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Chemical bonding and effective atomic states of actinides in higher oxide molecules

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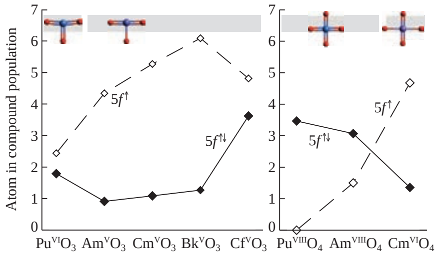
The new concept of atoms in compounds (AiC) is used to derive effective atomic configurations of plutonium and transplutonium elements in higher oxide molecules from the results of DFT calculations.



The possibility of reaching abnormally high oxidation states of plutonium and early transplutonium elements in their gas-phase oxides has been discussed during several decades (see refs. 1–5 and references therein). The results of recent relativistic density functional theory (DFT) calculations for An·4O and An·3O systems (An = Pu, Am, Cm, ...) indicate that the stability of higher oxide molecules with respect to the decay into lower oxides and oxygen as well as to the rearrangement to isomeric superoxides or peroxides should generally decrease along the actinide series from Pu onwards.[6–9] The analysis of the computed charge and magnetization density distributions and vibrational frequencies offered the possibility to depict chemical bonding in these systems in terms of bond orders and oxidation states and thus to detect some important general trends (for instance, gradual destabilization of higher oxidation states from Pu to Cf, with the only exception for the relatively stable $Bk^{V}O_3$). Several qualitative changes in the bonding picture in molecules within the series of oxides AnO_3 and AnO_4 have been predicted (the transition from hexavalency for Pu to pentavalency for heavier actinides in trioxides, the abrupt change of An oxidation state from VIII in PuO_4 and AmO_4 to VI in CmO_4). However, to complete the description of higher oxide molecules in conventional chemical terms one needs to determine effective states of actinide atoms.

In the present communication we analyze effective configurations of actinide atoms in simple molecules of their higher oxides using the adaptation of the recently proposed concept of effective atom in compound (AiC[10]) to the DFT framework. In contrast to most popular techniques of determining atomic orbital populations, the new approach avoids the arbitrariness arising from the dependence on the choice of basis set or some reference states and does not require the knowledge of the global one-electron density matrix. Furthermore, it is directly related by construction to so-called 'core' molecular properties which can be measured experimentally (chemical shifts of X-ray emission lines, Mössbauer spectra, hyperfine splittings, *etc*.[10–12]). To simplify the 'chemical' interpretation of the results, we restrict ourselves to the scalar relativistic formulation of the theory based on the use of averaged small-core relativistic pseudopotentials, which is satisfactory for this class of compounds[4] and justifies the use of collinear spin magnetization model.

The AiC approach is based on the analysis of the 'valence' part of the molecular one-electron density matrix, restricted to the vicinity of a chosen heavy nucleus. Within the DFT framework, we use the Kohn–Sham analogue of this entity

$$\rho_v^{<}(\boldsymbol{r}\eta,\boldsymbol{r}'\eta') = \begin{cases} \sum_i n_i \phi_i(\boldsymbol{r}\eta)\phi_i^{\dagger}(\boldsymbol{r}'\eta') & \text{if } |\boldsymbol{r}|,|\boldsymbol{r}'| \leqslant r_{\mathrm{c}}, \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$

Here $\boldsymbol{r}$ and η denote the spatial (with respect to the chosen nucleus) and spin electron coordinates, ϕ_i stands for the *i*th Kohn–Sham spinorbital (spinor) with its occupation number n_i. The summation runs over the valence (and possibly some subvalence) spinorbitals only; r_{c} is the radius of the 'core domain' of the atom. The AiC effective configuration is defined as a set of fractional occupancies for the free atom which yields atomic local Kohn–Sham density matrix (1) fitting in some averaged manner its molecular counterpart. To specify the latter requirement, consider the partial wave expansion of $\rho_v^{<}$

$$\rho_v^{<}(\boldsymbol{r}\eta,\boldsymbol{r}'\eta') = \sum_{ll'} \rho_v^{<ll'}(\boldsymbol{r}\eta,\boldsymbol{r}'\eta'), \tag{2}$$

where $\rho_v^{<ll'}$ stands for the sum of the terms proportional to the product of spherical harmonics $Y_{lm}(\boldsymbol{r}/|\boldsymbol{r}|)\,Y^{*}_{l'm'}(\boldsymbol{r}'/|\boldsymbol{r}'|)$. The quantities

$$q_v^l = \mathrm{tr}\,\rho_v^{<l} = \sum_{\eta} \int \rho_v^{<l}(\boldsymbol{r}\eta,\boldsymbol{r}\eta)\,\mathrm{d}\boldsymbol{r} \tag{3}$$

(partial *l*-wave charges[10]) can be regarded as contributions from the subshell(s) with the orbital moment *l* to the charge within the sphere of radius r_{c}; they are directly related to the values of certain 'core' properties.[10] Similarly, one can define partial *l*-waves of the spin magnetization component

$$\mu_{vz}^l = \mathrm{tr}(\rho_v^{<l}\sigma_z), \tag{4}$$

where σ_z is twice the spin *z* component operator, which describe the contributions of *l*-subshell(s) to the spin magnetization within the sphere $|\boldsymbol{r}| \leqslant r_c$. Now we can choose the overall paired and unpaired (spin-up) electron subshell populations so that the atomic local density matrix parameters q_ν^l and $\mu_{\nu z}^l$, for $l = 0$ through 3, coincide with those of the local molecular density matrix. Note that one cannot discern the contributions to q_ν^l ($\mu_{\nu z}^l$) from different subshells with the same *l* (for instance, 6*p* and 7*p*) because of the proportionality of the corresponding radial functions in the vicinity of the nucleus; to avoid ambiguities, we suppose that all but one (highest-energy) subshells with the given *l* were completely filled.

The core radius r_c is the key parameter of AiC techniques; theoretically, the r_c-independence of the results is guaranteed only for very small r_c.[10] Nevertheless, the results presented below were stable within 1% up to rather large r_c values (0.8–0.9 a.u.).

An important point of using DFT is that it does not provide the 'true' density matrix but only the Kohn–Sham one. Therefore, the legality of using different types of population analysis based on partial division of the density matrix such as natural bond orbitals, Mulliken populations, *etc*. is under a big question (in addition to other uncertainties of the schemes mentioned above). However, for the AiC case the legality is restored as we restrict our attention to the vicinity of a heavy nucleus where the strong field dominates over electron correlation and any mean-field approximation is more reliable than anywhere else. Furthermore, replacing the true density matrices by their Kohn–Sham counterparts both for the molecule and the free atom, one might expect some cancellation of errors.

The employed procedure of electronic structure calculations is essentially a scalar relativistic analogue of that described previously,[7,8] with only the basis set flexibility in the core domains having been significantly improved. The expansion (2) was analyzed using the described code.[12] The resulting effective paired-electron (bonding or lone-pair) and unpaired-electron subshell populations for actinide atoms are presented in Figure 1.

The following main features of the effective configurations are to be noticed.

(i) The unpaired-electron effective populations of 7*s* and 6*p* subshells are negligibly small (not shown in Figure 1). 7*s*-Shell populations do not vary strongly along both series, being in the range 0.45–0.64 in all cases. Fractional effective occupancies of 6*p* orbitals unambiguously indicate their valence, rather than subvalence, nature: overall 6*p* populations are markedly below six. This is in line with the findings of Teterin *et al*.[13] for solid oxides. The most significant loss of 6*p* electrons (0.4–0.5) occurs for $\mathrm{An^{VIII}}$ tetroxides.

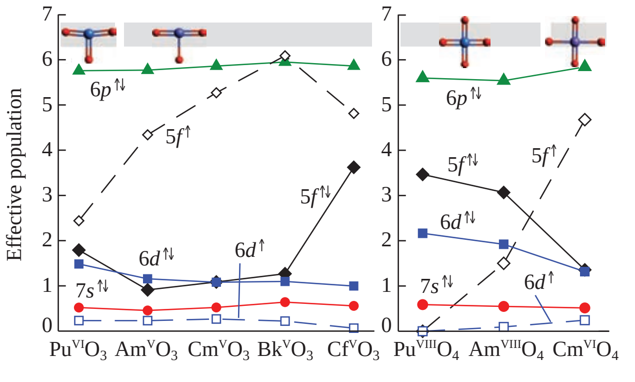


Figure 1 Effective populations of actinide atom subshells in trioxide and tetroxide molecules. Dashed lines and empty symbols: unpaired electron populations (↑), solid lines and filled symbols: paired electron populations (⇅). 7*s*, 6*p*, 6*d* and 5*f* populations are marked by circles, triangles, squares, and diamonds, respectively.

(ii) The overall paired-electron population of actinide 6*d* and 5*f* subshell in $\mathrm{AmO_3}$ is *ca*. 1.3 smaller than that in $\mathrm{PuO_3}$. Since here one cannot expect the formation of 5*f*–6*d* lone pairs, a removal of at least one 5*f*(6*d*) bonding electron in passing from $\mathrm{PuO_3}$ to $\mathrm{AmO_3}$ is to be supposed. Along with the data on magnetization density distributions[8] this should mean that one component of the double An–'equatorial' O bond which exists in $\mathrm{Pu^{VI}O_3}$ but disappears in $\mathrm{AmO_3}$–$\mathrm{CfO_3}$[8] is a An 5*f*(6*d*)–O 2*p* one. Similarly, the abrupt decrease of 5*f* and 6*d* paired-electron populations from $\mathrm{AmO_4}$ to $\mathrm{CmO_4}$ corresponds to the replacement of two double bonds by two single ones.

(iii) The number of unpaired 5*f* An electrons in $\mathrm{AnO_3}$ molecules as a function of atomic number peaks for An = Bk; the effective configuration approaches one with the half-filled *f*-shell as close as possible (the open shell population 7 cannot be reached because of significant paired electron population). This can explain relatively high stability of $\mathrm{Bk^VO_3}$ compared to its 'neighbours' $\mathrm{Cm^VO_3}$ and $\mathrm{Cf^VO_3}$.

(iv) Overall effective numbers of 5*f* electrons always markedly exceed those in the formal configurations ($5f^0$ for $\mathrm{Pu^{VIII}}$, $5f^1$ for $\mathrm{Am^{VIII}}$, $5f^2$ for $\mathrm{Pu^{VI}}$, *etc*.).

To summarize, the new AiC concept gives rise to a useful tool for representing the results of DFT calculations on *f*-element compounds in 'chemical' terms. It should be emphasized that the resulting effective configurations are just those which can be recommended for interpreting the data from several popular non-destructive experimental techniques, including X-ray and Mössbauer spectroscopy.[10] The effective atomic state analysis can be particularly useful for describing the properties of actinides in matrices, a valuable point in connection with the problem of nuclear waste immobilization.[14]

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References

1 V. P. Domanov and Yu. V. Lobanov, *Radiochemistry*, 2011, **53**, 453 (*Radiokhimiya*, 2011, **53**, 385).

2 V. P. Domanov, *Radiochemistry*, 2013, **55**, 46 (*Radiokhimiya*, 2013, **55**, 23).

3 Yu. M. Kiselev, M. V. Nikonov and B. F. Myasoedov, *Dokl. Chem*., 2013, **448**, 12 (*Dokl. Akad. Nauk*, 2013, **448**, 166).

4 A. Kovács, R. J. M. Konings, J. K. Gibson, I. Infante and L. Gagliardi, *Chem. Rev*., 2015, **115**, 1725.

5 W. Huang, P. Pyykkö and J. Li, *Inorg. Chem*., 2015, **54**, 8825.

6 W. Huang, W.-H. Xu, J. Su, W. H. E. Schwarz and J. Li, *Inorg. Chem*., 2013, **52**, 14237.

7 A. Zaitsevskii and W. H. E. Schwarz, *Phys. Chem. Chem. Phys*., 2014, **16**, 8997.

8 A. Zaitsevskii, *Phys. Chem. Chem. Phys*., 2015, **17**, 24831.

9 N. S. Mosyagin, A. V. Zaitsevskii, L. V. Skripnikov and A. V. Titov, *Int. J. Quantum Chem*., 2016, **116**, 301.

10 A. V. Titov, Yu. V. Lomachuk and L. V. Skripnikov, *Phys. Rev. A*, 2014, **90**, 052522.

11 Yu. V. Lomachuk and A. V. Titov, *Phys. Rev. A*, 2013, **88**, 062511.

12 L. V. Skripnikov and A. V. Titov, *Phys. Rev. A*, 2015, **91**, 042504.

13 Yu. A. Teterin, K. I. Maslakov, A. Yu. Teterin, K. E. Ivanov, M. V. Ryzhkov, V. G. Petrov, D. A. Enina and S. N. Kalmykov, *Phys. Rev. B*, 2013, **87**, 245108.

14 B. F. Myasoedov and S. N. Kalmykov, *Mendeleev Commun*., 2015, **25**, 319.

15 C. van Wüllen, *Z. Phys. Chem*., 2010, **224**, 413.

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