Projection population analysis for molecules with heavy and superheavy atoms

Alexander V. Oleynichenko$^{1, 2}$ and Andréi V. Zaitsevskii$^{1, 2}$

$^1$Petersburg Nuclear Physics Institute named by B.P. Konstantinov of National Research Center “Kurchatov Institute” (NRC “Kurchatov Institute” - PNPI), 1 Orlova roscha, Gatchina, 188300 Leningrad region, Russia

$^2$Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie gory 1/3, Moscow, 119991 Russia

A new iterative version of population projection analysis is formulated and applied to determine relativistic effective atomic configurations of superheavy elements Cn and Fl and their lighter homologues (Hg and Pb) in the molecules of their fluorides and oxides. The dependence of the computed populations on the initial reference atomic spinors is completely avoided. The difference in population of atomic spinors with the same orbital angular momentum and different total angular momenta is demonstrated to be essential for understanding the peculiarities of chemical bonding in superheavy element compounds.

INTRODUCTION

In the last two decades transactinide elements with atomic numbers exceeding 110 had been synthesized [1]. In spite of several successful chemical experiments with these species [2, 3], the bulk of information on their chemical properties is obtained from electronic structure modelling of their compounds. Due to very strong relativistic effects the bonding pattern in these compounds is rather unusual. Unfortunately, modern electronic structure theories provide few reliable tools for qualitative interpretation of relativistic models in “chemical” terms. Up to now, a straightforward relativistic generalization of Mulliken population analysis [4] remains the most popular tool for estimating the role of particular atomic spinors in chemical bond formation [5–7]. However, its results are not highly reliable because of their critical dependence on the basis set used to discretize the electronic Hamiltonian [8].

One of the most perspective relativistic population analysis techniques is so-called projection analysis (PA) proposed by Trond Saue and coworkers [9–11] and allowing to calculate effective configurations of atoms in molecules as sets of fractional occupancies of atomic spinors. The resulting configurations are much less sensitive to the basis set choice than those obtained via the Mulliken analysis. It is fully compatible with various tools of relativistic electronic structure calculations, including both all-electron four-component technologies and two-component methods using spin-orbit effective core potentials. Projection analysis is particularly well suited for cases where it is important to discern fractional occupancies of splitted subshells such as $p_{1/2}$ and $p_{3/2}$. Therefore the PA technique may be the best choice in the cases where the non-relativistic and even scalar relativistic description is fully inadequate, including those of superheavy element (SHE) compounds. However, projection analysis employs reference orbitals (spinors) of free atoms, which can depend strongly on the assumed reference atomic configurations. This gives rise to a certain arbitrariness of the computational scheme.

As mentioned above, copernicium (E112) and flerovium (E114) are the most studied in chemical sense among all superheavy elements. The chemistry of elements 112 and 114 is of great interest, since their atoms have quasi-closed-shell electron configurations $7s^2$ for Cn and $7s^27p_{1/2}^2$ for Fl with relativistically stabilized valence $7p_{1/2}$ electrons. This fact should lead to a relative inertness of these elements in most chemical interactions, which has been demonstrated both theoretically [12] and experimentally by thermochromatography on gold surfaces [3]. Due to their electron configurations Cn and Fl can also possess surprising bonding features in their “true” compounds with lighter elements. Unfortunately, the potential power of the projection analysis for predicting and interpreting the bonding patterns in SHE compounds was not yet widely applied, except hydrides of elements 116 [13] and 117 [9] and mixed diatomic molecules TIE117, E113At, E113E117 [10]. Therefore, the experience of application of projection analysis in this domain is still very scarce and not sufficient to make reliable conclusions about its advantages and drawbacks. The present paper reports the study of qualitative differences in chemical bonding in oxides and fluorides of superheavy elements and their lighter homologues, Cn vs Hg and Fl vs Pb through evaluating relativistic effective configurations of heavy atoms in compounds by the projection analysis. The latter technique is slightly modified in order to completely avoid the influence of arbitrary choice of atomic reference configurations on the results.

THEORY

The detailed description of the projection analysis technique was given in [11]. PA is based on the fact that every molecular spinor $|\psi_i^{MO}\rangle$ can be expanded in the spinors $|\chi_k^A\rangle$ of the constituent atoms, calculated in their own basis sets:

$$|\psi_i^{MO}\rangle = \sum_{A} \sum_{k \in A} c_{ki}^{A} |\chi_k^A\rangle + |\psi_i^{pol}\rangle$$
where $|\psi^\text{pol}_i\rangle$ stands for the component of $|\psi^\text{MO}_i\rangle$ outside of the linear span of reference atomic spinors $|\chi^A_k\rangle$.

The expansion coefficients $c^A_{qi}$ are found by solving the set of linear equations, obtained by projection:

$$
\langle \chi^B_k | \psi^\text{MO}_i \rangle = \sum_A \sum_{q \in A} \langle \chi^B_k | \chi^A_q \rangle c^A_{qi}
$$

In fact, we reexpand molecular spinors in the basis of atomic ones $|\chi^A_k\rangle$. Then fractional occupancies $N^A_k$ of the new basis orbitals $|\chi^A_k\rangle$ are calculated similarly to Mulliken analysis:

$$
N^A_k = \langle \text{pol} | \sum_q \text{occMOs} | \chi^A_q \rangle
$$

Note that in general the sum of fractional occupancies should not coincide with the total number of electrons $N$. Let us introduce the number $N_{\text{pol}}$ of electrons which are “lost” at the first projection step:

$$
N_{\text{pol}} = N_{\text{etec}} - \sum_A \sum_k N^A_k
$$

Obviously, if $N_{\text{pol}}$ is large the analysis becomes senseless because a significant fraction of electron density is not assigned to any atom.

In order to completely eliminate polarization contribution molecular spinors (or pseudospinors) can be transformed to "intrinsic" atomic spinors \cite{14}. However, it slightly distorts clear physical meaning of effective atomic configuration, since the "intrinsic" atomic spinors do not possess any definite angular momentum with respect to the nucleus of the corresponding atom.

As has been mentioned above, the resulting fractional occupancies $N^A_k$ depend on the particular choice of atomic spinors $|\chi^A_k\rangle$, which are in turn defined by the configurations of reference atoms chosen with an unavoidable degree of arbitrariness. Furthermore, certain spinors which are not occupied in ground-state atoms but play an important role in the bond formation are sometimes hardly usable for PA. For instance, reference atomic spinors obtained in conventional Hartree-Fock method (HF) or Kohn-Sham DFT method with integral spinor occupancies are as diffuse as allows the chosen basis set. Moreover, in some cases they even can have no physical meaning. This observation is particularly important since several heavy atoms are not capable to attach electron and thus have no electron affinity (for example, Hg and both Cn and Fl \cite{13}). Conventional PA underestimates populations of such spurious atomic spinors, whereas their compact counterparts are strongly involved in bond formation and should be taken into account while considering bonding features.

To avoid this shortcoming at least partially, we proposed an iterative version of the PA approach, based on the use of fractional-occupancy reference atomic configurations. The idea is very simple: the occupancies, obtained via the projection analysis at the first step, are used as input fractional occupancies for the new atomic calculation. The obtained atomic spinors are used as a new reference atomic in PA again. This loop is repeated until convergence. This procedure is shown to converge very fast and reduces significantly polarization contributions (see below).

The proposed method is suitable at least for atoms bearing positive net charges. Otherwise the atomic calculations for negative-charged ion must be carried out, this again can lead to unphysical and spatially blurred atomic spinors which cannot be corrected by introduction of fractional occupancies. In this case proposed iterative procedure does not converge and exhibits strong oscillations of subshell effective occupancies.

**COMPUTATIONAL DETAILS**

The iterative projection analysis (IPA) was applied to the molecules of oxides and difluorides of superheavy elements Cn, Fl and their lighter homologues (Hg and Pb respectively). All calculations were carried out by the two-component Kohn-Sham method with PBE0 functional \cite{10}, implemented in the DIRAC code \cite{17}. We replaced core electrons with spin-orbit semilocal relativistic effective core potentials by Mosyagin et al \cite{18} (60-e RECPs for Hg, Pb and 92-e RECPs for Cn, Fl). Valence and subvalence spinors of heavy atoms were represented using flexible uncontracted basis set from \cite{19}. We also used cc-pVTZ \cite{20} basis set for oxygen and fluorine. Before running population analysis the geometries of MF$_2$ and MO ($M = \text{Hg, Cn, Pb, Fl}$) were optimized (see Table 1). For performing one-step projection analysis we also used the code included in the DIRAC package.

In order to find trends in variations of typical bond strength in pairs Hg – Cn and Pb – Fl we also evaluated dissociation energies of all studies molecules. Since Kramers-restricted configuration-averaged approach is not well suited for DFT calculations of open-shell species, we used unrestricted two-component RDFT code by Christoph van Wüllen \cite{21} to calculate open-shell atomic ground states.

**RESULTS AND DISCUSSION**

Equilibrium geometry parameters (bond lengths and angles) and effective configurations of heavy atoms in the studied molecules are summarized in Table 1.

We found that the results of the iterative projection analysis are fully independent on the initial reference atomic orbitals and iterations converge very rapidly even
with nearly senseless starting atomic spinors (e.g., those of Cn$^{20+}$ ion; we recall that for Cn we use 92-e RECP).

Furthermore, during the iterations the polarization contribution decreases for every tried initial guess. We also studied the effect of the transformation of MOs to IAOs on results of projection analysis and found that it slightly affects the results (order of 0.01 of a atomic charge unit). Hence transformation to IAOs is not critical and can easily be avoided by an iterative procedure.

To interpret our results in intuitive "chemical" terms, let us recall that in the non-relativistic (and scalar-relativistic) models the formation of one or two covalent bond by an atom in a closed shell molecule implies the presence of one or two unpaired electron above the closed shell in the free atom. In the idealized case of purely covalent bonding, the overall populations of involved atomic orbitals remains the same upon the bond formation. If the atomic subshell population approaches that of the filled shell, the same holds for hole populations. Therefore the deviation of the atomic $l$-subshell occupancy from 0 (for low populations) or from $l(2l + 1)$ (for high populations) in a closed-shell molecule is related to the number of single covalent bonds formed by the atom. It is natural to suppose that this deviation should correlate with the covalent contribution to chemical bonding also in the case of fractional populations.

These considerations, however, should be modified to the relativistic case. Let us recall that the atomic two-component spinors are admixtures of spin-up and spin-down components. For example, $p$ spinors ($l = 1$ with the total spin projection $m_j > 0$ have the form

$$p_{1/2,1/2} = \left( \frac{1}{\sqrt{2}} p_0 \sqrt{2} p_1 \right)$$

$$p_{3/2,1/2} = \left( \frac{\sqrt{3}}{2} p_0 \sqrt{3} p_1 \right)$$

$$p_{3/2,3/2} = \left( p_1' \right)$$

where the radial parts of $p'$ and $p$ are different. Provided that we have a single electron on the $p$-subshell, the formation of a true $\sigma$-bond along an interatomic axis (let us call it z) implies the participation of an electron on the $p\sigma$ (or, the same, $l = 0$) component. However, neither any of the $p_{1/2}$ spinors nor any combination of these spinors is dominated by this component. The same holds for the $p_{3/2}$ spinors; to get a pure $p\sigma$ function, $p$ spinors with different $j$ are to be combined [22]. Such mixing is not efficient when the difference of energies and spatial distributions of the $j$-subshells with the same $l$ is large, as occurs in superheavy elements.

A large difference between the populations (per spinor) of the shells with the same $l$ and different $j$ indicates inefficient mixing and therefore weakening of $\sigma$-bonds. Note that the above considerations can be extended to other types of chemical bonds (but $\sigma$ bonds are the strongest).

These arguments can be used for interpretation of results obtained via the iterative PA technique. In case of compounds of group 12 elements (Hg and Cn) chemical bonds are formed mainly by $s$ electrons (See Figure 1).

We may assert that the covalent component of chemical bonds is stronger in HgF$_2$ than in CnF$_2$ since the fractional occupancy of the $s$-shell approaches 1. Furthermore, though hole population of the Cn $d_{5/2}$ subshell is significant, it does not strongly contribute to $\sigma$-bonding since the very small hole population of $d_{3/2}$ indicates the inefficiency of $d_{5/2} - d_{3/2}$ mixing required to form $d\sigma$ components. However, $d$-subshells seems not to be as inert as in the case of Hg where they are nearly filled, that characterizes Cn as a real transition element.

This qualitative picture agrees with the bond energy estimates (2.8 eV for Hg–F bond and 2.2 eV for Cn–F one). The smallness of Hg–O and Cn–O bond energies block the possibility of searching the correlations between the bonding pattern and bond strength in this case.

A different bonding pattern is observed for the compounds of Pb and F. In this case the results of the iterative projection analysis are consistent with the simple

| Molecule  | $s_{1/2}$ | $p_{1/2}$ | $p_{3/2}$ | $d_{3/2}$ | Bond  | Valence  | $E_{\text{M} - \text{X}},$ |
|-----------|-----------|-----------|-----------|-----------|-------|----------|-----------------|
| HgO       | 0.65      | 0.05      | 0.07      | 3.96      | 5.90  | 1.875    | 0.06            |
| CnO       | 1.71      | 0.33      | 0.10      | 3.94      | 5.45  | 1.681    | 0.23            |
| HgF$_2$   | 0.94      | 0.11      | 0.15      | 3.92      | 5.80  | 1.902    | 180.0           |
| CnF$_2$   | 1.50      | 0.16      | 0.10      | 3.88      | 5.46  | 1.931    | 180.0           |
| PbO       | 1.88      | 0.69      | 0.63      | 3.99      | 5.99  | 1.898    | 3.69            |
| FIO       | 1.93      | 1.18      | 0.28      | 3.98      | 5.97  | 2.038    | 0.83            |
| PbF$_2$   | 1.88      | 0.39      | 0.46      | 4.00      | 5.99  | 2.023    | 95.6            |
| FIF$_2$   | 1.95      | 0.63      | 0.28      | 3.99      | 5.98  | 2.154    | 96.9            |
chemical intuition: subvalence $d$- and valence $s$-shells are actually quasi inactive in bond formation, and these two elements exhibit typical $p$-element behavior. Again, from Pb to Fl, mixing between the subshells with the same $l$ and becomes less efficient, and the significantly populated $p_{3/2}$ subshell in FlO and FlF$_2$ cannot greatly contribute to covalent bonding due to the imbalance of $p_{1/2}$ and $p_{3/2}$ occupancies. This leads to a weakening of bonds involving flerovium atom with respect to those formed by Pb. This conclusion is also consistent with decreasing of calculated M–F bond energy from 4.2 eV for PbF$_2$ to 2.2 eV for FlF$_2$. Essentially the same pattern is observed for the corresponding oxides.

Finally, we should point out that all results obtained with iterative PA qualitatively coincide with the predictions of the AiC analysis [23, 24] (see Figure 2). Both PA and AiC approaches give grounds to assert that bonds in

PbF$_2$ and FlF$_2$ are formed entirely by $p$-electrons.

**CONCLUSIONS**

To summarise, the new iterative approach to projection population analysis was proposed and shown to be rapidly converging and fully insensitive to the initial choice of reference atomic configuration. Based on conventional projection analysis technique, it can be easily used on the top of any quantum chemistry code implementing fractional-occupancy two- or four-component relativistic Hartree-Fock or DFT methods.

The application of iterative projection analysis to the molecules of Hg, Cn, Pb and Fl oxides and difluorides gives some insight into the peculiarities of chemical bonding in superheavy element compounds. The decrease of the covalent component of bonds in Cn compound with respect to their Hg-containing counterparts is related to the increase of the $s$-subshell population approaching that of the closed shell. Furthermore, the large difference of hole populations of $d_{3/2}$ and $d_{5/2}$ subshells prevents their admixture necessary for strong $\sigma$-bonding. A similar imbalance of $p_{1/2}$ and $p_{3/2}$ occupancies results in weakening of covalent bonding in Fl compounds. The separate determination of effective populations for the subshells with the same orbital angular momentum but different total angular momenta is thus crucial for interpreting the bonding pattern on superheavy element compounds.

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