% Cl and 25% U in character. Interestingly, the U contribution to the $3t_2$ orbital is primarily from the 6d orbital while that in the $3a_1$ orbital is an equal admixture of 5f and 7s. This orbital exhibits a sizable downward shift upon relativistic correction as would be expected for an orbital containing significant s character. The Cl π lone pair levels, which contain only small (<10%) contributions from the U atom, are scarcely affected by the inclusion of relativistic effects.

Also included in Fig. 1 is a comparison of the minimal and extended basis set calculations on UCl_4. It is seen that the addition of more partial waves barely perturbs the orbital energies, and we have concluded that the smaller basis set is adequate for these systems.

The primarily U 5f orbitals are essentially unsplit by the Cl ligands, an indication that they may be more contracted than the d orbitals of early transition metal systems. The separation of the $5t_2$ and $4a_1$ orbitals is only 0.1 eV, and it will be seen that this low degree of splitting is evident in organo-f-element complexes as well.

Cp_4U

The replacement of four chloride ligands by four Cp ligands about a U atom necessarily reduces the overall symmetry of the molecule from T_d, although structurally the molecule is known to have virtually T_d symmetry with respect to the U–Cp (centroid) bonds [15]. While the crystallographic symmetry of UCp_4 is only S_4, we have idealized the coordinates to D_{2d} symmetry, a change which only involves rotation of the Cp ligands about the U–Cp (centroid) bonds.

Figure 2 shows a comparison of the converged RXα energy levels for Cp_4U as compared to those for UCl_4. The Cp orbitals shown are those derived from the $a_2''(\pi_1)$ and $e_1''(\pi_2)$ orbitals of the four Cp ligands; there is virtually no interaction, as expected, between the Cp σ system and the U atom. It is seen that although the molecule has D_{2d} symmetry, the highest occupied orbitals are energetically grouped as if the molecule were tetrahedral and, for

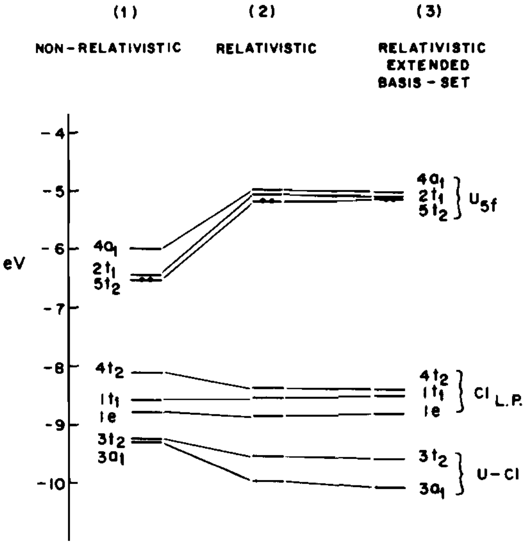

Fig. 1. Converged upper valence orbitals of UCl_4 from: (1) non-relativistic, (2) quasi-relativistic, minimal basis, and (3) quasi-relativistic, extended basis Xα-SW calculations.

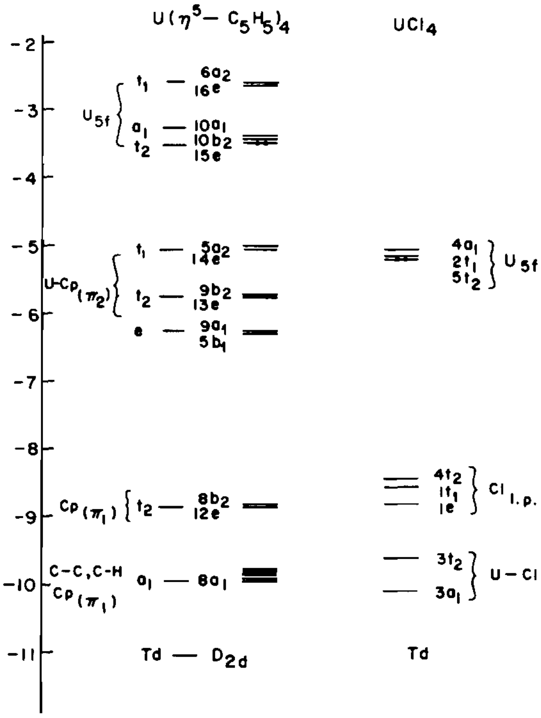

Fig. 2. A comparison of the converged quasi-relativistic Xα-SW orbital energies for $(\eta^5\text{-}C_5H_5)_4U$ and UCl_4.

convenience, the orbitals will be discussed as if the molecule were truly T_d symmetry. The ligand π_2 orbitals yield combinations of $t_1(a_2 + e)$, $t_2(b_2 + e)$, and $e(a_1 + b_1)$ symmetry, thus affording a separation of the interactions of the ligand orbitals with the U 5f and 6d atomic orbitals; the t_1 orbital can interact only with the 5f, the e only with the 6d, and the t_2 with both the 5f and 6d. Table II lists the upper valence orbitals of the complex and the U contributions to each. It can be seen that donation into the U 6d orbitals is as important as that into the 5f orbitals, and that the e π_2 orbital is stabilized by >1 eV relative to the t_1 π_2 orbital. It would thus appear that donation into the 6d, when facilitated by appropriate orbitals on the ligands, is actually a more stabilizing interaction than donation into the 5f.

TABLE II. Upper Valence Orbitals of Cp_4U from the Quasi-relativistic Xα-SW Calculation and the U Contributions to each.

Orbital energy (eV)	Symmetry		% U Contributions		
	D_{2d}	T_d	5f	6d	7p
−2.60	a_2	t_1	75	–	–
−2.62	e		75	–	–
−3.38	a_1	a_1	94	–	–
−3.43	b_2	t_2	87	3	–
−3.47[a]	e		86	3	–
−5.03	a_2	t_1	23	–	–
−5.05	e		23	–	–
−5.74	b_2	t_2	1	8	2
−5.77	e		1	8	2
−6.26	a_1	e	–	17	–
−6.28	b_1		–	17	–

[a] Highest occupied molecular orbital. In a closed-shell approximation, this orbital contains two electrons.

A comparison of the electronic structure of Cp_4U to that of UCl_4 leads to several noteworthy conclusions. The primarily U 5f orbitals of Cp_4U are significantly higher in energy than those of UCl_4, and they are more greatly split by the Cp ligands than by Cl. Both of these observations lead to the conclusion that Cp is a stronger donor to the U atom than is Cl, a consequence of the higher energy of the Cp π_2 orbitals as compared to the lone pairs of the Cl ligands. This conclusion is in good accord with the ionization data for Cp_4U and UCl_4: the first ionization potential of UCl_4 is 9.97 eV [46] while that of Cp_4U is 6.34 eV [47, 48] and in both cases the ionization can unequivocally be assigned to removal of a primarily 5f electron. The greater donor ability of Cp relative to Cl can also be seen in a comparison of the contour plots of the t_2 orbitals of each complex, as shown in Fig. 3.

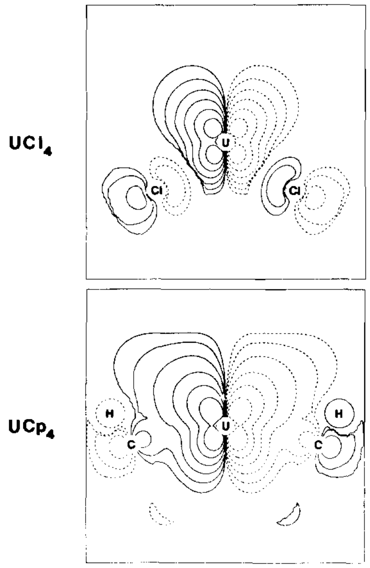

Fig. 3. Contour plots of the t_2 HOMO of UCl_4 and Cp_4U.

The 5f orbital of Cp_4U is more diffuse than that of UCl_4, reflective of the more electron-rich nature of the U atom in the former than in the latter.

Cp_2UCl_2

As a model of the $Cp^*_2MX_n$ systems which are ubiquitous in organo-f-element chemistry [4], we have chosen Cp_2UCl_2 where for computational expedience we have replaced the pentamethylcyclopentadienyl ligands with unsubstituted cyclopentadienyl ligands. We have found that the electronic differences between Cp and Cp* to be rather small [49], and it is our belief that methylation of the ring primarily affects the steric rather then electronic properties of the ligands. We have already reported RXα calculations comparing the electronic structures of Cp_2UCl_2 and Cp_2UMe_2 [11] so the focus of this discussion will be on the comparison of the low symmetry Cp_2UCl_2 species with its higher symmetry 'parents' UCl_4 and Cp_4U. Such a comparison will directly indicate whether Cp or Cl dominates the metal–ligand interactions if an equal number of each is present.

The orbital energetics of Cp_2UCl_2 are compared to those of UCl_4 and Cp_4U in Fig. 4. Rather than showing individual energy levels, we have chosen for clarity to correlate the three molecules via their distinct bands of orbitals. The position of the U 5f based MO's in Cp_2UCl_2 is of particular interest. As is evident, these are energetically closer to the corresponding band of orbitals in Cp_4U than in UCl_4. We interpret this as evidence that the Cp ligands are dominating the position of the 5f orbitals and that two Cp ligands are enough to greatly

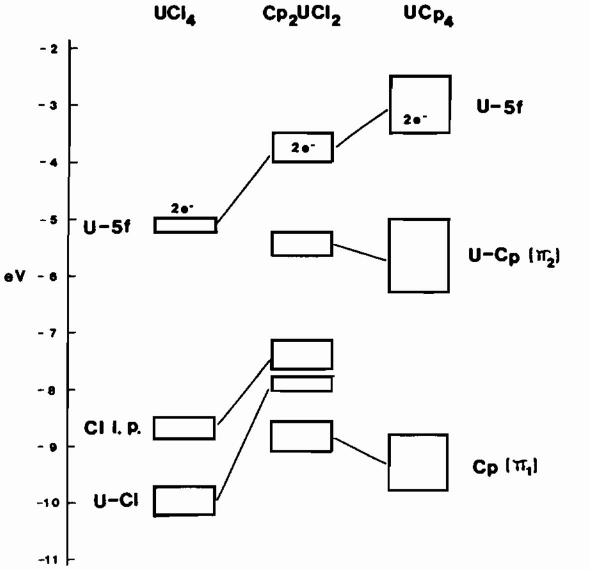

Fig. 4. A comparison of the bands of orbitals of Cp_2UCl_2 to those of UCl_4 and Cp_4U.

increase the electron density at the uranium center. The splitting of the 5f orbitals in Cp_2UCl_2 is intermediate between that of UCl_4 and Cp_4U, but these seven orbitals still occupy a very narrow (0.5 eV) band of energies. We have pointed out [11] that this is consistent with the observed paramagnetism of $Cp^*_2UCl_2$ *vis-à-vis* the diamagnetism of Cp_2MoCl_2, for which we have calculated a 2.2 eV HOMO/LUMO gap.

The Cl-based levels of Cp_2UCl_2 rise in energy relative to UCl_4, no doubt a consequence of the greater electron density on the uranium atom which will decrease the coulombic stabilization of the Cl levels. The Cp based levels are not split as much as they are in Cp_4U and energetically they are quite similar.

The dominance of the Cp ligands with regard to the U 5f electrons is experimentally evident in the photoelectron spectrum of $Cp^*_2UCl_2$ [50]. The first ionization of the molecule, which is due to U 5f electrons, occurs at 6.85 eV, much closer to the first ionization potential of Cp_4U than to that of UCl_4. It is expected that the replacement of Cp by Cp* ligands will affect the ionization potential somewhat but not enough to change the argument; for $CpM(CO)_3$ *vs.* $Cp^*M(CO)_3$, (M = Mn, Re), the ionization potential for the Cp* complex is only about 0.5 eV lower than that of the Cp complex [51]. In fact, it appears that Cp donation truly governs the U 5f energies for the first ionization potential of $Cp^*_2UMe_2$ is only 0.2 eV lower than that of $Cp^*_2UCl_2$ despite the replacement of the Cl ligands by the much stronger σ-donating Me ligands [50].

Acknowledgments

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