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ELECTRONIC STRUCTURE AND BONDING OF ACTINIDE COMPLEXES

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ABSTRACT

This investigation is for the study of the electronic structure of actinide complexes. Accurate Hartree-Fock self-consistent-field computations have been performed in the recently developed X_α -Multiple-Scattering approximation. The goal of the investigation is to interpret the optical and magnetic properties of the actinide compounds and to estimate the degree to which covalency must be taken into account in order to understand the role of the 5f electrons in both molecular and metallic bonding.

The compounds to be investigated will include the actinyl ions as well as the hexafluoride and oxide complexes of Uranium, Neptunium, and Plutonium. In addition, it is proposed to investigate small metallic clusters which reflect the complex geometry of the unit cell found in the metallic phase of the actinide elements.

I. Introduction

This report outlines some of the preliminary progress made in the study of the electronic structure of actinide complexes in the Hartree-Fock self-consistent-field approximation. Our goal is to interpret the optical and magnetic properties of these compounds and to estimate the degree to which covalency must be taken into account in order to understand the role of the 5f electrons in both molecular and metallic bonding. The specific compounds to be investigated will include both the hexafluoride and oxide complexes as well as small metallic clusters which reflect the complex geometry of the unit cell found in the metallic phase of these elements.

Historically the spectra of actinide compounds have been discussed in terms of crystal field theory in which the optical spectra is interpreted in terms of the Slater-Condon parameters (arising from electronic repulsion), the spin orbit coupling parameter, and the crystal field splitting parameters (due to the electrostatic field of the ligands). On comparison with experiment one finds both the Slater-Condon parameters and the spin orbit parameters are reduced from the free atom values. This change from the free atom parameters is interpreted to arise from the covalent mixing of ligand orbitals into the metal d and f functions. The covalency effects in actinide complexes are generally thought to be intermediate between that of the well shielded 4f electrons of the rare earths and the strong covalent bonding found in many transition metal ions.^{1,2}

Indeed, recently, Hill³ has argued that the 5f electrons are often better compared to the 3d electrons of the first transition series than to the 4f electrons of the rare-earth series. The results of recent band structure calculations by Kmetko⁴ and Koelling and Freeman⁵ would seem to give weight to this hypothesis.

In an attempt to understand covalency effects in transition metal ions we have recently carried out Hartree-Fock self-consistent-field calculations on the NiF_6^{4-} cluster.⁶ The molecular orbitals of the complex were expanded in a basis of Gaussian functions which included sufficient flexibility to allow for orbital relaxation in the field of the ligands. All 86 electrons were included and all multicenter integrals were accurately calculated. Even for this ionic complex extensive covalent mixing of metal 3d and ligand 2s and 2p functions was found. The resulting wave function was used to compute the crystal field splitting parameter, $10Dq$, and the transferred hyperfine interaction parameters. Comparison with experiment led to the conclusion that a Hartree-Fock description of the cluster gave reasonably good charge densities and excitation energies.

Unfortunately these techniques are not at present applicable to actinide complexes. In Section II below we summarize in some detail a recent variant of the Hartree-Fock approximation (the self-consistent-field- X_α multiple scattering method) which is feasible for actinide complexes and in Section III we report some preliminary results for the Uranyl ion (UO_2^{++}) and Uranium Hexafluoride⁷ done in collaboration with M. Boring and J. Wood of the University of California Los Alamos Scientific Laboratory.

Section IV reviews the systems we propose for future investigation and finally in Section V we briefly speculate on the possibility of using the results obtained from the multiple scattering method to guide the formulation of atomic pseudopotentials to replace the actinide core electrons.

II. The Self-Consistent-Field-X Multiple Scattering Method

The Hartree-Fock self-consistent-field model⁸ is a one electron approximation in which the true many electron wavefunction is approximated as an antisymmetrized product of one electron spin orbitals, u_i . From these spin orbitals we can set up a charge density

$$\rho(1) = \sum_i n_i u_i^*(1) u_i(1)$$

where the n_i are occupation numbers with the value zero or unity. The expectation value of the total energy then takes the form

$$\langle E \rangle = \sum_i n_i \int u_i^*(1) f_1 u_i(1) dv_1 + \frac{1}{2} \int \rho(1) \left[\int \rho(2) g_{12} dv_2 + U(1) \right] dv_1$$

where f_1 is a one electron operator consisting of the kinetic energy and the potential energy of an electron in the field of the nuclei and g_{12} represents the coulomb repulsion between a pair of electrons. The first term represents the average of the one electron operators. The second term represents one half the integral of the charge density multiplied by an effective potential energy. This potential energy is made up of the coulomb interaction, $\int \rho(2) g_{12} dv_2$, which includes the self-interaction of the electron and of the term $U(1)$, a negative term which subtracts the self-interaction and also takes account of all exchange terms.

The one-electron Schrödinger equations used for determining the spin orbitals u_i are now derived by applying the variation principle to the expression for the total energy.

$$[-\nabla_1^2 + V_c(1) + V_{\text{xHF}}(1)]u_1(1) = E_1 u_1(1)$$

Here $-\nabla_1^2$ is the kinetic energy and $V_c(1)$ is the electrostatic potential energy, both electronic and nuclear, computed classically. The quantity $V_{\text{xHF}}(1)$ is the exchange potential. Up to this point the formulation is exact within the framework of the one electron model.

The Hartree-Fock equations may be solved exactly by numerical integration for atomic systems. For molecules they may be solved approximately by expanding the molecular spin orbitals in terms of a finite linear combination of atomic orbitals (Gaussian or Slater) centered on the constituent atoms.

At this point two further approximations to the Hartree-Fock equations have been introduced which allow their practical extension to actinide complexes. The first is the statistical approximation for the exchange potential V_{xHF} ,⁹

$$V_{\text{x}\alpha}(1) = -6\alpha\{3/8\pi\rho(1)\}^{1/3}$$

where α is a constant to be determined. The criterion used is that α should give as good a description as possible of the separated atoms. Slater and Wood¹⁰ have shown that if one chooses α so that $\langle E_{\text{x}\alpha} \rangle$ agrees exactly with the Hartree-Fock energy of the same atom then the X_α spin orbitals agree closely with the Hartree-Fock spin orbitals.

The second approximation introduced by Slater, Johnson, and Connolly¹¹ is to approximate the one electron potential by the so-called "muffin-tin" approximation. That is, each atom is

surrounded by a sphere (Region I) and inside each of these spheres the exact potential is replaced by a spherical average. In the region between the spheres (Region II) the potential is replaced by a constant. The entire molecule is now surrounded by a sphere and in this extra-molecular region (Region III) the exact potential is replaced by a spherical average.

In carrying through a self-consistent-field calculation one may start with an assumed potential (i.e., a superposition of atomic potentials), solve the one electron equations for that potential, finding spin orbitals u_i with eigenvalues E_i . The charge density arising from the occupied spin-orbitals then determines a new potential used as the starting point of the next iteration.

The computational method used for solving the one electron Hartree-Fock equations was formulated by Johnson¹² and is known as the multiple scattering method. Inside each atomic sphere in Region I there is a spherically symmetric potential. The solution of Schrödinger's equation can be expanded as a linear combination of spherical harmonics and numerically determined radial functions depending on the angular momentum number l and the energy E_i . The spherically symmetric Region III outside the molecule may be treated in a like manner. In the Region II (the intersphere region) there is a constant potential. The solution can be taken to be a sum of free-space scattering functions (products of spherical harmonics and the proper combinations of spherical Bessel, Neumann, or Hankel functions) which fall off in the proper

exponential manner as one goes away from an atom. The satisfaction of the proper boundary conditions on the surface of the atomic spheres leads to the determination of the unknown expansion coefficients as well as the eigenvalues E_1 .

These equations have been programmed by Johnson and Connolly¹³ and can be solved very efficiently. The expansion of the wavefunction converges very rapidly as not many values of angular momentum are required for each atomic sphere. The final wavefunction has the physical features of a linear combination of atomic orbitals. In the traditional Hartree-Fock approach one obtains these molecular orbitals as a highly approximate solution to the correct one-electron Hamiltonian. In the multiple-scattering method one solves a model Hamiltonian exactly with great speed and efficiency. It has recently been shown by Rösch, Klemperer, and Johnson¹⁴ that approximate non-muffin-tin corrections can be introduced into the method through the use of overlapping atomic spheres. It should also be pointed out that the transition energies calculated in the multiple-scattering method are weighted averages of the multiplets arising from a given atomic or molecular configuration.

The multiple-scattering method has been applied with excellent results to a variety of molecular systems.¹¹ In this laboratory we have recently completed successful investigations of: (1) the rydberg states of water¹⁵; (2) the electronic spectra of the solvated electron¹⁶; (3) the electronic spectra of various halogen substituted permanganates and chromates¹⁷; and (4) a study of metal-metal bonding in $\text{Re}_2\text{Cl}_8^{2-}$ ¹⁸.

III. Preliminary Results

Over a decade ago McGlynn and Smith¹⁴ interpreted the electronic structure of the actinyl ions based upon a molecular orbital picture. They postulated the ground state of the linear UO_2^{++} ion to be of $1\Sigma_g^+$ symmetry with configuration,

$$1\sigma_u^2 1\sigma_g^2 1\pi_u^4 1\pi_g^4 .$$

The molecular orbitals were constructed from 2p orbitals on each oxygen and 5f, 6d, 7s, and 7p orbitals centered on the uranium atom. In the Russell-Saunders (Hund's case a) coupling scheme the first excited state arises from either the configuration $1\Sigma_g + 1\pi_g^3 \phi_u^1 (1,3\Delta_u, 1,3\Gamma_u)$ which is orbitally forbidden or the configuration $1\Sigma_g + 1\pi_g^3 \delta_u^1 (1,3\Pi_u, 1,3\Phi_u)$ the $\Sigma + \Pi$ component of which is allowed. Upon analysis of the UO_2^{++} absorption and emission spectra in solution McGlynn and Smith assign the first three bands to the components of a $3\Pi_u$ state.

Newman²⁰ has recently interpreted the near visible absorption spectra of UO_2^{++} in the cesium uranyl nitrate crystal. He emphasizes the importance of spin-orbit coupling and suggests that jj -coupling (Hund's case c) is dominant in the uranyl ion. In addition Newman postulates a different orbital ordering in the ground state based on U-O overlap integrals computed with numerical Hartree-Fock function ($1\pi_g^4 1\sigma_g^2 1\pi_u^4 1\sigma_u^2$).

Most recently, Görrler-Walrand and de Jaegere²¹ reported a systematic study of a large number of uranyl complexes. The visible absorption spectra of these complexes could be classified

into six distinct categories differing in the number and relative intensity of the electronic transitions involved. To each of these spectral categories could be associated a given geometry. By analyzing these results by means of group theory and simple molecular orbital theory, Görller-Walrand and Vanquickenborne²² have shown that the band system situated at 20000-22000 cm^{-1} is only consistent with a ${}^1\Sigma_g + {}^1\Phi_g$ transition ($\sigma_u^1 \phi_u^1$), while the band system at 22500-27000 cm^{-1} is consistent with a ${}^1\Sigma_g + {}^1\Delta_g$ transition ($\sigma_u^1 \delta_u^1$). In addition they have shown that it is possible to use the small equatorial perturbation due to the ligands as a physical probe to examine the coupling situation in the excited uranyl Φ_g and Δ_g states.²³ They conclude that only a Russell-Saunders coupling scheme allows a satisfactory explanation of the observed splitting and intensity.

In our computations on the uranyl ion⁷ a starting potential for the multiple scattering method was generated by superimposing atomic charge densities. For the U^{++} ion a relativistic atomic (Dirac-Slater) charge density²⁴ was superimposed with a non-relativistic oxygen atomic ($V_{\text{x}\alpha}$) charge density.¹⁰ The valence electrons for the U^{++} ion were considered to be $6s^2 6p^6 5f^2 6d^1 7s^1$ while the remaining electrons of the core were held fixed. In the case of the oxygen atoms only the $1s^2$ electrons were considered part of the core. Once a starting potential was obtained by superimposed atomic potentials the calculations were taken to self-consistency. We summarize below the results for linear UO_2^{++} at $R = 1.73 \text{ \AA}$ (3.269 a.u.).

First, the four highest occupied molecular orbitals fell in the order $\pi_u^4 \sigma_u^2 \pi_g^4 \sigma_g^2$. These orbitals show heavy mixing between the uranium 5f and 6d orbitals and the oxygen 2p orbitals with little participation of the uranium 7s or 7p orbitals or the oxygen 2s orbital. The covalency is thus surprisingly large. The total number of electrons in each region for these four molecular orbitals is as follows: uranium sphere (total 3.66, .02s, .1p, .58d, 2.96f); in each oxygen sphere (total 2.06, 2.06p); outer sphere (total .36, .04s, .04p, .18d, .10f); intersphere region (total 3.86). Although it is difficult to assign the outersphere and intersphere charge to a particular atom most of the charge probably belongs to the oxygens. This is due to the fact that the atomic spheres were not allowed to overlap resulting in a far larger uranium (2.3344 a.u.) than oxygen (0.9346 a.u.) atomic sphere radius. The uranium radius was set by requiring it to contain the entire core charge density. The calculations thus show, depending upon how the charge is partitioned, a slight ligand to metal charge transfer.

We have also examined the electronic transition energies for the excitation $^1\Sigma_g \rightarrow ^1,3\Phi_g(\sigma_u^1 \phi_u^1)$ which falls at $16,457 \text{ cm}^{-1}$ and the transition $^1\Sigma_g \rightarrow ^1,3\Pi_u, ^1,3\Phi_u(\pi_g^3 \delta_u^1)$ which falls at 21942 cm^{-1} . It must be remembered that in the multiple-scattering method the transition energies represent weighted averages of the multiplets arising from a given molecular configuration. The results are thus suggestive but certainly not conclusive that the interpretation of Görller-Walrand et. al.²¹⁻²³ are correct.

We report briefly on some preliminary results on the charge distribution in UF_6 and on the optical spectra of UF_6^- . A detailed review of the absorption spectra of actinide compounds has been published recently by Ryan.²⁵ In addition $5f^1$ transitions, in particular pentavalent uranium have been reviewed by Selbin et. al.,²⁸ and Riesfeld and Crosby.²⁹ The $5f^1$ configuration gives rise in octahedral symmetry to a $^2A_{2u}$ ground state and a $^2T_{2u}$ and $^2T_{1u}$ excited states. In the intermediate coupling scheme the ground state is $^2\Gamma_7$ while $^2T_{2u}$ is split by spin orbit coupling into $^4\Gamma_8$ and $^2\Gamma'_7$ and $^2T_{1u}$ is split into $^4\Gamma'_8$ and $^2\Gamma_6$. Experimentally we would thus predict at least four low energy transitions to be observed, although Jahn-Teller splitting of the Γ_8 and Γ'_8 states is possible. Riesfeld and Crosby²⁹ assign the spectrum as follows: $A_{2u} \rightarrow T_{2u}(\Gamma_8, \Gamma'_7)$ at 4587 cm^{-1} and 6928 cm^{-1} ; $A_{2u} \rightarrow T_{1u}(\Gamma'_8, \Gamma_6)$ at 12705 cm^{-1} and 14245 cm^{-1} .

The calculation we performed on uranium hexafluoride was carried out in an essentially equivalent manner to that reported above for the uranyl ion. All electrons below the 6s and 6p level of uranium were treated as part of the core along with the 1s electrons of the fluorine atoms. The covalent mixing of the metal 5f orbitals with the ligand 2p orbitals was again surprisingly large. The distribution of the 56 valence electrons was as follows: uranium sphere (total 10.72, 1.96s, 5.19p, .7d, 2.87f); in each fluorine sphere (total 5.55, 1.62s, 3.93p); outersphere (total .75, .05s, .15p, .27d, .28f); intersphere region (total 11.25). The 2.87f electrons found in the uranium sphere may be contrasted to the 3.7f electrons found by Hill and

Kmetko⁴ as a result of their band structure calculation for metallic uranium. We have also performed a series of computations upon UF_6^- and computed the one electron excitation energies $A_{2u} \rightarrow T_{2u}$ (4388 cm^{-1}) and $A_{2u} \rightarrow T_{1u}$ (17005 cm^{-1}). These are seen to be in fair agreement with the experimental results. It should be remembered that within the multiple scattering formulation one electron transitions of this type are computed exactly; i.e., there is no problem arising from the separation of multiplets.

IV. Proposed Investigations

The results of the calculations reported above strongly suggest the possibility of obtaining both qualitative and quantitative information about the electronic structure and bonding of actinide complexes by means of the self-consistent-field multiple scattering model. The recent work¹⁴ on overlapping atomic spheres gives hope of partially sidestepping the effects of the muffin-tin approximation and thus reducing the number of electrons assigned to the intersphere region. One should also investigate the changes that might be expected if relativistic corrections were included for the valence electrons as well as for the frozen core. It should be possible to put the relativistic corrections directly into the Hamiltonian as is done in relativistic band structure calculations.³⁰ We propose here as a first step in that direction to compute the spin-orbit splitting of the upper few molecular orbitals as a perturbation correction in a manner similar to that used by Wood³¹ in atomic X_α computations.

We now summarize briefly some of the systems that seem fruitful for future investigation.

A. Actinyl ions

We propose to complete the series of calculations begun with UO_2^{++} to include NpO_2^{++} , PuO_2^{++} , and AmO_2^{++} whose spectra are reasonably well characterized. These systems are small enough to allow experimentation with the method in order to

develop improved computational techniques. This is particularly true for NpO_2^{++} where the configuration $5f^1$ allows simple interpretation of the spectra in the multiple-scattering model.

B. Actinide Hexahalides and Oxides

The reviews of Ryan²⁵ (halides), Selbin and Ortega²⁶ (U^{5+}), and the recent work of Hecht, Lewis, and Eastman¹ (oxides) indicate the extraordinary range of experimental information available on the electronic structure of actinide complexes and in particular those with the configuration $5f^1$. We propose to continue our investigation of UF_6 and UF_6^- and extend the computation to other halide ligands. In addition we plan to investigate NpF_6 , the $5f^1$ oxides of uranium (UO_3^+ , UO_2^+ , UO_3^- , UO_4^{3-} , and $\text{U}_2\text{O}_6^{2-}$), and several compounds of plutonium. It is proposed to perform spin-polarized computations in order to compute the ligand transferred hyperfine parameters.

C. Metal Clusters

The actinide metals exhibit a wide variety of interesting magnetic, optical, and superconducting properties. In recent years a number of band structure calculations have been performed in order to gain better theoretical understanding into their origin^{3,4,5}. Unfortunately the metals have complex crystal structures with many atoms per unit cell and low symmetry³². Thus recent computations on uranium have considered only such phases as γ -uranium with body centered cubic (bcc) structure.

We propose to perform a self-consistent-field multiple-scattering calculation on a nine atom bcc uranium cluster and compare the results to the band structure calculations of Kmetko and Hill⁴ in order to calibrate our results. It will then be possible to perform computations on the five atom cluster of α -uranium (C_{2v} symmetry). The extension of this technique to the atomic clusters arising from the different phases of neptunium and plutonium would be straightforward and should yield interesting information about the participation of 5f electrons in different bonding situations.

V. Atomic Pseudopotentials

The multiple-scattered-wave formalism developed by Slater and Johnson is, as discussed above, the only practicable method which may be applied to the study of the electronic structure of actinide complexes. Its great strength is the ease and economy with which it may be applied to systems containing heavy metals. The predictions of charge distributions and photo-electron spectra have been encouraging. The prediction of optical properties is more difficult as the method is only capable of separating multiplets in situations of low symmetry. The method seems least appropriate when discussing stability or conformation of molecular complexes. The necessity to compute total energy arises in the prediction of vibrational force constants and anharmonicity constants important in the discussion of isotope separation, for example, that of UF_6 .

An alternate technique to the multiple-scattering method would be to replace the core electrons of the metal with an atomic pseudopotential³³. We are in this laboratory at present engaged in implementing a set of atomic pseudopotential programs based on the work of Goddard, Kahn, and Melius³⁴. If we can successfully apply this method to transition metal complexes it should be possible to extend the formulation to the actinides. However, unlike the transition metal complexes which are reasonable well understood, it will be crucial to have the results of the multiple-scattering computations to guide the application of pseudopotential methods. We propose to follow this promising line of research.

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