

Global and local approaches to population analysis: bonding patterns in superheavy element compounds

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Introduction

- ▶ Strong spin-orbit interaction in superheavy element (SHE) compounds requires full-relativistic description of such systems.
- ▶ Modern electronic structure theory provides few reliable tools for interpretation of relativistic models in “chemical” terms.
- ▶ A promising way to describe chemical bonds is to define the so-called effective configuration of atom in compound:

$$\mathbf{n}^A = \{n_{s_{1/2}}^A, n_{p_{1/2}}^A, n_{p_{3/2}}^A, n_{d_{3/2}}^A, n_{d_{5/2}}^A, \dots\}$$

where n_{lj} are fractional occupancies of lj -shells.

Global approach: projection analysis (PA)

- ▶ Molecular spinors are approximately re-expanded over all space in the (nearly) minimal set of atomic spinors $|\chi_k^A\rangle$ obtained as solutions of some SCF-like problem for constituent free atoms:

$$|\psi_i^{MO}\rangle = \sum_A \sum_{k \in A} c_{ki}^A |\psi_k^A\rangle + |\psi_i^{pol}\rangle$$

- ▶ Fractional occupancies n_k^A of these new basis spinors $|\chi_k^A\rangle$ are calculated similarly to Mulliken analysis [1].
- ▶ Some part of electron density is not assigned to any atom.
- ▶ PA is well suited for the cases where it is important to discern fractional occupancies of splitted subshells ($p_{1/2}$ and $p_{3/2}$, etc).
- ▶ Depends strongly on the assumed configurations of free atoms.
- ▶ This dependence can be avoided if one determines these configurations by iterations until self-consistency [2]. Resulting fractional occupancies n_i should coincide with ones used to obtain reference spinors $|\chi_k^A\rangle$.

Local approach: Atom-in-Compound (AiC)

- ▶ The partial-wave expansion of the molecular density matrix in the vicinity of chosen heavy nucleus is considered [3]:

$$\rho_{r \leq R_c}(\mathbf{r}|\mathbf{r}') \approx \sum_{ljm, l'j'm'} \Delta_{ljm, l'j'm'} \eta_{ljm}(\mathbf{r}) \eta_{l'j'm'}^\dagger(\mathbf{r}'), \quad |\mathbf{r}|, |\mathbf{r}'| \leq R_c$$

- ▶ Universal reference functions $\eta_{ljm}(\mathbf{r}) = f_{lj}(|\mathbf{r}|) Y_{ljm}(\mathbf{r}/|\mathbf{r}|)$ are constructed to be orthonormal at $|\mathbf{r}| \leq R_c$.
- ▶ The effective configuration of a atom A is defined as a set of fractional occupation numbers in SCF (e.g. Kohn-Sham) calculation of the free atom for which partial lj -wave charges q_{lj} coincide with the molecular ones:

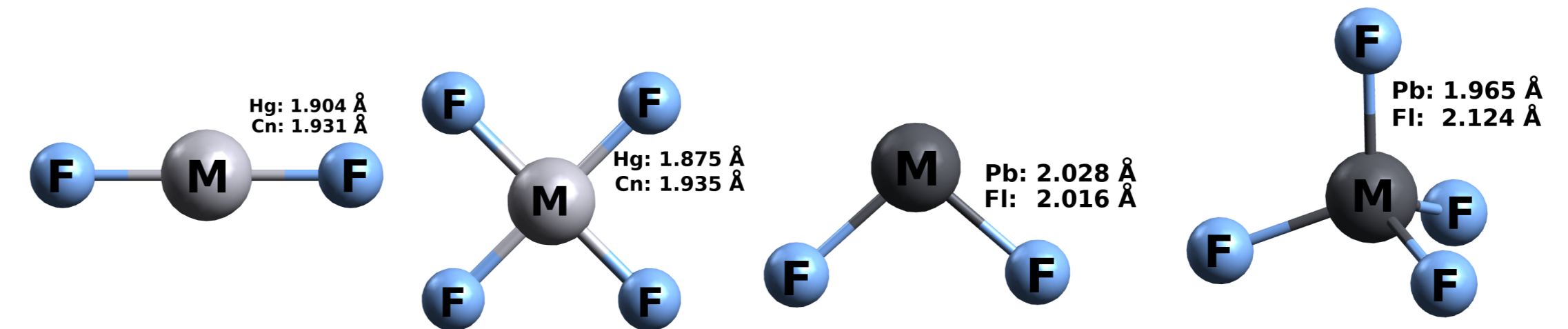
$$q_{lj}^{mol}(A) = \sum_m \Delta_{ljm, lj} = q_{lj}^{atom}(n_s, n_{p_{1/2}}, n_{p_{3/2}}, n_{d_{3/2}}, n_{d_{5/2}}) \quad \forall l, j$$

- ▶ Partial wave charges q_{lj} are the contributions from the lj -subshells to the electronic charge within the sphere of radius R_c .
- ▶ Partial wave charges q_{lj} are directly related to experimentally observable “core” properties.
- ▶ No arbitrary atomic reference state should be defined.

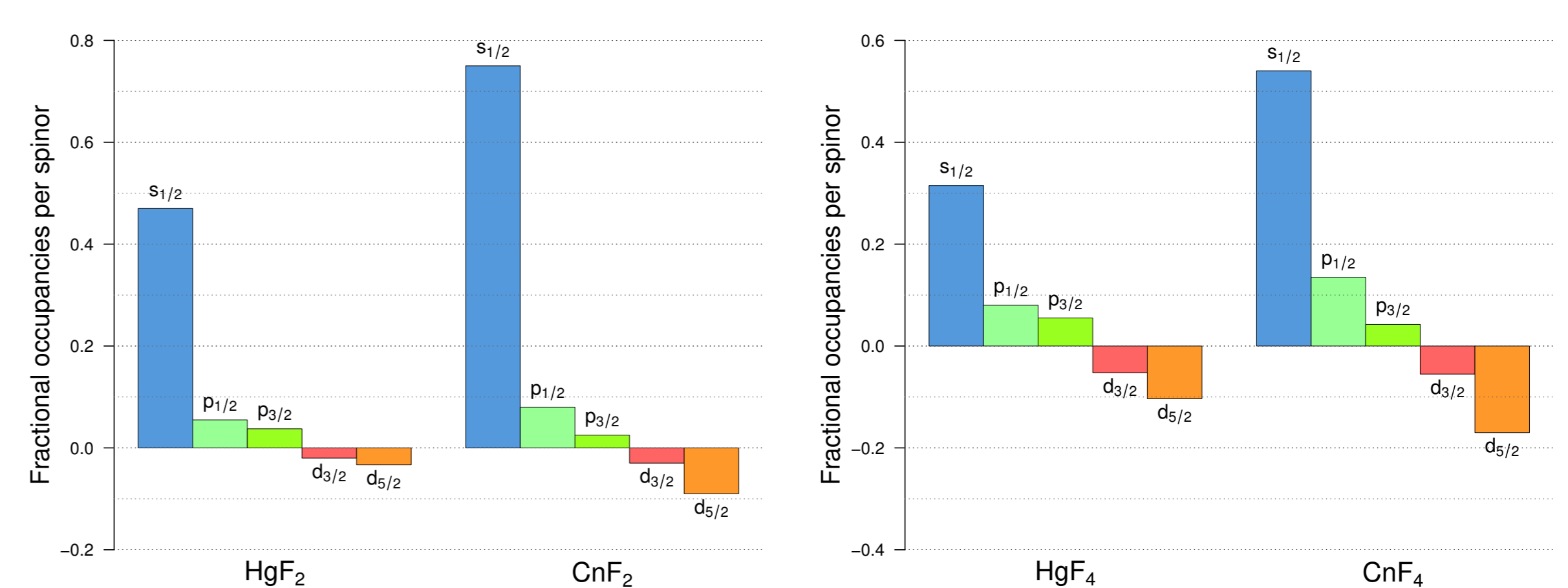
Results

In order to investigate bonding features in SHE compounds, both iterative projection analysis and Atom-in-Compound techniques were applied to molecules of fluorides and oxides MF_2 , MF_4 , MO ($M = \text{Hg, Pb, Cn, Fl}$) as well as hydroxides MOH ($M = \text{Ti, Nh}$).

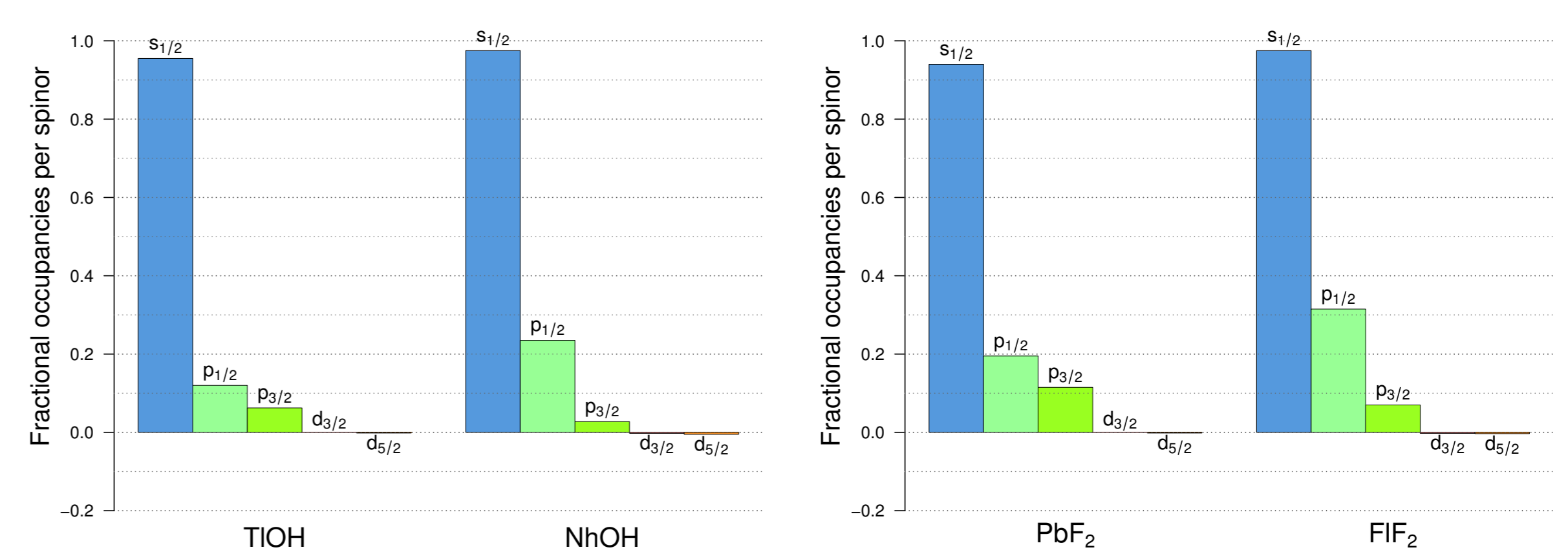
- ▶ All molecular and atomic calculations were performed using 2c-RDFT/PBE0 method [4, 5]; core electrons were replaced with SO-ECPs by Mosyagin et al [6]. Population analysis was performed for optimal molecular geometries:



- ▶ To get a σ -bond, p -spinors with different j are to be combined. Such mixing is hindered by large differences of energies and spatial distributions of the j -subshells with the same l .
- ▶ A large difference between the populations (per spinor) of the splitted lj -shells indicates inefficient mixing \rightarrow covalent σ -bonds becomes weaker (2.8 eV in HgF_2 vs 2.2 eV in CnF_2).
- ▶ In Ha and Cn compounds chemical bonds are formed mainly by s -electrons; d -subshells are not inert in Cn compounds \rightarrow Cn is a real transition element.



- ▶ Ti, Nh, Pb, Fl exhibit typical p -element behavior; d -spinors occupancies correspond to filled subvalence d -subshell.



Conclusions

- ▶ Both local and global analysis yield essentially the same relativistic effective configurations.
- ▶ The separate determination of effective populations for the subshells with the same l but different j is crucial for interpreting the bonding pattern in superheavy element compounds.

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