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Relativistic effects on atomic and molecular properties of the heaviest elements

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Abstract. Interaction of superheavy element 112 and its homolog Hg with inert and gold surfaces was studied on the basis of atomic and molecular fully-relativistic (4-component) DFT electronic structure calculations. Performance of additional non-relativistic calculations allowed one to demonstrate the role and magnitude of relativistic effects on adsorption energies and bond distances of the studied systems. For example, on quartz, element 112 will be stronger adsorbed than Hg by about 5 kJ/mol (or at 5 degrees higher temperatures) due to the stronger van der Waals interaction. This is caused by the relativistically contracted smallest atomic radius of element 112. Non-relativistically, the trend would be opposite. On surface of gold, element 112 will be about 20 kJ/mol weaker adsorbed than Hg (i.e., it will be deposited at about 100 degrees lower temperatures than Hg). Such a decrease in ΔH_{ads} comes at the account of the weaker interaction of the relativistically stabilized $7s_{1/2}(112)$ orbital with valence orbitals of gold. Still, the relatively large adsorption energy of element 112 is indicative that it is a transition metal forming intermetallic compounds with Au and other metals due to the involvement of the relativistically destabilized $6d$ orbitals. The influence of relativistic effects on the adsorption energy depends, however, on the adsorption position.

PACS. 31.15.Ew Density-functional theory – 27.90.+b $220 \leq A$

1 Introduction

It is presently well established that relativistic effects play a crucial role in the electronic structures and related properties of the heaviest elements [1,2]. They were shown [3] to define trends in chemical properties in the chemical groups in going over to the elements of the 7th row, but could also lead to some deviations. Element 112 is the most interesting from this point of view due to the maximum of relativistic effects on its electronic shells [4]. It was expected to be very volatile and inert similar to noble gases due to the closed electronic shells and inaccessibility of the relativistically stabilized $7s_{1/2}$ orbital for bonding [5]. The reactivity of element 112 depends, however, on the chemical environment and the way it is supposed to be experimentally identified [6,7]. In this work, we consider the ways by which element 112 will be chemically identified, i.e., we study its adsorption on quartz and gold surfaces, as well as we study the influence of relativistic effects on its behaviour upon adsorption along with that of Hg. The study is based on results of fully relativistic atomic, molecular and cluster electronic structure calculations. Non-relativistic calculations were performed to establish the role and magnitude of relativistic effects.

2 Method and details of the calculations

Atomic properties of the heaviest elements and their homologs were calculated with the use of the Dirac-Fock (DF) and 4-component Density Functional Theory (4c-DFT) methods. For molecular calculations, the recently created version of the 4c-DFT method — the spin polarized (SP) — was used. Some of its features are described below.

Within the non-collinear Density Functional Theory (DFT) the total energy of a molecular system is given by the following expression

$$E = \sum_{i=1}^{M} n_i \left\langle \psi_i \,\middle|\, \hat{t} \,\middle|\, \psi_i \right\rangle + \int V^N \rho \, d^3\mathbf{r} + \frac{1}{2} \int V^H \rho \, d^3\mathbf{r} + E^{xc}[\rho, \mathbf{m}] + \sum_{p>q} \frac{Z_p \, Z_q}{|\mathbf{R}_p - \mathbf{R}_q|} \qquad (1)$$

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with the density ρ and magnetization density $\mathbf{m}$ which are defined by

$$\rho(\mathbf{r}) = \sum_{i=1}^{M} n_i\, \psi_i^{+}(\mathbf{r})\psi_i(\mathbf{r}), \tag{2}$$

$$\mathbf{m}(\mathbf{r}) = -\mu_B \sum_{i=1}^{M} n_i \psi_i^{+}(\mathbf{r})\beta\boldsymbol{\Sigma}\psi_i(\mathbf{r}). \tag{3}$$

Here n_i are the occupation numbers, $\mathbf{r}$, $\mathbf{R}_q$ are the electronic and nuclear coordinates respectively and μ_B is the Bohr-magneton. The index i runs over all occupied molecular orbitals M, which in our case are four-component Dirac-spinors. The four-component spin-operator $\boldsymbol{\Sigma} = (\Sigma_x, \Sigma_y, \Sigma_z)$ is built from the two component Pauli matrices σ. The Dirac kinetic energy operator has the form (we use atomic units throughout)

$$\hat{t} = c\,\alpha \cdot \hat{\mathbf{p}} + c^2(\beta - I), \tag{4}$$

where $\alpha = (\alpha_x, \alpha_y, \alpha_z)$ and β are the four-component Dirac matrices in the standard representation and I is the four-component unit matrix.

V^N is the nuclear potential

$$V^N = \sum_p -\frac{Z_p}{|\mathbf{r} - \mathbf{R}_p|}, \tag{5}$$

where the index p runs over all nuclei in the molecular system.

E^{xc} is the exchange-correlation energy functional.

V^H is the electronic Hartree potential

$$V^H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}\,')}{|\mathbf{r} - \mathbf{r}\,'|}\, d^3\,\mathbf{r}\,'. \tag{6}$$

Since the calculation of the Hartree potential from the SCF-density (2) is very time-consuming, we approximate ρ in (2) by a model-density $\tilde{\rho}$. We expand our model-density into series of 'atomic' multipole-densities centered on the nuclei.

The variation of the energy functional (1) leads to the relativistic Kohn-Sham (KS) equations in their general form for the molecular Kohn-Sham orbitals ψ_i

$$\begin{aligned} \Big\{\hat{t} + V^N + \ &\tilde{V}^H + \frac{\delta E^{xc}[\rho, \mathbf{m}]}{\delta\rho} \\ &-\mu_B\beta\boldsymbol{\Sigma} \cdot \frac{\delta E^{xc}[\rho, \mathbf{m}]}{\delta\mathbf{m}}\Big\}\psi_i = \epsilon_i\psi_i \qquad (7) \\ &i = 1, ..., M'. \end{aligned}$$

Here $\tilde{V}^H$ is the Hartree potential from the model-density and $M' \geq M$ is the number of molecular orbitals.

This general formulation is called a non-collinear description which allows the magnetization density to point in any direction at any point of the system under consideration. Because often the z-component of the magnetization density is physically important, an approximation of this expression is used which is called the collinear description. It means that now, all the stated with the magnetic quantum number m_j can be explicitly described. For details, see references [9,10,13].

Table 1. Atomic properties — atomic radii (AR), ionisation potentials (IP), polarisabilities (α), and adsorption enthalpies (ΔH_{ads}) of Hg and element 112 on quartz.

Property	Hg		112		Ref.
	nr	rel	nr	rel	
IP (eV)	8.98	10.43	8.25	11.97	[8]
α (a.u.)	57.83	33.91	74.66	25.8	[4]
AR (a.u.)	3.911	3.43	4.318	3.259	this work
$-\Delta H_{ads}$ (kJ/mol)	41.3	40.8	40.2	44.5	[12]

Calculations for the dimers of Hg and element 112 were performed with the extended optimized basis sets which include neutral valence occupied orbitals plus up to the $5g$ virtual ones of the ionized metal atoms. The calculations for the metal-cluster systems were performed with smaller basis sets where additional orbitals beyond the minimal basis were the np and $(n-1)d$ of the ionised atoms (+1.5).

3 Results and discussion

3.1 Atomic calculations

Knowledge of atomic properties is important for calculations of adsorption energy upon deposition of Hg and element 112 on inert surface of detectors (e.g., quartz) in a gas-phase chromatography column. In Table 1, atomic properties of these elements which contribute to the energy of the dispersion interaction with such a surface are given.

One can see that trends in the relativistic and nonrelativistic IPs, AR (half of the bond length in the dimer) and α change in opposite ways from Hg to element 112, so that their influence on the adsorption energy and its trend in the group should be partially canceled. This is, indeed, the case, which is seen from the equation for the dispersion interaction with an inert surface (Eq. (6) of [12]). Thus, the trend in the adsorption energy from Hg to element 112 will be determined by the trend in the AR, and, will, consequently, be also opposite for the relativistic and nonrelativistic cases. The values of ΔH_{ads} are given in Table 1. Thus, relativistically, element 112 will interact stronger with an inert surface due to its relativistically decreased AR(112) = 1.725 Å. Non-relativistically, the trend is just opposite.

3.2 Molecular calculations

In the presently designed experiments with element 112, the detectors are covered with gold [6,7]. So, the interaction of element 112 and Hg with gold and other transition elements is an important case of the theoretical study. The trend in the binding energy of Hg and element 112 with gold can already be seen from our earlier RGGA DFT

Table 2. Bond lengths (R_e) and bond energies (D_e) of some compounds of Au, Hg and element 112.

Molecule	R_e (Å)	D_e (eV)	Ref.
Au_2	2.50	2.30	[14]
	2.47	2.29	exp.
Hg_2	3.63	0.01	this work
	3.63	0.043	exp.
$(112)_2$	3.45	0.05	this work
HgAu	2.71	0.67	this work
112Au	2.75	0.51	this work

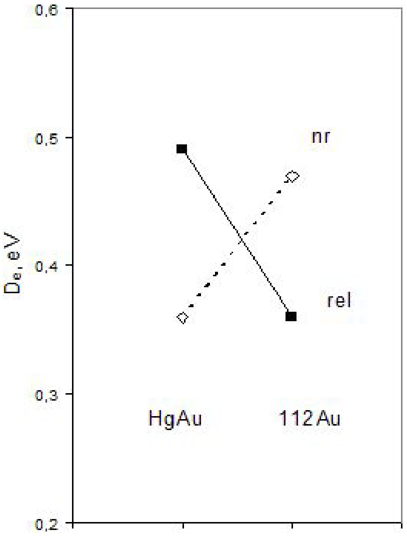

Fig. 1. Relativistic effects on binding energies (D_e) of HgAu and 112Au [12].

Table 3. Influence of relativistic effects on the binding energy (D_e, eV) of Hg and element 112 with small gold clusters at different adsorption positions.

System	Case	Hg		112		Ref.
		nr	rel	nr	rel	
MAu_{14}	top	0.64	0.86	0.70	0.71	[12]
MAu_9	hollow	0.41	0.85	0.52	0.79	[12]
MAu_{14}	bridge	–	1.00	–	0.82	this work

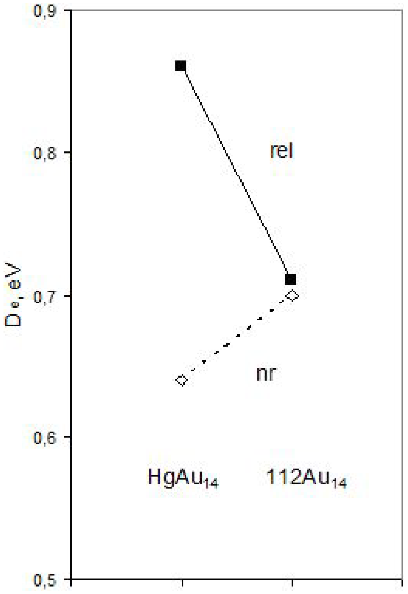

Fig. 2. Relativistic effects on binding energies (D_e) of MAu_{14} (M = Hg and element 112) in the on-top position of M [12].

calculations for the dimers [11]. Results of our present SP calculations for HgAu and 112Au are shown in Table 2 together with those for some other compounds of Hg and Au, where experimental spectroscopical properties are available in order to demonstrate the achieved accuracy.

Comparison with experiment where available is excellent for both the bond lengths (R_e) and binding energies (D_e). For the wan der Waals system, Hg_2, where DFT has still some deficiency due to the lack of suitable density functionals, agreement is also satisfactory, at least D_e is of the same order of magnitude. The bond length for Hg_2 is in perfect agreement with experiment, which assures that R_e of $(112)_2$ is very accurate. The knowledge of the latter is very important, since half of it is the atomic radius (AR) of element 112. It was used to define the wan der Waals interaction energy of the element with a quartz surface (Tab. 1).

Relativistic effects on spectroscopic properties of HgAu and 112Au were studied in [12]. There, the calculations were performed without spin-polarization and with a smaller basis set, so that the relativistic binding energies are smaller than those of our present calculations. Nevertheless, the comparison of the relativistic and non-relativistic values of that study is valid (both relativistic and non-relativistic calculations were preformed with the same type of the basis sets). The relativistic and non-relativistic D_es are shown in Figure 1. Thus, relativistic effects increase bonding in HgAu by 0.13 eV, but they decrease it by about the same value (0.12 eV) in 112Au. This different action of relativistic effects on bonding in HgAu and 112Au makes trends in the non-relativistic versus relativistic D_e values opposite from HgAu to 112Au, so that D_e^{nr}(112Au) > D_e^{nr}(HgAu), while D_e^{rel}(112Au) < D_e^{rel}(HgAu). The bond lengths are decreased by relativistic effects in both systems, though slightly to a larger extent in 112Au than in HgAu. The trends stay, however, the same both for the non-relativistic and relativistic values. Relativistic effects increase vibrational frequencies in each compound, but to a much lesser extent in 112Au than in HgAu, which makes trends in the relativistic and non-relativistic values opposite from HgAu to 112Au.

3.3 Cluster calculations

In Table 3, results of our calculations for M-Au_n(cluster) systems, where n = 14, 14 and 9 for the on-top, bridge and hollow positions of M, respectively, are summarized. They are indicative that element 112 should form rather strong bonding with gold-clusters, which is only 0.15 eV weaker than that of Hg for the top and bridge positions and of only about 0.06 eV weaker for the hollow position.

Such different differences in D_e between Hg and element 112 for various adsorption positions of M — on-top, bridge or hollow — on a metal lattice are explained by participation of different valence orbitals of these elements in

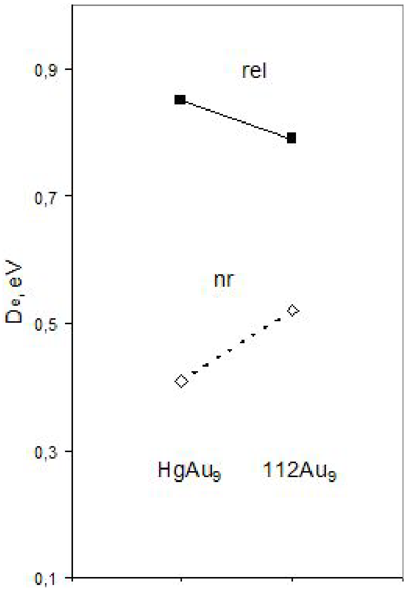

Fig. 3. Relativistic effects on binding energies of MAu_9 (M = Hg and element 112) in the hollow position of M [12].

bonding in each case, and, hence, different action of relativistic effects on the interaction energy. Thus, in the top-position, the ns and $np_{1/2}$ orbitals are predominantly involved in bonding with orbitals of the surface atoms of gold, which makes the difference in the relativistic values of D_e between Hg and element 112 larger due to the relativistic stabilization of the $7s$(112)-AO. On the contrary, the difference in the non-relativistic values is small. In the hollow position (Fig. 3), the $(n-1)d$ orbitals of both the adsorbed atom and the surface gold atoms are predominantly involved in bonding. The relativistic destabilization and expansion of the $6d$ AOs of element 112 bring them closer to the valence $5d$ AOs of Hg, so that the difference in the non-relativistic binding energies between the Hg and element 112 systems becomes smaller. The difference in the non-relativistic values is, on the contrary, larger.

4 Conclusions

The study of relativistic effects on the adsorption energy of Hg and element 112 has shown that their influence is different depending on the surface of the adsorbent and the adsorption position. Thus, upon adsorption on inert surfaces, relativistic effects increase the interaction energy of element 112 with the surface due to the relativistically contracted atomic radius, so that relativistically, the trend in ΔH_{ads} in the group is Hg < 112. Non-relativistically, the trend is opposite.

Upon adsorption of Hg and element 112 on gold clusters, the influence of relativistic effects on the adsorption energy depends on the adsorption position. For example, relativistic effects do not increase or even decrease the adsorption energy of element 112 when adsorbed in the on-top position, so that it will be the most volatile in group 12. This is due to a drastic decrease of the participation of the relativistically stabilized $7s$ orbital in bonding. Non-relativistically, element 112 would have been the least volatile in the group. On the contrary, when adsorbed in the hollow position, relativistic effects increase the interaction energy of element 112 with the gold cluster, so that relativistically it will be less volatile than non-relativistically. This is due to the involvement of the relativistically destabilized $6d_{3/2}$ and $6d_{5/2}$ orbitals. In both cases, element 112 will, however, be more volatile than Hg when adsorbed on the gold (100) surface, with the difference in the adsorption energies between the two elements being smaller for the adsorption in the hollow position than in the top position. Calculations have demonstrated that trends in the relativistic and non-relativistic properties in group 12 are opposite due to the opposite action of relativistic and orbital effects.

References

1. B. Fricke, Struct. Bond. **21**, 89 (1975)
2. P. Pyykkö, Chem. Rev. **88**, 563 (1988)
3. V. Pershina, Chem. Rev. **96**, 1977 (1996)
4. P. Schwerdtfeger, M. Seth, *Encyclopedia on Calculational Chemistry* (Wiley, NY, 1998), Vol. 4, p. 2480
5. K. Pitzer, J. Chem. Phys. **63**, 1032 (1975)
6. A.B. Yakushev et al., Radiochim. Acta. **89**, 743 (2001)
7. S. Soverna et al., Presentation at the GDCh Conference, Würzburg, Germany, September 2001; J.-P. Niklaus et al., PSI Annual Report 2002, p. 8
8. E. Eliav et al., Phys. Rev. A **52**, 2765 (1995)
9. T. Bastug et al., Chem. Phys. Lett. **211**, 119 (1993)
10. S. Varga et al., J. Chem. Phys. **112**, 2499 (2000)
11. V. Pershina et al., Chem. Phys. Lett. **265**, 176 (2002)
12. V. Pershina, T. Bastug, Chem. Phys. **311**, 139 (2005)
13. J. Anton, B. Fricke, E. Engel, Phys. Rev. A **69**, 012505 (2004)
14. J. Anton, B. Fricke, P. Schwerdtfeger, Chem. Phys. **311**, 200 (2005)