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Energy Near-Degeneracy Driven Covalency Analyzed by a Two-Electron Two-Orbital Model

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Abstract: A simple model based on the two-electron two-orbital textbook problem is presented and used to analyze pairwise interatomic interactions in metal-ligand bonding. In particular the two types of covalency discussed during the last decade for actinide-ligand interactions, overlap/interaction driven and energy-near-degeneracy driven covalency, as well as their influence on the bond strengths and interatomic charge build-up are discussed. The hydration complexes $M(H_2O)_n^{4+}$ of selected tetravalent lanthanide and actinide ions are used to probe the performance of the model for an analysis of calculations as well as for predictions.

Key words: bonding, covalency, actinides, lanthanides.

1. Introduction

The involvement of actinide 5f orbitals in chemical bonding was already discussed as early as 1954 by Seaborg and coworkers [1] and has been a hotly debated topic of numerous research articles since then, which are summarized in several reviews [2-15]. Actinide-ligand bonding is a very complicated topic, due to the influence of many factors such as relativistic and correlation effects, numerous low-lying electronic states on the actinide center in case of open 5f shells, the changing character of the 5f shell from initially diffuse Rydberg type in Fr and Ra, over valence-type to rather core-like along the actinide row, as well as a competitive participation in bonding of 5f, 6d, 7p and 7s orbitals with different abilities or preferences for ionic and covalent interactions. In so far it is somewhat surprising that simple ideas from molecular orbital theory still are able to offer some insight.

Recently two concepts to explain reasons for covalent bonding in actinide complexes have been proposed [16] and extensively used [17-25], i.e., orbital overlap or interaction driven and energy (near-)degeneracy driven covalency. Following the original article of Neidig et al. [16] these types of covalency can be briefly explained as follows. The theoretical foundation is a perturbative approach of MO-LCAO (molecular orbitals by linear combination of atomic orbitals) theory to actinide-ligand bonding, starting with an ionic picture of a complex, i.e., $M^{n+}(L^{m-})_k$, as zeroth order. A metal orbital ϕ_M with orbital energy ϵ_M, and a ligand orbital ϕ_L with orbital energy ϵ_L, can mix leading to an antibonding

$$\varphi_a = \frac{1}{\sqrt{1 + 2\lambda S_{ML} + \lambda^2}}(\phi_M + \lambda\phi_L) \qquad (1)$$

and a bonding

$$\varphi_b = \frac{1}{\sqrt{1 - 2\lambda S_{ML} + \lambda^2}}(\phi_L - \lambda\phi_M) \qquad (2)$$

linear combination, with S_{LM} being the overlap integral between ϕ_M and ϕ_L. We note that, probably due to their intention to analyze, e.g., K-edge X-ray absorption spectroscopy (XAS) results, the authors focus on the antibonding, in the ground state unoccupied linear combination φ_a with a leading metal contribution ($\lambda \leq 0$). In the core excited states probed by spectroscopy this orbital becomes occupied and its An 5f contributions are related to spectroscopic features. In a two-orbital model orthogonality then determines the bonding orbital φ_b occupied in the ground state and thus allows to calculate An 5f contributions. Using these ideas An 5f covalency in the ground state can be experimentally 'measured'. However, some problems might arise since the unoccupied orbital probed by XAS is probably best described as a canonical orbital, whereas for bonding discussions localized occupied orbitals are more appropriate.

The mixing coefficient λ is given by first-order perturbation theory as

$$\lambda = \frac{H_{ML}}{\epsilon_M - \epsilon_L} \qquad (3).$$

Note that $\epsilon_M > \epsilon_L$ and $H_{ML} \leq 0$ leads to $\lambda \leq 0$, i.e., the antibonding and bonding linear combinations in eqns. 1 and 2, respectively. According to the Wolfsberg-Helmholz model the Hamiltonian matrix element H_{ML} is proportional to the overlap integral S_{ML} [26]. A parameter $\lambda = 0$ results in the ionic case without orbital mixing, i.e., an unoccupied metal orbital $\varphi_a = \phi_M$ and an occupied ligand orbital $\varphi_b = \phi_L$, whereas $\lambda = -1$ corresponds to the antibonding $\varphi_a \sim \phi_M - \phi_L$ and bonding $\varphi_b \sim \phi_L + \phi_M$ linear combinations of a homonuclear diatomic such as H_2. As noted by Neidig et al. [16] a corresponding two-electron covalent bond has still 50% ionic and 50% covalent contributions, as becomes obvious from expanding the delocalized orbital product for the bonding orbital $\varphi_b \sim \phi_M + \phi_L$ into two ionic and two covalent terms with localized orbitals

$$\varphi_b(1)\varphi_b(2) \sim \phi_L(1)\phi_L(2) + \phi_M(1)\phi_M(2) + \phi_L(1)\phi_M(2)$$

$$+ \phi_M(1)\phi_L(2) \qquad (4).$$

It was argued that according to eqn. 3 covalent interactions may be realized in two ways:

- a large (absolute value of the) Hamiltonian matrix element H_{ML} in the numerator, i.e., a large overlap matrix element S_{ML}, which is thus refered to as overlap driven covalency, or
- a vanishing denominator $\epsilon_M - \epsilon_L$, which is denoted as near degeneracy driven covalency.

The 'traditional' idea of covalent bonding in chemistry is that the interaction leads to orbital mixing and as a consequence to a buildup of charge between the atoms, at the same time leading to a stabilization of the bonding orbital, whereas in the physical community a mixing of atomic orbitals in canonical molecular orbitals is often considered as covalency. Neidig et al. [16] point out that the charge buildup between the metal atom and the ligand depends on the type of covalency. Near-degeneracy driven covalency may result in orbital delocalization and not necessarily a large charge redistribution. Moreover, orbital mixing termed as covalency by the physics community does not need to be accompanied by stronger bonds as expected for covalency in the chemistry community, since the energy associated with covalent mixing in second-order perturbation theory is given as

$$\Delta E = \frac{|H_{ML}|^2}{\epsilon_M - \epsilon_L} = \lambda H_{ML} \qquad (5).$$

Two bonds with the same mixing coefficient λ may have different covalent contributions to the bonding energy depending on the Hamiltonian matrix element H_{ML}. Finally, Neidig et al. [16] remarked that both types of covalency may be operative for different classes of complexes, depending on the ligand and the metal oxidation state.

It has to be mentioned that recently Sergentu and Autschbach criticized the usage of the concept of energy-driven covalency, or orbital mixing without overlap, applied previously for the interpretation of K-edge X-ray absorption near edge structure (XANES) spectra of $AnCl_6^{2-}$ (An=Th-Pu) complexes [23] in contrast to the conventional covalency based on overlap and orbital mixing as unnecessary [27]. Recent related work analyzes the covalency in CeX_6^{2-} complexes [28]. In an earlier article they in addition emphasized that, as shown by relativistic multi-configurational ab initio calculations, actinide-ligand covalency in core excited states such as probed by XANES spectroscopy may be different from the covalency in the ground state [29].

In the following we use the ideas of Neidig et al. [16] as a starting point for a related minimalistic model, which is based on a variational rather than a perturbative approach for a two-electron two-orbital bond [30]. Schwarz and collaborators discussed the covalent binding energy contributions in lanthanide trihalides molecules in terms of such a model [31]. They emphasize that the covalent bond stabilization is limited by $2H_{ML}$, i.e., there is no covalency in the sense of a bond stabilization without a metal-ligand interaction $H_{ML} \neq 0$. In addition, a nonvanishing positive bond order can result for orbital mixing without interaction, i.e., for a vanishing bond stabilization. As for the model of Neidig et al. [16] the focus of the present work is only on metal-ligand bonding, i.e., bonding between two centers, a positively charged metal ion with (partially) unoccupied valence orbitals and a ligand atom able to donate electron density into these. By no means it is intended to establish an universally applicable approach to analyze other bonding situations, such as, e.g., multiple-center covalent bonding, metallic bonding, van der Waals bonding, etc..

Kaltsoyannis, Dognon, Kerridge and other experts in the field actually strongly advocate analytic approaches which do not rely on the sometimes not uniquely defined orbitals, but rather on observables as the electron density [10, 11, 13, 15], e.g., the quantum theory of atoms in molecules (QTAIM) by Bader [32]. In fact multi-configurational treatments combined with subsequent orbital localization might result for many cases in orbital sets which are more useful for interpretation than commonly used single-reference based approaches such as density functional theory (DFT), and remove signs of 'interactions' which are rather due to the restriction to one configuration than to physical interactions. For example, it is well known that treating H_2 $^1\Sigma_g^+$ at large distance with both the $\varphi_b^2 = \sigma_g^2$ bonding and $\varphi_a^2 = \sigma_u^2$ antibonding configurations allows to form a $\varphi_b^2 - \varphi_a^2$ linear combination and thus to remove the ionic terms mentioned above from the wavefunction. After orbital localization one can write the resulting spatial wavefunction in terms of the contributing atomic orbitals $\phi_L = 1s_A$ and $\phi_M = 1s_B$, i.e., $\phi_L(1)\phi_M(2) + \phi_M(1)\phi_L(2)$, which reflects much more correctly the picture of two noninteracting neutral H atoms in their $1s^1$ ^2S ground states. We also note that it was found by Kaltsoyannis that (sometimes) different tools yield different conclusions [9], and probably for this reason Dognon recommended always to use various complementary tools for analysis of actinide-ligand bonding [10]. Nevertheless, sticking despite its limitations deliberately to a single configuration approach and to orbitals, which are familiar to and popular among chemists, it is hoped that results obtained with such a low-level model bring easily to remember insight in the terms overlap/interaction driven and energy (near-)degeneracy driven covalency. Finally we want to point out that when digging deeper even ordinary covalency for systems such as H_2 is by no means a simple topic [33].