MOLECULAR CLUSTER THEORY OF CHEMICAL BONDING IN ACTINIDE OXIDES

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Prepared for

3rd International Conference on
the Electronic Structure of the Actinides
Grenoble, France
August 30 to September 1, 1978

U of C-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY

MOLECULAR CLUSTER THEORY OF CHEMICAL BONDING IN ACTINIDE OXIDES

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La structure électronique des oxydes et bioxydes d'actinides, AcO et AcO_2, où Ac= Th, U, Np, Pu, Am, Cm et Bk, a été étudiée selon des méthodes de groupes moléculaires basées sur la théorie de premiers principes de densité locale d'un électron. Les orbitales moléculaires des groupes voisins les plus proches AcO_6 et AcO_8, représentatifs des treillis d'oxyde et de bioxyde ont été obtenues à l'aide de modèles Hartree-Fock-Slater spin-restreints et spin-polarisés non relativistes utilisés pour toute la série. Des calculs Dirac-Slater totalement relativistes ont été effectués pour ThO, UO et NpO afin d'explorer la grandeur des fragmentations d'orbite de spin et des changements de niveau en structure de valence. Des calculs constants en eux-mêmes ont été répétés pour NpO, le groupe NpO_6 étant enfoncé dans le champ moléculaire du solide. Enfin, un modèle de "moment polarisé" combinant à la fois et de façon constante polarisation de spin et effets relativistes, a été appliqué au système NpO.

Les résultats indiquent qu'un mélange covalent de niveaux d'oxygène 2p et Ac 5f augmente rapidement dans la série d'actinides; ils indiquent aussi que la covalence s, p, d du métal est presque constante. L'analyse Mulliken de la population de l'orbitale atomique relative aux fonctions de poids des groupes montre que les modèles de champ cristallin d'ions libres sont peu sûrs, à l'exception des actinides de lumière. La forme des lignes de photoélectrons de rayons X a été calculée et les résultats indiquent qu'elles correspondent assez bien aux données expérimentales sur les bioxydes.

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The electronic structure of actinide monoxides AcO and dioxides AcO_2, where Ac = Th, U, Np, Pu, Am, Cm and Bk has been studied by molecular cluster methods based on the first-principles one-electron local density theory. Molecular orbitals for nearest neighbor clusters AcO_6^{10-} and AcO_8^{12-} representative of monoxide and dioxide lattices were obtained using non-relativistic spin-restricted and spin-polarized Hartree-Fock-Slater models for the entire series. Fully relativistic Dirac-Slater calculations were performed for ThO, UO and NpO in order to explore magnitude of spin-orbit splittings and level shifts in valence structure. Self-consistent iterations were carried out for NpO, in which the NpO_6 cluster was embedded in the molecular field of the solid. Finally,a "moment polarized" model which combines both spin-polarization and relativistic effects in a consistent fashion was applied to the NpO system.

Covalent mixing of oxygen 2p and Ac 5f orbitals was found to increase rapidly across the actinide series; metal s,p,d covalency was found to be nearly constant. Mulliken atomic orbital population analysis of cluster eigenvectors shows that free-ion crystal field models are unreliable, except for the light actinides. X-ray photoelectron line shapes have been calculated and are found to compare rather well with experimental data on the dioxides.

Recent advances in one-electron local density theory have made it possible to perform quantitative first-principles studies of the electronic structure of molecules containing actinide atoms(1-5). Results for free molecules like UF_6 have been compared with photoelectron and optical data, showing that many features of the spectra can be understood in terms of simplified orbital models, which differ from the traditional free ion approach by the covalent mixing of actinide (Ac) and ligand levels. Active participation of Ac 5f states in the metal-ligand bond has been demonstrated.

The nature of chemical bonding in solid compounds of the actinides can be explored through use of molecular cluster models; here we briefly present some results from an ongoing study of the monoxides and dioxides. Wavefunctions and molecular orbital (MO) energies have been obtained for AcO_6^{10-} and AcO_8^{12-} clusters representative of the monoxide and dioxide

lattices making use of a discrete variational method described previously (6). Numerical free atom wavefunctions were used as a basis set in the variational procedure; overlap and hamiltonian matrix elements were calculated by a numerical sampling algorithm.

Within the local density formalism one may choose models of varying degrees of complexity, i.e. nonrelativistic (spin-restricted or spin-polarized) and relativistic (restricted or polarized). It is useful to compare predictions of these models in order to identify the source of observed features in the MO structure. Complete calculations within a given model require self-consistent iterations, using the occupied MO's the produce a charge density and potential. Treatment of solids involves the further complication of developing embedding constraints on the cluster due to the crystal environment(7). As a first approach we have considered nonself-consistent models in which the input atomic configurations were chosen empirically to produce "reasonable" cluster energy levels which compare well with available photoelectron data(8). Our findings are discussed in detail in forthcoming publications(9,10). We can summarize the results as follows:

In a nonself-consistent (NSC) model cluster charge densities were formed by superposition of free atom densities, and used to construct the one-electron potential. A satisfactory MO level scheme for the entire AcO and AcO_2 series was found in nonrelativistic (NR) spin-restricted and spin-polarized models with the use of <u>free atom</u> oxygen $2s^2 2p^4$ and actinide $5f^n 6d^0 7s^2$ configurations. The MO levels can be described as a practically constant framework, consisting of Ac 6d,7s,7p and O 2s,2p states in which $5f\uparrow$ and $5f\downarrow$ states shift systematically toward greater binding energies with increasing atomic number. In the NSC model a maximum "5f" exchange splitting of 4.5 eV was found for AmO, corresponding to the assumed high spin state of the atom. Crystal field splittings of 1.2-1.4 eV were calculated for the MO's of predominant 5f character. However when such "5f" levels approach and overlap with the O 2p band (as for example $5f\uparrow$ in PuO) the free ion crystal field model loses its utility. In any case a significant amount of 5f and 6d character is found in the "O 2p" valence band, leading to effective Ac ion configurations quite

different from those of the free ion.

Decomposition of cluster eigenvectors into atomic orbital contributions was carried out using Mulliken population analysis. The resulting atomic orbital populations provide a quantitative (but basis dependent) picture of the effective atomic configuration in the solid, and can be used to define an approximate self-consistent-charge (SCC) scheme for iteration(6). Populations determined for individual MO levels have been used to calculate X-ray photoelectron line shapes, which compare well with experimental data on the dioxides(8). The main discrepancy concerns relative intensity of Ac 5f and O 2p contributions to the photoemission. It remains an interesting problem to determine whether this discrepancy is altered by self-consistent iterations (it seems unlikely) or whether the theoretical atomic cross-sections used in the lineshape calculation represent an inadequate approximation.

Table 1. Total actinide valence atomic orbital populations for spin-unrestricted AcO_6^{10-} and AcO_8^{12-} clusters, using potentials generated from superimposed free atom charge densities.

	monoxide				dioxide			
	5f	6d	7s	7p	5f	6d	7s	7p
Th	2.37	0.87	0.01	0.02	0.48	1.02	0.01	0.02
U	4.44	0.86	0.02	0.02	2.71	1.07	0.01	0.02
Np	5.44	0.81	0.03	0.03	4.00	1.08	0.01	0.02
Pu	6.54	0.83	0.03	0.03	5.21	1.07	0.01	0.02
Am	7.18	0.79	0.04	0.03	6.60	1.08	0.01	0.02
Cm	8.34	0.77	0.04	0.03	7.34	1.08	0.01	0.02
Bk	9.95	0.75	0.04	0.04	8.16	1.07	0.01	0.02

In Table 2 are shown the valence MO levels for NpO_6^{10-} obtained by SCC spin-polarized iterations, for a cluster embedded in the potential field of the NpO lattice represented by superposition of Np^{2+} and O^{2-} charge densities. Some quantitative differences can be noted in comparison with the NSC results(10), but the overall level structure is rather similar. In principle we intend to continue iterations by modifying the crystal environment until mutual consistency is reached. It should be noted that there is no reason to suppose that the iterated

ground state will provide a better model for binding energies than NSC models, because of the rather large Coulomb corrections and relaxation shift associated with the ionization process. The position of Ac 5f levels is notably sensitive to configuration changes. Slater's transition state scheme provides a feasible method for SC treatment of these effects, but in principle independent calculations must be done for each ionization level(11).

Table 2. Self-consistent-charge spin-polarized valence levels (in eV) for NpO_6^{10-} clusters embedded in the NpO lattice.

MO	↑ spin	↓	MO	↑ spin	↓	MO	↑ spin	↓
$7e_g$	0.2	0.0[a]	$11t_{1u}$	6.2 (5f)	6.4[b]	$9t_{1u}$	10.2	10.4
$5t_{2g}$	3.9	3.8	$1t_{1g}$	8.4	8.9	$4t_{2g}$	10.8	10.0
$12t_{1u}$	5.7	4.8	$10t_{1u}$	8.4	8.6	$8t_{1u}$	20.9	20.5
$3t_{2u}$	6.4[b] (5f)	5.3	$2t_{2u}$	8.9	9.2	$8a_{1g}$	23.1	23.5
$10a_{1g}$	5.5	5.7	$9a_{1g}$	9.4	9.6	$5e_g$	23.2	23.5
$2a_{2u}$	7.0 (5f)	5.9	$6e_g$	9.9	10.2	$7t_{1u}$	24.3	24.4

a) Arbitrary zero of energy b) First occupied levels

Space limitation prevents discussion of SC relativistic results obtained to date; these will be published elsewhere.

Acknowledgement: DEE acknowledges support by NSF (Grant No. DMR77-22646) and by the U.S. Department of Energy

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