# Lawrence Berkeley National Laboratory

**Title**

A QUASI-RELATIVISTIC SCF X-a STUDY OF OCTAHEDRAL 5F1 COMPLEXES

**Permalink**

https://escholarship.org/uc/item/7rf7v0j8

**Author**

Thornton, G.

**Publication Date**

1979-09-01

# ⊞ Lawrence Berkeley Laboratory
## UNIVERSITY OF CALIFORNIA

## Materials & Molecular Research Division

A QUASI-RELATIVISTIC SCF X-α STUDY OF OCTAHEDRAL $5f^1$ COMPLEXES

Geoffrey Thornton, Notker Rösch, and Norman Edelstein

RECEIVED
LAWRENCE
BERKELEY LABORATORY.

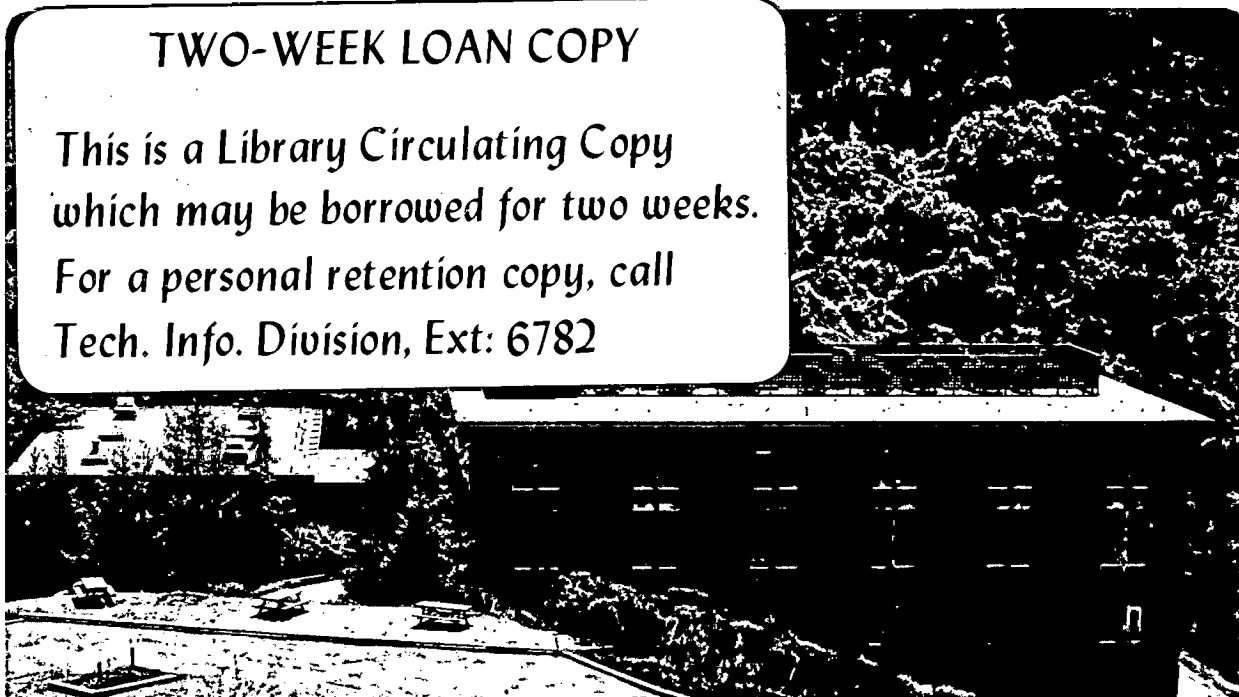NOV 16 1979

September 1979

LIBRARY AND
DOCUMENTS SECTION

LBL-9693 c.2

## DISCLAIMER

A Quasi-Relativistic SCF X-$\alpha$ Study of Octahedral $5f^1$ Complexes[a]

Geoffrey Thornton,[b] Notker Rösch,[c] and Norman Edelstein

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

September 1979

ABSTRACT

Quasi-relativistic SCF X-$\alpha$ calculations have been carried out for the octahedral $5f^1$ complexes $Pa^{IV}X_6^{2-}$, $U^V X_6^-$ (X = F, Cl, Br, I) and $Np^{VI}F_6$. The $5f \rightarrow 5f$ excitation energies calculated using the transition-state method agree well with the available absorption spectra. Ionic effects appear to dominate the trends observed in the f-orbital ligand field splitting.

---

[b]Present address: Department of Chemistry, University of Manchester, Manchester M13 9PL, England.

[c]Present address: Lehrstuhl fur Theoretische Chemie, Technische Universitat Munchen, 8046 Garching, W. Germany.

INTRODUCTION

Although ab-initio calculations of $ML_N$ complexes have been carried out extensively for the situation in which M is a transition metal or main group element,[1] lanthanide and actinide complexes have been somewhat neglected. Such calculations are computationally difficult for traditional LCAO schemes, although the multiple scattering X-$\alpha$ (MSX$\alpha$) method is capable of solving such a problem without undue cost, even when relativistic effects are included. The X-$\alpha$ method has been applied to the neutral species $UF_5$,[2] $UF_6$,[2-6] $UCl_6$,[7] $NpF_6$,[4,5] and $PuF_6$.[4,5] Considerable success was obtained in their agreement with photoelectron and absorption spectra.

In the present study, quasi-relativistic SCF X-$\alpha$ calculations were carried out on a series of $5f^1$ complexes: $PaX_6^{2-}$, $UX_6^{-}$ (X = F, Cl, Br, I) and $NpF_6$. The study of such series has aided the interpretation of the electronic structure in terms of parameters commonly used in inorganic chemistry. In this case, the main object of study was the nature of the 5f ligand field splitting relative to the oxidation state of the metal ion and to the halide ion. Previously, only the relative extent of $\sigma$ and $\pi$ type ligand-f-orbital interactions has been discussed, in terms of the semi-empirical angular-overlap model.[8]

As a test of the SCF X-$\alpha$ calculations, 5f $\rightarrow$ 5f excitation energies were determined to compare with available experimental results.[9-11]

## COMPUTATIONAL DETAILS

The calculations were performed using a version of the MS X-α routine described by Slater,[12] modified, in the Dirac-Slater framework, to include relativistic effects. The Dirac-Slater MO model has previously been solved for a number of polyatomic systems, using the discrete variational method.[4] The computational effort necessary, however, is substantial but may be reduced considerably by constraining the potential to muffin-tin form. This allows the use of the efficient scattered-wave (SW) formalism either via a Green's function technique[13] or by means of the elimination method.[14] The resulting secular equation for the orbital energies $\varepsilon_i$ is of the same form as in the nonrelativistic SW formalism:[15]

$$\det\left| G_{pq}(\varepsilon) - t_p^{-1}(\varepsilon)\, \delta_{pq} \right| = 0$$

The propagators $G_{pq}(\varepsilon)$ describe the scattering of the waves in the region of constant potential from sphere p to sphere q; they only depend on the muffin-tin geometry. The scattering factors $t_p(\varepsilon)$ characterize the phase shift experienced by a wave on reflection at sphere p; it is a function of the logarithmic derivative of the large component of the wave function evaluated at the sphere boundary.[14,15]

In this study we use a nonperturbative self-consistent approximation to the SW treatment of the relativistic X-α

model that should be well-suited for MO calculations of very large molecules. The chemically relevant information is contained in the energies and wave functions of the valence shell molecular orbitals. Core levels do not participate directly in the formation of chemical bonds and remain well-localized in the vicinity of a nucleus. The SW model with its underlying muffin-tin geometry takes advantage of this fact in that it confines core levels to one atomic sphere, thereby treating them essentially as in atomic problems. For atoms, of course, the solution of the Dirac-Slater model is well-established.[16]

In order to simplify the relativistic SW problems for valence shell MO's, we briefly analyze the magnitude of various relativistic effects for such orbitals. The spin-orbit splitting in molecules is usually smaller than in isolated atoms, and at most ∿1 eV for MO's with bonding energies less than ca. 20 eV. This has to be compared to errors in the orbital energies due to the muffin-tin form of the potential, which may be up to about the same size. The mass-velocity correction and the Darwin shift of MO energies may be 10 times larger. They affect the wavefunction where-ever the quantity

$$q \ = \ \frac{1}{2c^2} \ (\varepsilon \ - \ V(r))$$

is large, i.e., inside the atomic muffin-tin spheres. In

the intersphere region where $|\varepsilon - V(r)| \leqslant 4$ a.u. these rela-
tivistic effects are completely negligible: $|q| \leqslant 10^{-4}$
($c = 137$ a.u.). The solution of the Dirac-Slater equation
is therefore restricted to the interior of the atomic spheres.[16]
The SW problem in the intersphere region is then identical to
the nonrelativistic treatment except for the use of scattering
factors $t_p(\varepsilon)$ calculated from the large component of the
wavefunction inside the atomic spheres. A similar but more
formal treatment, with applications mainly to atoms, has
recently been presented by Wood and Boring.[17]

This approximation has the chemical appeal of reducing
to the nonrelativistic treatment whenever the atomic number Z
is small ($Z \leqslant 56$), or when c is made very large deliberately
($c \sim 10^6$ a.u.). The same irreducible representations may be
used as in the nonrelativistic case, and double groups
necessary in the SW solution of the Dirac-Slater equation for
molecules can be avoided. Spin-orbit splittings have to be
estimated using perturbation theory. The resulting errors
will be tolerable since they are of the same size as those
from the muffin-tin model.

The protactinium, uranium, and neptunium core electron
charge densities were derived from relativistic calculations.[16]
The interatomic distances used in the calculations (Table 1)
were taken from structural studies when available,[18,19] or
by reference to ionic radii tables.[20] The muffin-tin radii
(Table 1) were chosen as follows: An SCF X-$\alpha$

calculation of $UF_6$ was performed, and the sphere radii were
adjusted to give the best overall agreement with the Discrete
Variational X-α calculation of Koelling et al.[4] To obtain
this agreement the U and F spheres were overlapped. The U
sphere radius was held constant at this value, while the
other ligand radii were chosen to touch an imaginary sphere
corresponding to a 10% reduction in the U sphere radius. The
10% overlap of the U sphere corresponds approximately to that
present in the $UF_6$ calculation. The same ligand radii were
then used for calculations on $NpF_6$ and $PaX_6^{2-}$. In these cases,
the metal radii were chosen to give a 10% overlap. In all
cases, the outer sphere was chosen to touch the ligand spheres,
and for the anionic species a Watson sphere of the same
radius was used. This carried a charge of +1 for $UX_6^-$ and
+2 for $PaX_6^{2-}$.

The atomic exchange scaling parameters, α, were taken
from values tabulated by Schwartz,[21,22] or extrapolated from
them.

$$\alpha_{Pa,U,Np} = 0.69208, 0.6920, 0.6916;$$
$$\alpha_{F,Cl,Br,I} = 0,73732, 0.72325, 0.70606, 0.70008$$

Extramolecular and intersphere scaling parameters were obtained
by averaging the atomic parameters. Core electron densities
for Pa, U, and Np ([Xe]$4f^{14}$) were frozen at their atomic values
as were the F([He]), Cl([Ne]), Br([Ar]), and I([Kr]) electron
densities. All other electrons were considered fully in the

SCF calculations, spin-orbit coupling being neglected. The X-α one-electron energies found in the calculations are shown in Figure 1, and the electron charge within each muffin-tin sphere is presented in Table 1.

DISCUSSION

An appropriate test for the calculations presented here is to compare the calculated 5f - 5f excitation energies with corresponding absorption spectra. Table 2 shows this comparison and it can be seen that the agreement between theory and experiment is remarkably good. The excitation energies were calculated using the transition-state procedure of Slater.[12]

The trend in the calculated ligand field splittings observed in Figure 1 follows that found experimentally and that expected from the spectrochemical series, i.e., $F^- > Cl^- > Br^- > I^-$. Also, the order $Np^{6+} > U^{5+} > Pa^{4+}$, expected on purely ionic grounds is observed. In the MS X-α scheme a charge fraction analysis of each of the orbitals can reveal the relative σ and π contributions in each of the spheres. Following the work of Rösch et al.,[23] the intersphere charge density is divided between the metal (1 part) and ligand spheres (6 parts) and the charge density in the outer sphere is given to the ligands. Table 3 shows the results of this charge fraction analysis for the antibonding[24] and bonding $t_{1u}$ and $t_{2u}$ orbitals and the nonbonding $a_{2u}$ orbitals that

contain the f electron. Although the absolute numbers are probably not meaningful, the relative values should be qualitatively correct.

The following trends are apparent on comparing the relative ligand contribution to the antibonding orbitals, or the metal contributions to the bonding orbitals. The fluoride complexes are the most ionic in each of the various ionic groups, and the ligand contribution increases as the halide ion becomes heavier. Within a particular halide-complex series, the heavier the metal ion (and the lesser the total ionic charge) the greater the ligand contribution. In particular, $NpF_6$ appears to be the most covalent complex in the entire hexahalide series.

Considering only the $t_{1u}$ antibonding orbitals, the percentage of ligand $\sigma$ bonding increases from 17.4% ($UF_6^-$) and 7.8% ($PaF_6^{2-}$) to 26.6% ($UI_6^-$) and 12.7% ($PaI_6^{2-}$). The ligand $\pi$ bonding component in the $t_{1u}$ antibonding orbital increases from 2.3% and 2.6% in $UF_6^-$ and $PaF_6^{2-}$ to 5.5% and 3.9% in $UI_6^-$ and $PaI_6^{2-}$. For the antibonding $t_{2u}$ orbital (where only $\pi$ bonding with the f orbitals can occur), the ligand $\pi$ bonding increases from 8.5% and 4.8% for $UF_6^-$ and $PaF_6^{2-}$ to 11.6% and 6.2% for $UI_6^-$ and $PaI_6^{2-}$.

The increase in both $\sigma$ and $\pi$ bonding as the halide becomes heavier is substantial. However, it is small when compared with the dramatic decrease in the f orbital splitting as the ligand is changed from $F^-$ to $I^-$ (see Table 2). These

results suggest that the f orbital splittings of these hexahalide complexes are dominated by ionic effects with a lesser contribution from covalent bonding. It appears that the decrease in ionic effects due to changes in bond length outweighs the gain in covalent bonding on descending the halogen series.

Another measure of the covalent/ionic nature of the complexes can be found in the gross atomic charge assigned to the metal and ligand, as shown in Table 4. This is equivalent to a Mulliken population analysis in the LCAO scheme. The pattern obtained here is different from that discussed previously considering only the f orbitals. Clearly, $NpF_6$ is the most covalent but $PaF_6^{2-}$ appears more covalent than $UF_6^-$. However, if the bonding is mainly ionic then these results are consistent, i.e., the greater the charge on the complex as a whole the smaller the charge on the central ion. Since the $F^-$ ion is the smallest and least polarizable halide ion, an overall charge on the complex will result in more charge being placed on the central metal ion. There appears to be little difference for the other halide ions.

SUMMARY

This paper has described a systematic study of the 5f ligand field splitting in the $5f^1$ complexes $Pa^{IV}X_6^{2-}$, $U^V X_6^-$ (X = F, Cl, Br, I) and $Np^{VI}F_6$. A quasi-relativistic MS X-$\alpha$ routine was used for this purpose. The trends observed

in the f orbital ligand field splitting appear to be
principally ionic in nature.

REFERENCES

1.  W.G. Richards, P.R. Scott, E.A. Calbourn, and A.S. March-
    ington, Bibliography of ab initio molecular wavefunctions
    --supplement for 1976-1977, Oxford University Press,
    Oxford, 1978; and earlier publications in this series.

2.  D.H. Maylotte, R.L. St. Peters, and R.P. Messmer, Chem.
    Phys. Lett. 38, 181 (1976).

3.  M. Boring and J.W. Moskowitz, Chem. Phys. Lett. 38, 185
    (1976).

4.  D.D. Koelling, D.E. Ellis, and R.J. Bartlett, J. Chem.
    Phys. 65, 3331 (1976).

5.  M. Boring and H.G. Hecht, J. Chem. Phys. 69, 112 (1978).

6.  M. Boring and J.H. Wood, J. Chem. Phys. 71, 32 (1979).

7.  G. Thornton, N. Edelstein, N. Rösch, R.G. Egdell, and
    D.R. Woodwark, J. Chem. Phys. 70, 5218 (1979).

8.  K.D. Warren, Inorg. Chem. 16, 2008 (1977).

9.  D. Brown, P. Lidster, B. Whittaker, and N. Edelstein,
    Inorg. Chem. 15, 511 (1976).

10. N. Edelstein, D. Brown, and B. Whittaker, Inorg. Chem.
    13, 563 (1974)

11. W. Wagner, N. Edelstein, B. Whittaker, and D. Brown,
    Inorg. Chem. 16, 1021 (1977).

12. J.C. Slater, The Self-Consistent Molecular Field  for
    Molecules and Solids (McGraw-Hill,  New York, 1974).

13. C.Y. Yang and S. Rabii, Phys. Rev. A12, 362 (1975);
    and C.Y. Yang, Chem. Phys. Lett. 41, 578 (1976).

14. R. Rosicky, P. Weinberger, and F. Mark, J. Phys. B9,
    2971 (1976).

15. N. Rösch, in "Electrons in Finite and Infinite Systems,"
    NATO Advanced Study Institute, ed. P. Phariseau and
    L. Scheire, Plenum Press, New York 1977.

16. D.A. Liberman, J.T. Waber, and D.T. Cromer, Phys. Rev.
    137A, 27 (1965).

17. J.H. Wood and A.M. Boring, Phys. Rev. B18, 2701 (1978).

18. D. Brown, in "Comprehensive Inorganic Chemistry," Vol. 5,
    Pergamon Press, New York 1973.

19. A. Rosenzweig and D.T. Cromer, Acta. Cryst. 23, 865 (1967).

20. R.D. Shannon, Acta. Cryst. A32, 2446 (1972).

21. K. Schwartz, Phys. Rev. 85, 2446 (1972).

22. K. Schwartz, Theor. Chim. Acta. 34, 225 (1974).

23. N. Rösch, V.H. Smith, Jr., and M.H. Whangbo, Inorg. Chem.
    15, 1768 (1976).

24. In the case of the antibonding orbitals, the analysis
    is of virtual charge.

TABLE I. Sphere radii and interatomic distances used in the MS X-$\alpha$ calculations (a.u.), and the charge found within each sphere for the ground state complexes.

| | $R_M$ | $R_L$ | $R_{OUT}$ | $D_{ML}$ | $Q_M$ | $Q_{HAL}$ | $Q_{INT}$ | $Q_{OUT}$ |
|---|---|---|---|---|---|---|---|---|
| $PaF_6^{2-}$ | 3.212 | 1.3781 | 5.6767 | 2.274 | 89.582 | 7.843 | 9.148 | 1.208 |
| $PaCl_6^{2-}$ | 3.212 | 2.2856 | 7.4920 | 2.754 | 89.351 | 16.039 | 8.482 | 0.925 |
| $PaBr_6^{2-}$ | 3.212 | 2.5690 | 8.0586 | 2.904 | 89.414 | 34.031 | 8.480 | 0.891 |
| $PaI_6^{2-}$ | 3.212 | 3.0280 | 8.9713 | 3.144 | 89.437 | 52.078 | 8.235 | 0.812 |
| $UF_6^{-}$ | 2.789 | 1.3781 | 5.2666 | 3.888 | 90.879 | 7.803 | 8.927 | 1.197 |
| $UCl_6^{-}$ | 2.789 | 2.2856 | 7.0816 | 4.796 | 89.879 | 16.018 | 8.147 | 0.859 |
| $UBr_6^{-}$ | 2.789 | 2.5690 | 7.6484 | 5.079 | 89.982 | 34.014 | 8.093 | 0.815 |
| $UI_6^{-}$ | 2.789 | 3.0280 | 8.5670 | 5.539 | 90.022 | 52.070 | 7.781 | 0.729 |
| $NpF_6$ | 2.763 | 1.2322 | 4.9765 | 3.744 | 91.457 | 7.294 | 10.359 | 1.412 |

TABLE II.  $5f \to 5f$ excitation energies; theoretical and experimental[10-12] $(cm^{-1})$

| | $a_{2u} \to t_{2u}$ | | $a_{2u} \to t_{1u}$ | |
|---|---|---|---|---|
| | calc | exptl | calc | exptl |
| $PaF_6^{2-}$ | 2381 | 3074 | 6979 | 7576 |
| $PaCl_6^{2-}$ | 1350 | 1634 | 4521 | 3507 |
| $PaBr_6^{2-}$ | 1218 | 1707 | 4104 | 2975 |
| $PaI_6^{2-}$ | 944 | 1546 | 3424 | 2378 |
| $UF_6^{-}$ | 4148 | 4479 | 17130 | 11361 |
| $UCl_6^{-}$ | 2294 | 2936 | 8658 | 6307 |
| $UBr_6^{-}$ | 2008 | 2935 | 7725 | 5310 |
| $UI_6^{-}$ | 1525 | -- | 6277 | -- |
| $NpF_6$ | 5662 | 5619 | 18676 | 23117 |

14

TABLE III. The energies and composition of the $a_{2u}$, $t_{1u}$, and $t_{2u}$ "5f" orbitals

| Molecule | Orbital | Energy (Ryd) | % metal (f) | % metal (p) | % ligand (σ) | % ligand (π) |
|---|---|---|---|---|---|---|
| $PaF_6^{2-}$ | $a_{2u}$ | -.3117 | 96.56 | | | |
| | $t_{1u}$ | -.2483* | 88.39 | 1.27 | 7.76 | 2.58 |
| | | -.6592 | 5.71 | 8.28 | 63.56 | 22.46 |
| | | -.7170 | 10.78 | 0.11 | 21.54 | 67.56 |
| | $t_{2u}$ | -.2900* | 95.19 | | | 4.81 |
| | | -.7045 | 7.22 | | | 92.78 |
| $PaCl_6^{2-}$ | $a_{2u}$ | -.3691 | 97.29 | | | |
| | $t_{1u}$ | -.3285* | 86.13 | 0.74 | 10.11 | 3.01 |
| | | -.5754 | 10.72 | 4.64 | 81.94 | 2.71 |
| | | -.5941 | 7.19 | 0.30 | 2.31 | 90.19 |
| | $t_{2u}$ | -.3568* | 94.68 | | | 5.33 |
| | | -.5861 | 6.96 | | | 93.04 |
| $PaBr_6^{2-}$ | $a_{2u}$ | -.3570 | 97.16 | | | |
| | $t_{1u}$ | -.3202* | 84.69 | .67 | 11.26 | 3.38 |
| | | -.5311 | 14.38 | 3.39 | 81.69 | .54 |
| | | -.5493 | 3.94 | 1.96 | 1.05 | 93.05 |
| | $t_{2u}$ | -.3459* | 94.22 | | | 5.79 |
| | | -.5393 | 7.26 | | | 92.74 |

TABLE III. The energies and composition of the $a_{2u}$, $t_{1u}$, and $t_{2u}$ "5f" orbitals (Continued)

| Molecule | Orbital | Energy (Ryd) | % metal (f) | % metal (p) | % ligand (σ) | % ligand (π) |
|---|---|---|---|---|---|---|
| PaI$_6^{2-}$ | $a_{2u}$ | -.3551 | 97.28 | | | |
| | $t_{1u}$ | -.3246* | 82.89 | .55 | 12.66 | 3.89 |
| | | -.4884 | 17.27 | 1.90 | 70.54 | 10.29 |
| | | -.5107 | .22 | 4.78 | 13.21 | 81.80 |
| | $t_{2u}$ | -.3465* | 93.84 | | | 6.16 |
| | | -.4959 | 7.31 | | | 92.69 |
| UF$_6^-$ | $a_{2u}$ | -.4740 | 96.28 | | | |
| | $t_{1u}$ | -.3479* | 77.93 | 2.40 | 17.42 | 2.25 |
| | | -.7205 | 10.76 | 9.57 | 50.94 | 28.74 |
| | | -.8452 | 15.92 | 10.17 | 22.84 | 61.06 |
| | $t_{2u}$ | -.4363* | 91.52 | | | 8.48 |
| | | -.8221 | 10.27 | | | 89.73 |
| UCl$_6^-$ | $a_{2u}$ | -.5111 | 96.75 | | | |
| | $t_{1u}$ | -.4333* | 71.96 | 1.34 | 22.91 | 3.77 |
| | | -.6561 | 16.37 | 4.48 | 64.04 | 5.11 |
| | | -.6985 | 14.67 | 0.00 | 9.99 | 75.34 |
| | $t_{2u}$ | -.4902* | 89.83 | | | 10.17 |
| | | -.6866 | 10.90 | | | 89.10 |

**TABLE III.** The energies and composition of the $a_{2u}$, $t_{1u}$, and $t_{2u}$ "5f" orbitals (Continued).

| Molecule | Orbital | Energy (Ryd) | % metal (f) | % metal (p) | % ligand ($\sigma$) | % ligand ($\pi$) |
|---|---|---|---|---|---|---|
| $UBr_6^-$ | $a_{2u}$ | -.4857 | 96.64 | | | |
| | $t_{1u}$ | -.4171* | 69.96 | 1.13 | 24.53 | 4.38 |
| | | -.6117 | 21.51 | 3.49 | 69.38 | 5.62 |
| | | -.6444 | 11.52 | .16 | 2.72 | 85.60 |
| | $t_{2u}$ | -.4676* | 89.22 | | | 10.78 |
| | | -.6329 | 11.29 | | | 88.71 |
| $UI_6^-$ | $a_{2u}$ | -.4706 | 96.61 | | | |
| | $t_{1u}$ | -.4150* | 67.01 | .86 | 26.64 | 5.47 |
| | | -.5690 | 29.80 | 1.95 | 67.93 | .32 |
| | | -.5953 | 5.06 | 1.26 | 2.14 | 91.53 |
| | $t_{2u}$ | -.4568* | 88.70 | | | 11.30 |
| | | -.5815 | 11.48 | | | 88.52 |
| $NpF_6$ | $a_{2u}$ | -.6307 | 97.0 | | | |
| | $t_{1u}$ | -.4631* | 67.9 | 3.87 | 26.35 | 1.91 |
| | | -.7753 | 14.09 | 8.97 | 37.48 | 39.45 |
| | | -.9258 | 24.83 | .30 | 26.34 | 48.53 |
| | $t_{2u}$ | -.5795* | 86.45 | | | 13.55 |
| | | -.8917 | 16.71 | | | 83.29 |

TABLE III. The energies and composition of the $a_{2u}$, $t_{1u}$, and $t_{2u}$ "5f" orbitals (Continued)

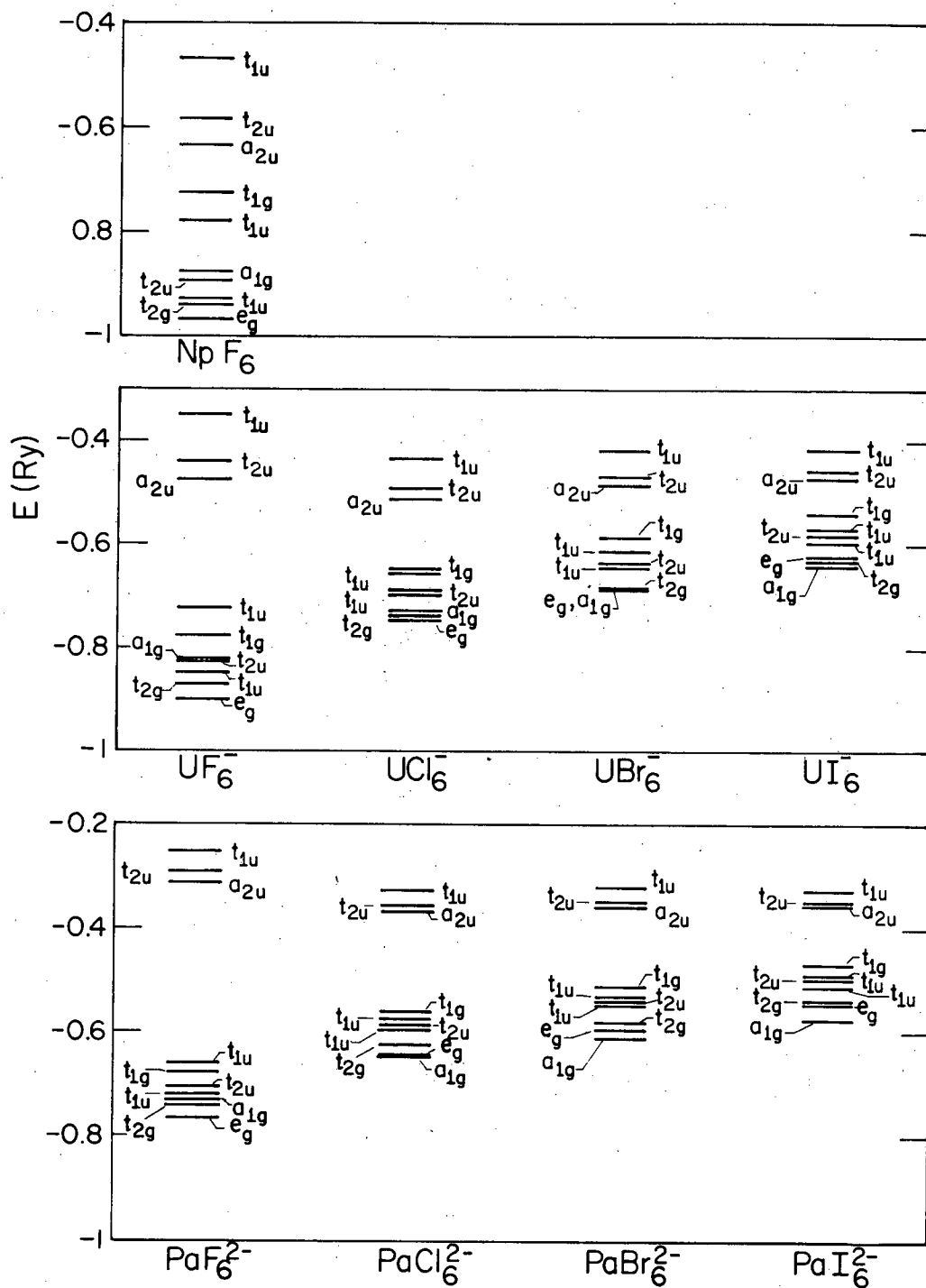| Molecule | Orbital | Energy (Ryd) | % metal (f) | % metal (p) | % ligand (σ) | % ligand (π) |
|---|---|---|---|---|---|---|

* Antibonding orbital

+ Intersphere charge 1/7 given to metal sphere, 6/7 to ligands; within a ligand or metal orbital the intersphere charge is divided proportionately among the various components according to the percentage of charge density for each partial wave. The outer sphere charge density is distributed only on the ligands in the same fashion.

TABLE IV.  Gross atomic charges

| | M | L |
|---|---|---|
| $PaF_6^{2-}$ | 0.11 | -0.35 |
| $PaCl_6^{2-}$ | 0.44 | -0.41 |
| $PaBr_6^{2-}$ | 0.38 | -0.39 |
| $PaI_6^{2-}$ | 0.39 | -0.39 |
| $UF_6^{-}$ | 0.68 | -0.28 |
| $UCl_6^{-}$ | 0.96 | -0.33 |
| $UBr_6^{-}$ | 0.86 | -0.31 |
| $UI_6^{-}$ | 0.87 | -0.30 |
| $NpF_6$ | 0.06 | -0.01 |

Figure Caption

Figure 1.    Calculated one-electron energies for the $5f^1$ hexahalide complexes.

Figure 1

XBL797-2171