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Molecular cluster theory of chemical bonding in actinide oxides ([†])

D. E. Ellis, V. A. Gubanov (*), and A. Rosén (**)

Northwestern University, Evanston, Ill. and Argonne National Laboratory, Argonne, Ill., U.S.A.

(*) Institute of Chemistry, Ural Science Centre, Academy of Sciences, Sverdlovsk, U.S.S.R.

(**) Chalmers University of Technology, Göteborg, Sweden

Résumé. — La structure électronique des mono-oxydes et des dioxydes d'actinides AcO et AcO₂ (où Ac = Th, U, Np, Pu, Am, Cm et Bk) est étudiée à l'aide de modèles moléculaires dans le cadre du formalisme de la densité locale. Les orbitales moléculaires des systèmes AcO₆¹⁰⁻ et AcO₈¹²⁻ utilisés comme modèles pour les mono- et dioxydes, ont été calculées pour toute la série des actinides dans l'approximation Hartree-Fock-Slater non relativiste avec et sans polarisation de spin. Pour ThO, UO et NpO, nous utilisons le modèle complètement relativiste de Dirac-Slater afin d'évaluer l'importance du couplage spin-orbite et des déplacements des niveaux. Nous effectuons un calcul self-consistent dans le cas de NpO, le groupement NpO₆ étant placé dans le champ moléculaire du solide. Finalement, nous appliquons au composé NpO un modèle de *moment polarisé* tenant compte de façon cohérente de la polarisation de spin et des effets relativistes.

Abstract. — The electronic structure of actinide monoxides AcO and dioxides AcO₂, 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 neighbour clusters AcO₆¹⁰⁻ and AcO₈¹²⁻ 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 NpO₆ 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.

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 UF₆ 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 AcO₆¹⁰⁻ and AcO₈¹²⁻ 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 to 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 AcO₂ series was found in nonrelativistic (NR) spin-restricted and spin-polarized models with the use of *free atom* oxygen 2s² 2p⁴ and actinide 5fⁿ 6d⁰ 7s² configurations. The MO levels can be described as a practically constant

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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

Table I. — *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

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.

In table II 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].

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

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

MO	$\uparrow$ spin	$\downarrow$	MO	$\uparrow$ spin	$\downarrow$	MO	$\uparrow$ spin	$\downarrow$
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.

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