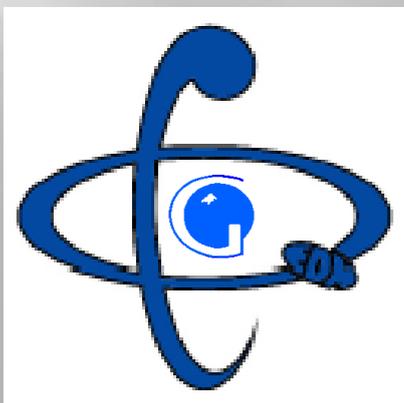


# Relativistic DFT and *ab initio* calculations on the seventh-row superheavy elements: E113 - E114

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Oriented targeted basic research on key interdisciplinary topics

# Motivation

- Analysis of atomic data and accurate calculations of diatomics with SHEs Cn, E113 and E114 is not sufficient for reliable prediction of their adsorption properties on gold surface.
- Disagreement of different RDFT studies with the exptl value of adsorption of Hg on gold clusters is too high, whereas it is rather good for Pb on gold. In turn, the exptl statistics with SHEs is yet rather poor.
- Discrepancies in RDFT studies of the binding energies of Hg & Cn on gold surface are rather high (LDA vs. GGA & hybrid RDFT: factor of 2).
- Applicability of RDFT with primitive XC functionals to more or less complex systems with Cn was never examined in details.
- To-date, the problem of adsorption of E112-E114 is most interesting us from theoretical point of view in connections with SHEs. It cannot be solved by "brute-force" improvement in computational (quantum chemical) technique but require involving some new ideas to overcome it.

# SHEs in the “island of stability” subperiodic structure

43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
				closed shells $6d_{5/2}^6 7s^2$		closed (sub)shells $6d_{5/2}^6 7s^2 7p_{1/2}^2$			closed shells $6d_{5/2}^6 7s^2$ $7p_{1/2}^2 7p_{3/2}^4$			
75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo	

subperiod:

$6d_{5/2}$  is being filled

subperiod:

$7p_{1/2}$  is  
being filled

subperiod:

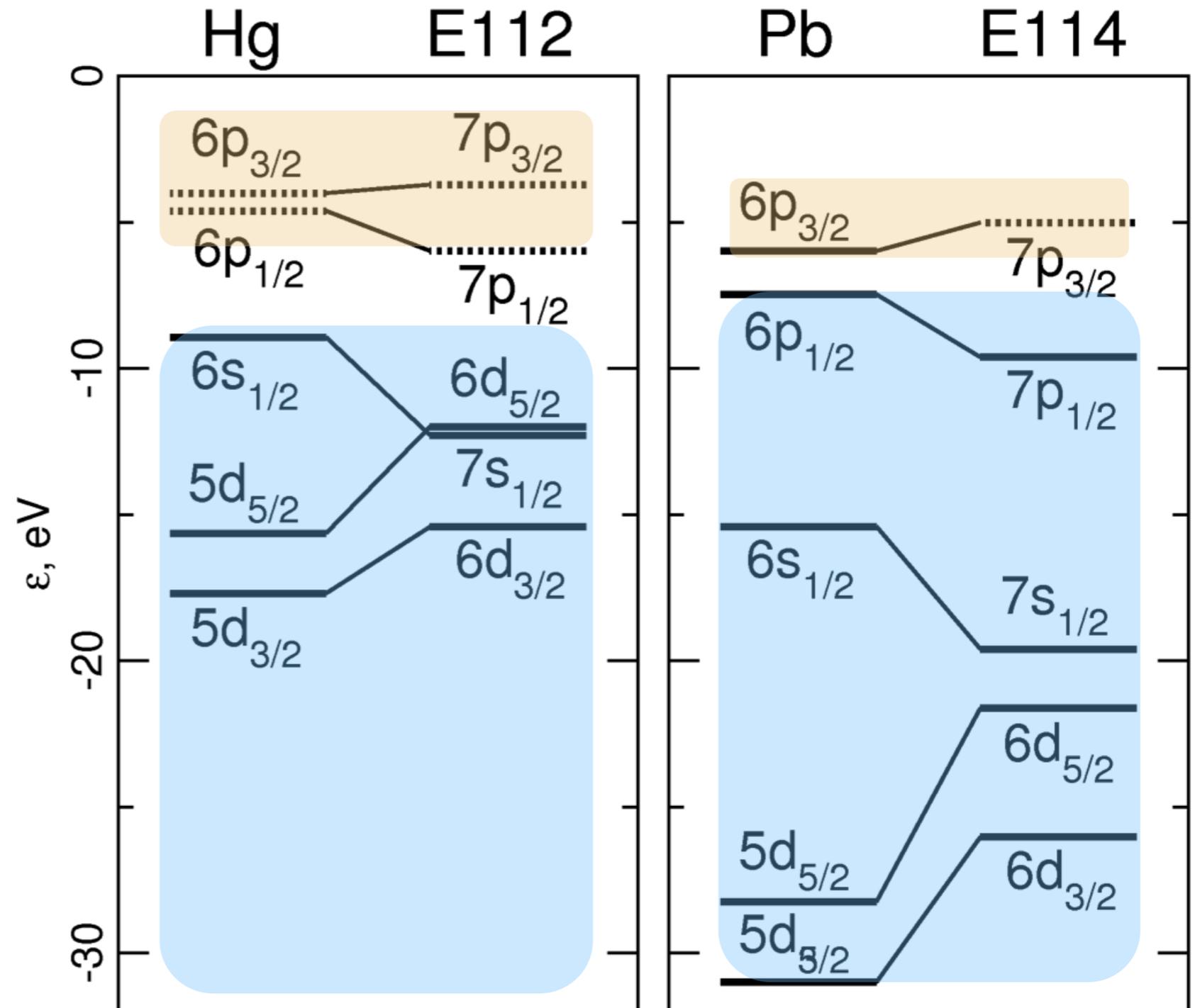
$7p_{3/2}$  is being filled

# Features of even elements of VII<sup>th</sup> period

⊙ contraction and stabilization of s- and p<sub>1/2</sub>- shells

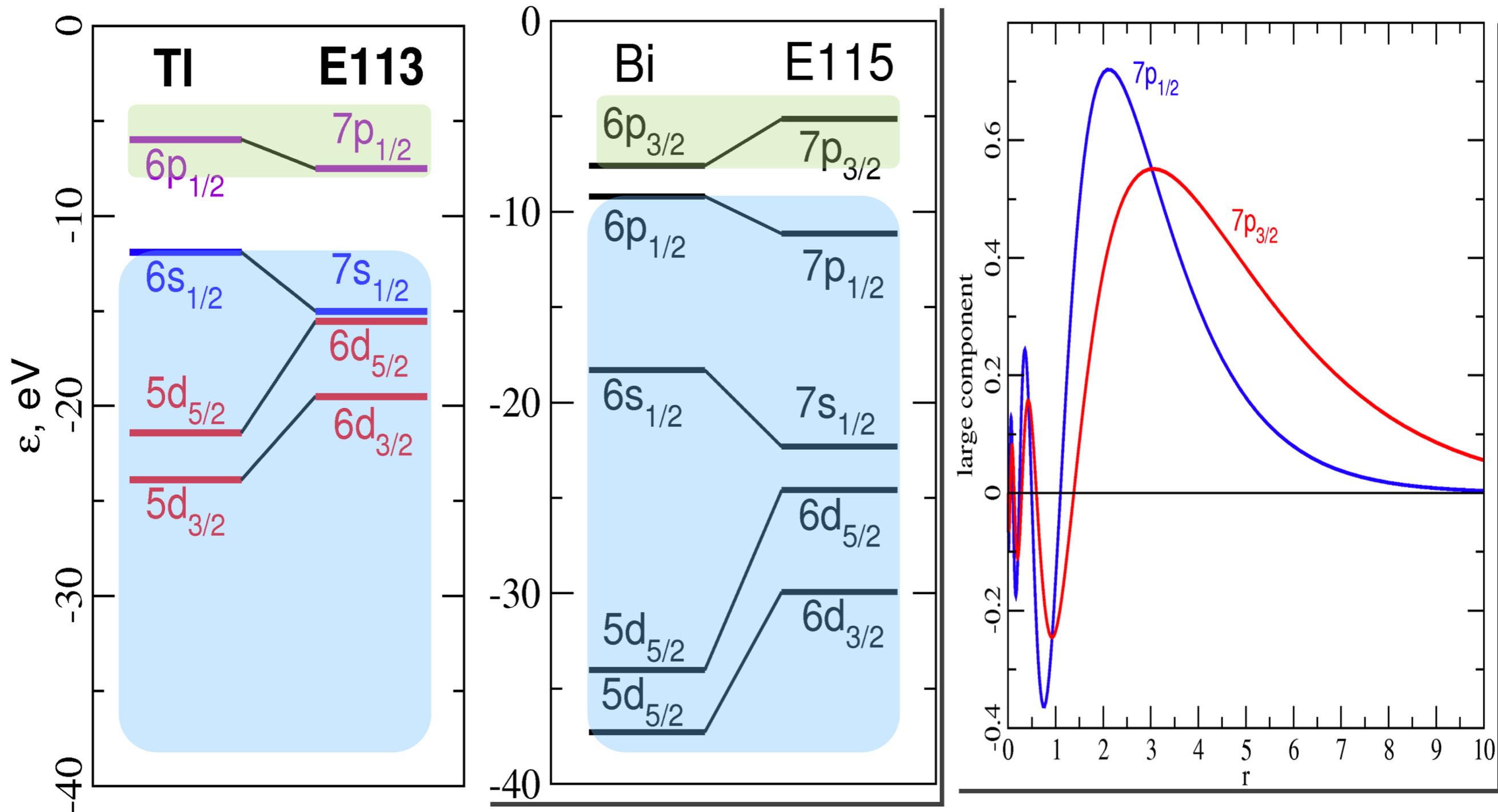
⊙ large spin-orbit splitting p<sub>1/2</sub> - p<sub>3/2</sub>

⊙ rather diffuse and unstable sub-valence d-shell)



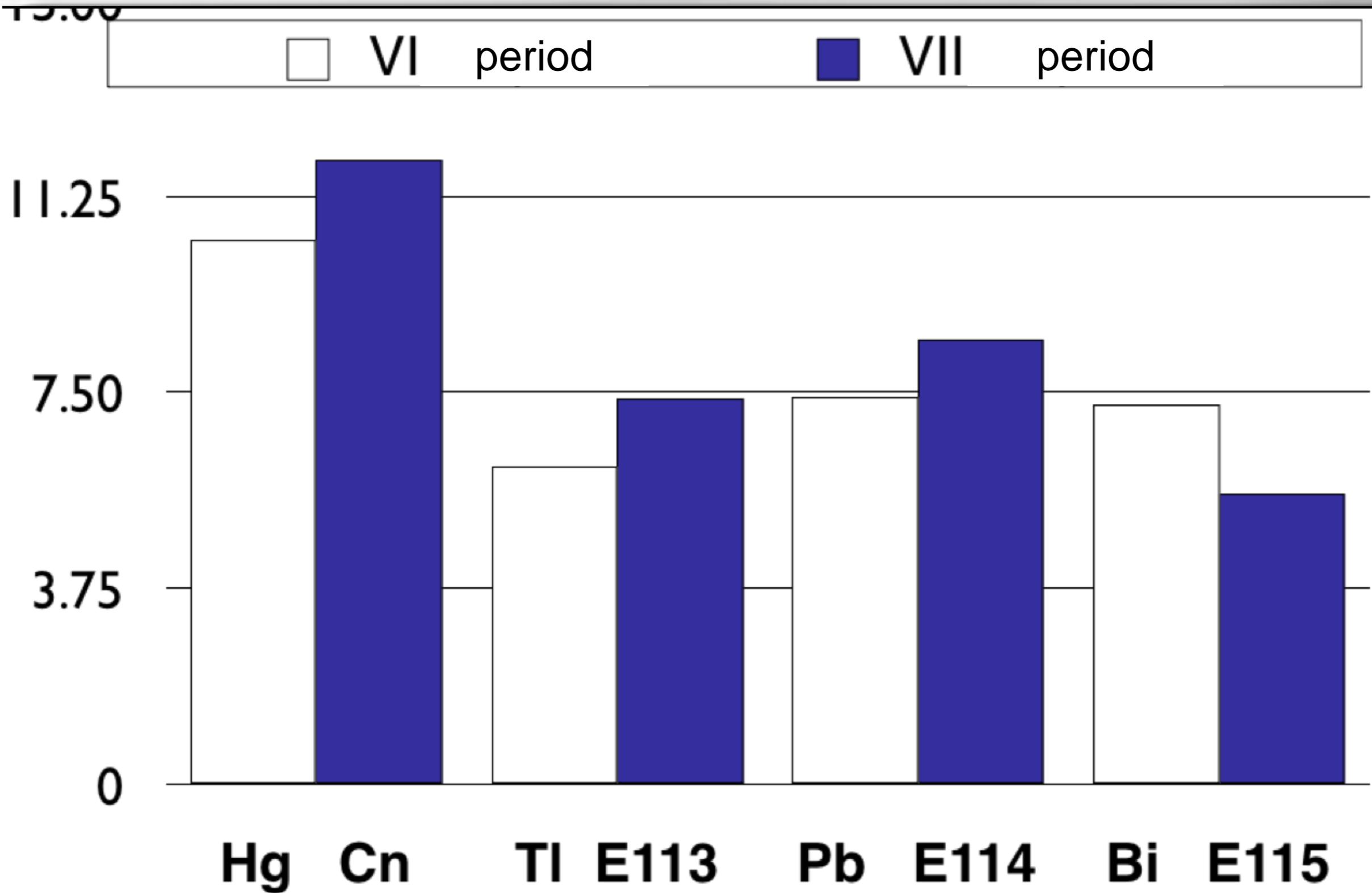
**Cn(E112) & E114: closed-shell like structure**

# Features of odd elements of VII<sup>th</sup> period

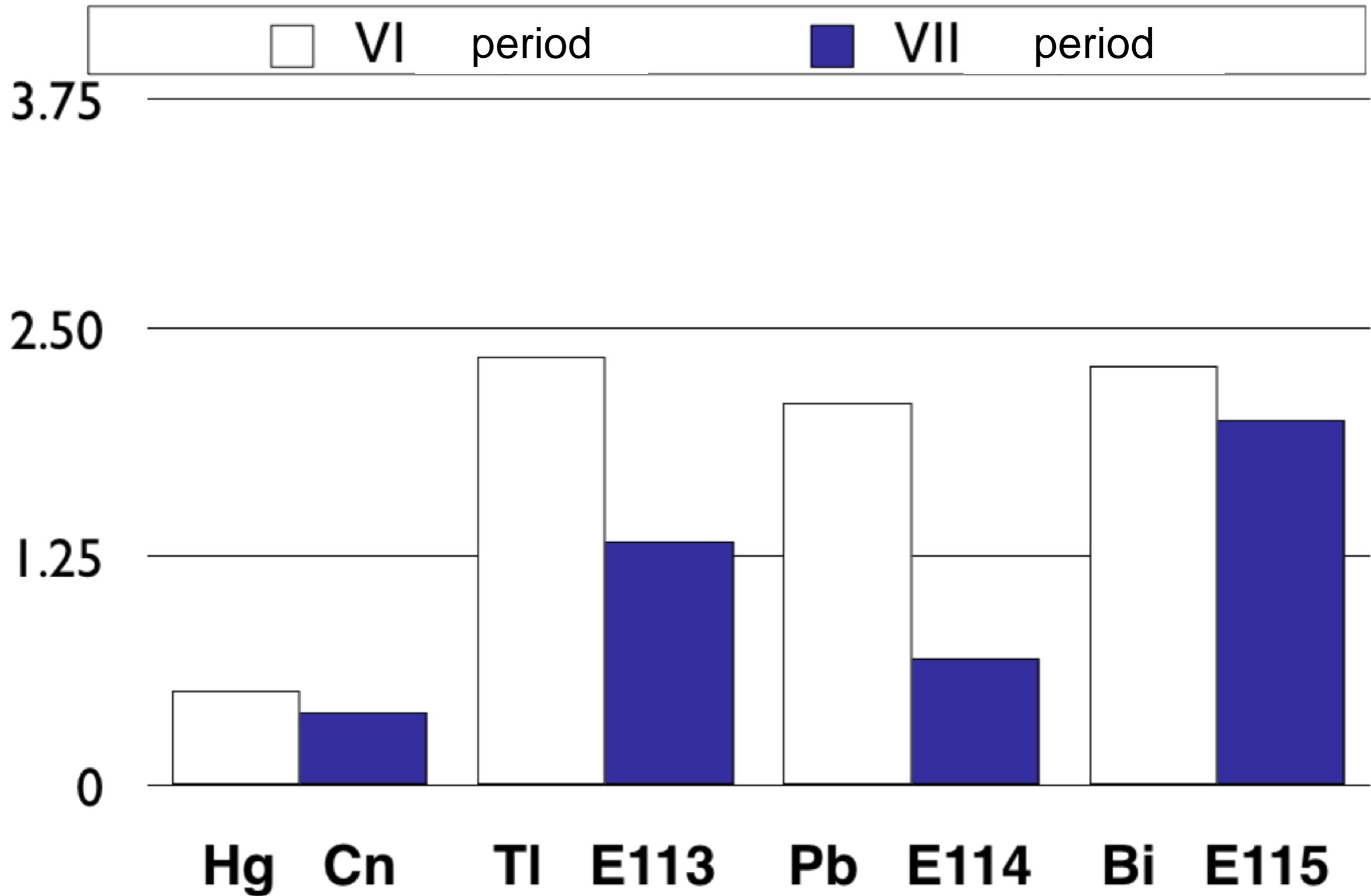


**E113 & E115: 1 electron over the closed shell**

# Ionization potentials, eV



# Binding energy M-Au in diatomics MAu, eV



# Binding energy M-M in dimer $M_2$ , eV

□ VI period

■ VII period

2.50

1.25

0

**Hg**

**Cn**

**Tl**

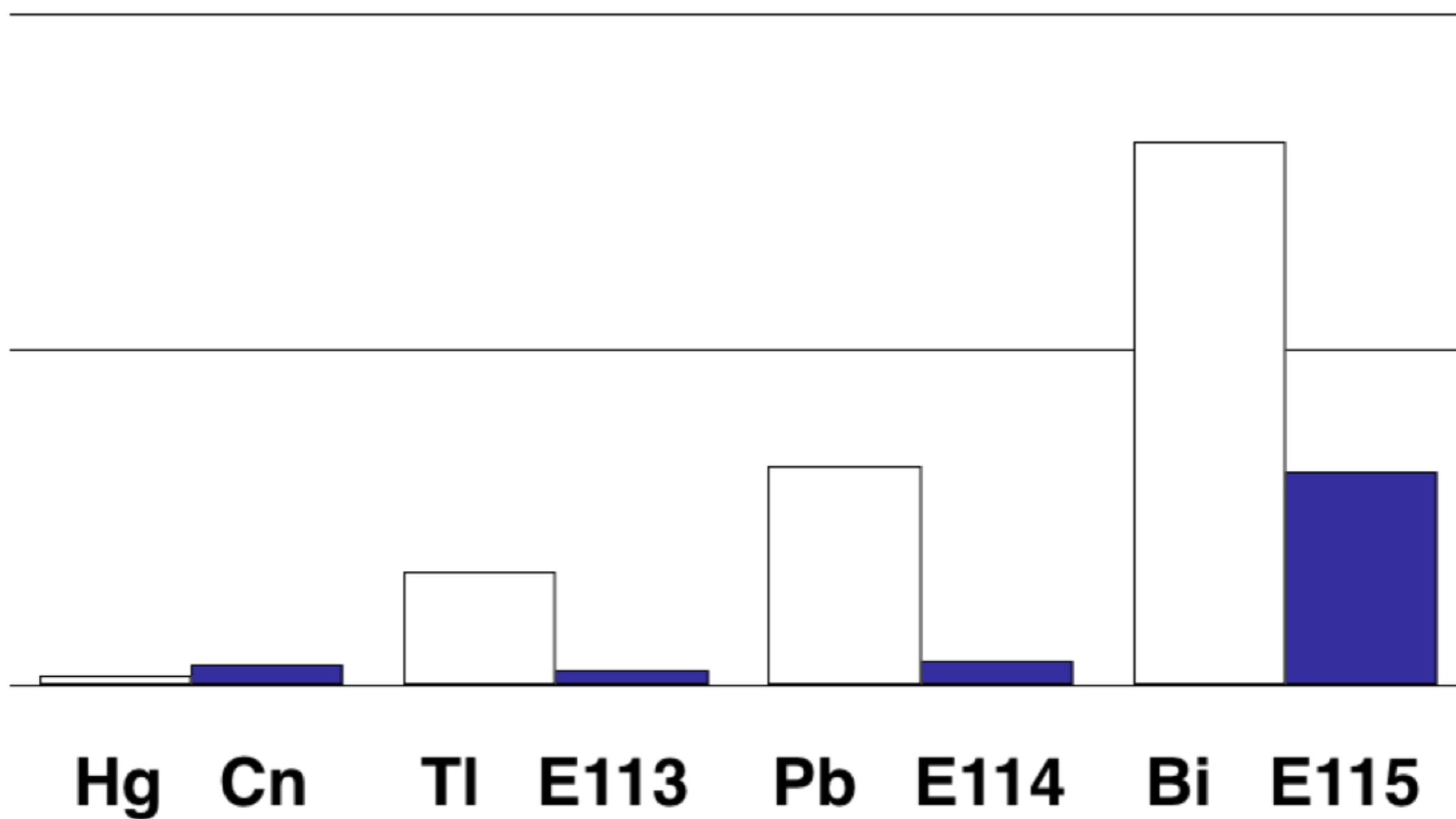
**E113**

**Pb**

**E114**

**Bi**

**E115**

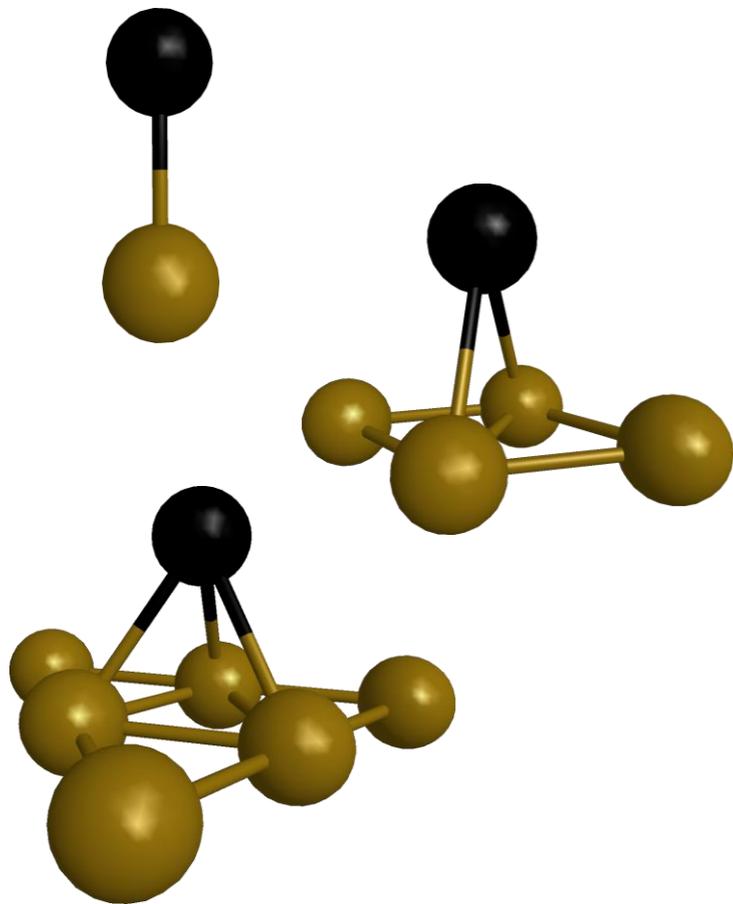


# Interaction energy of $C_n$ - $Au_n$ & E113- $Au_n$ : RDFT vs. *ab initio*

**MBPT+SO (pilot):**

[A.Zaitsevskii *et al.*, JCP **132**, 081102 (2010)]

**CCSD(T), CBS+SO (reliable):** [A.Zaitsevskii *et al.*, to be published (2011)]



- Very time consuming calculations, thus:
- The Au-Au distances are *experimental (bulk)*;
- Only the **distance adatom-Au plane is optimized**:
  - to check influence of dispersion-like int-n;
  - to reduce computational efforts;
  - to forbid forming plane structures ( $C_n / Au$ )
- ***The only goal is to assess the DFT applicability***

We **never declared** and even thought smth like:

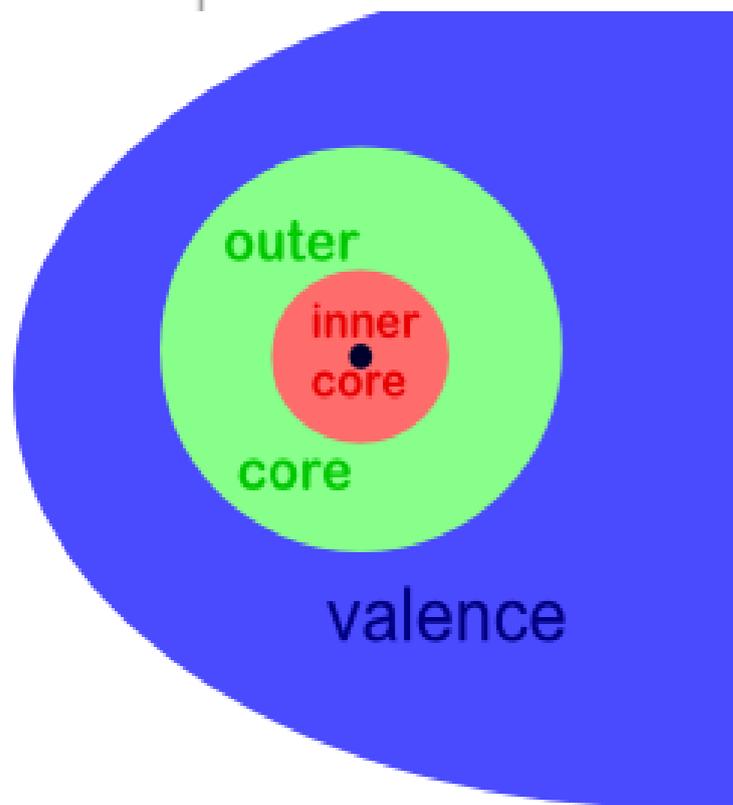
*“the opposite trend in  $C_n/A_n$  vs.  $Hg/Au$  binding energies in some tests means inapplicability of DFT to these ‘closed shell’ systems”*

# Model features:

## Small-core relativistic pseudopotential (Gatchina)

[Mosyagin *et al.*, *Progr.Theor.Chem.Phys.* **B15**, 229 (2006),  
Zaitsevskii *et al.*, *Russ.Chem.Rev.*, **78**, 1173, (2009),  
Mosyagin *et al.*, *Int.Rev.At.Mol.Phys.* **1**, 63 (2010)]

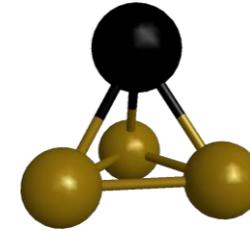
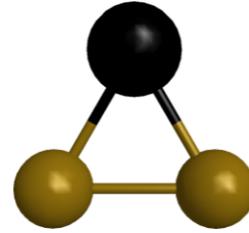
inner core is simulated by relativistic pseudopotential;  
outer core:  $6s^2 6p^6 6d^{10}$  & valence:  $7s 7p$  (E112 - E115),  
 $5s^2 5p^6 5d^{10}$   $6s 6p$  (Au, Hg - Bi)  
are treated explicitly (small-core PP)



- “non-relativistic-type”  $n$ -electron system in a spin-dependent pseudopotential (radially(semi)-local or generalized)
- nonrelativistic symmetry for scalar studies
- relativistic symmetry for spin-dependent ones

“*chemical accuracy*” (and better!) is **attainable & sufficient** ( $\sim 1$  kcal/mol  $\approx 0.043$  eV  $\approx 350$  cm $^{-1}$ ) for potential curves etc.

# *Ab initio study of simple models of adsorption complexes $C_n-Au_n$ и E113- $Au_n$*



## **full two-component *ab initio* calculation:**

- ⊙ low symmetry => huge number of calculations
- ⊙ extremely slow convergence on the basis set extension, in which the Hamiltonian is discretized

**calculations are very expensive even for diatomic molecules**



## **scalar-relativistic:**

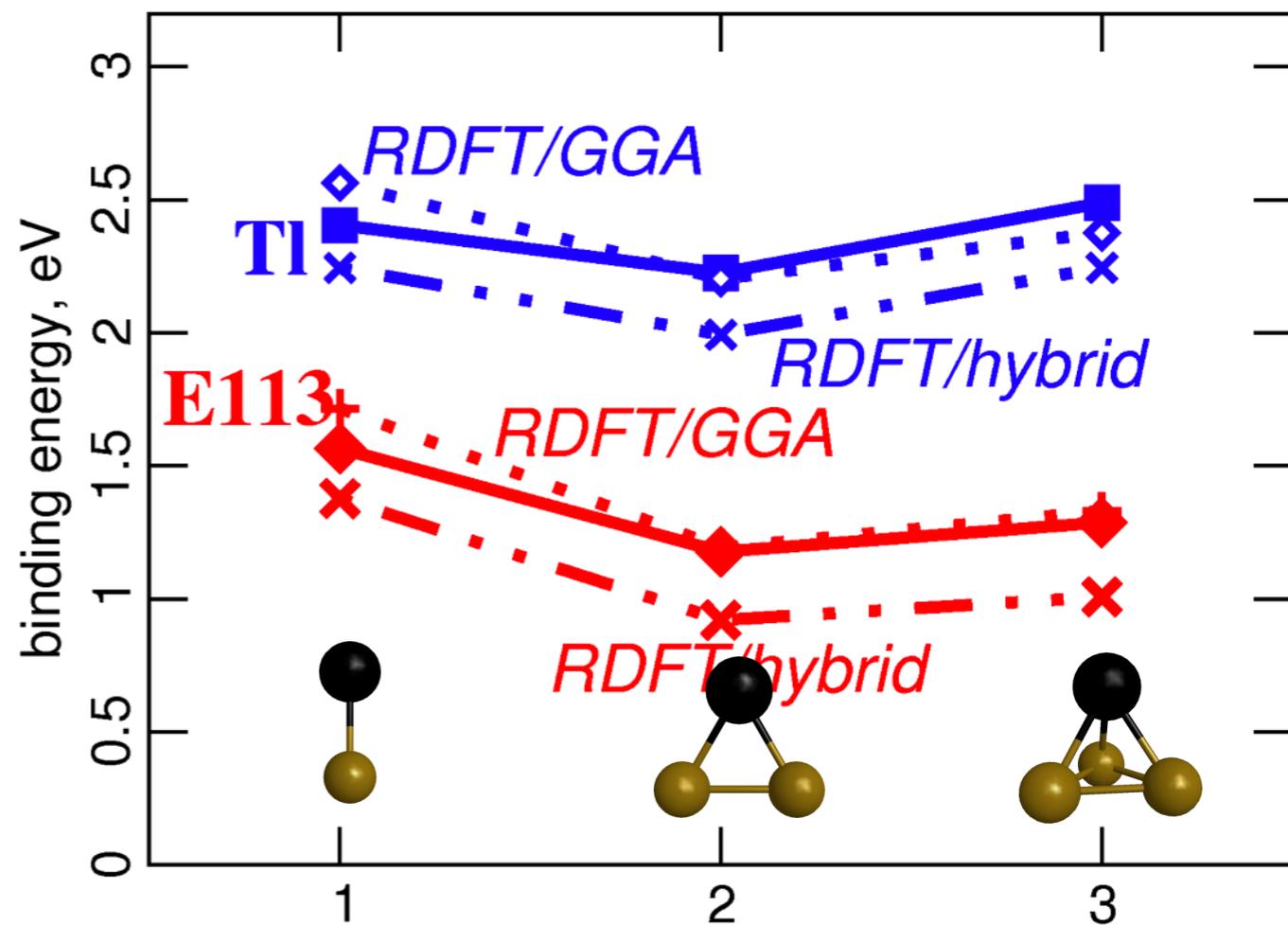
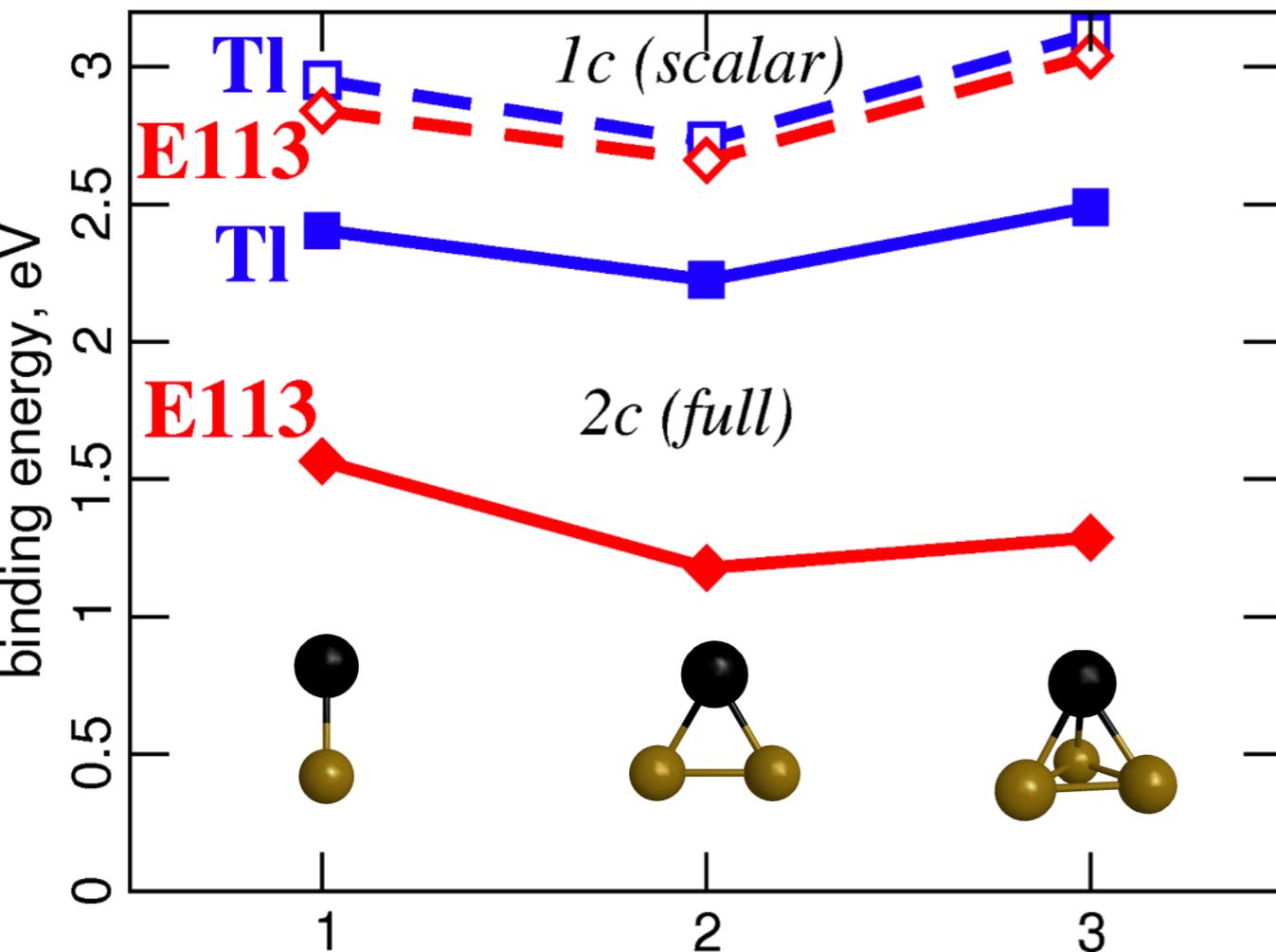
- ⊙ CCSD(T) as a means of describing the electron correlations
- ⊙ sequence of *correlation-consistent* Gaussian bases
  - complete basis set (CBS) limit

**effects of magnetic interactions: 1comp. vs. 2comp. RDFT**

# E113-Au<sub>n</sub> vs. Tl-Au<sub>n</sub>

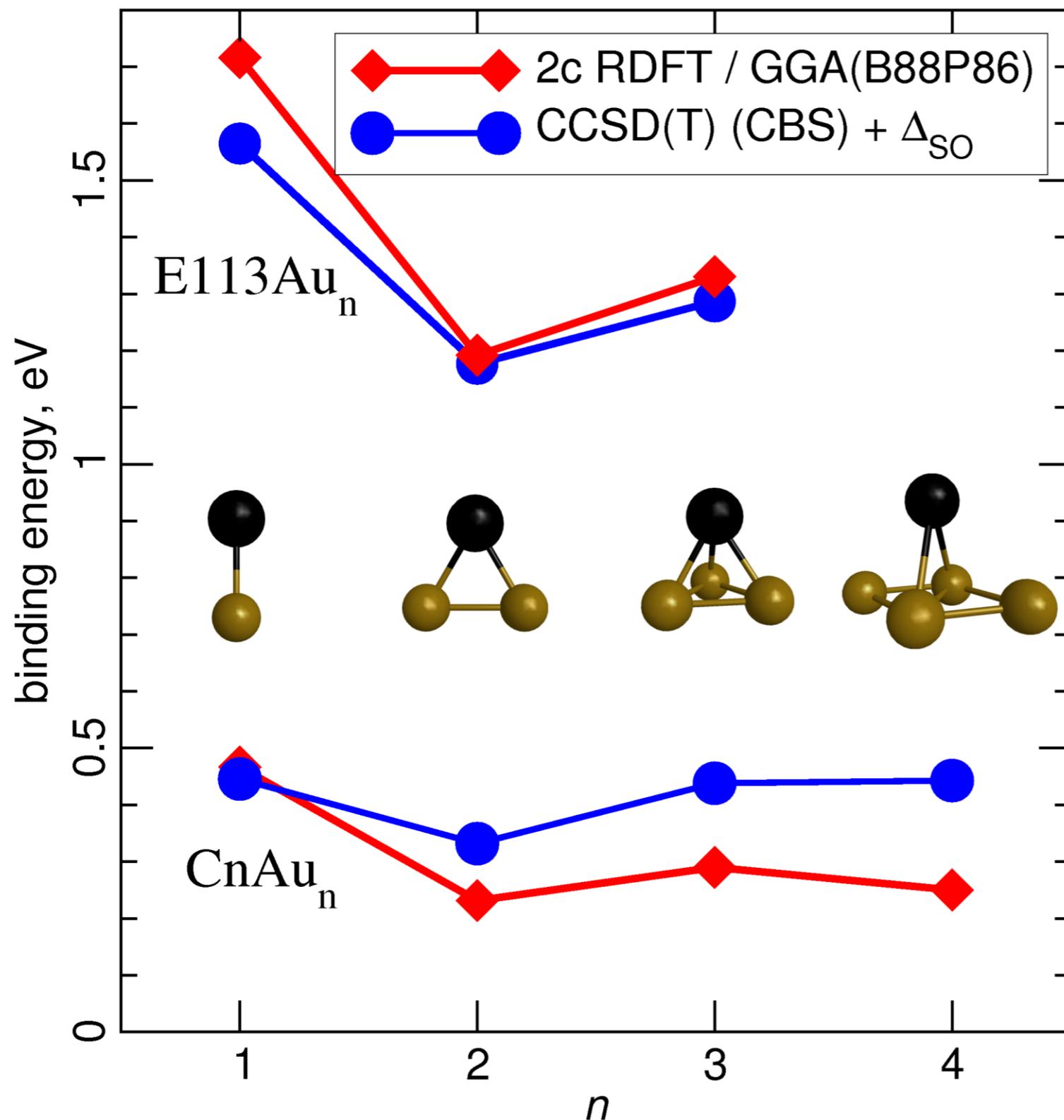
CCSD(T): accurate scalar-relativist. model; contribution of magnetic effects within RDFT

RDFT: quite reasonable approximation, **but** calibration on diatomic data is not reliable



**contribution** of correlations involving **6d-shell** of **E113** to the binding energy  $\sim 0.3$  eV/bond; *is it transition element?*

# E113-Au<sub>n</sub> and Cn-Au<sub>n</sub>: RDFT vs. CCSD(T)



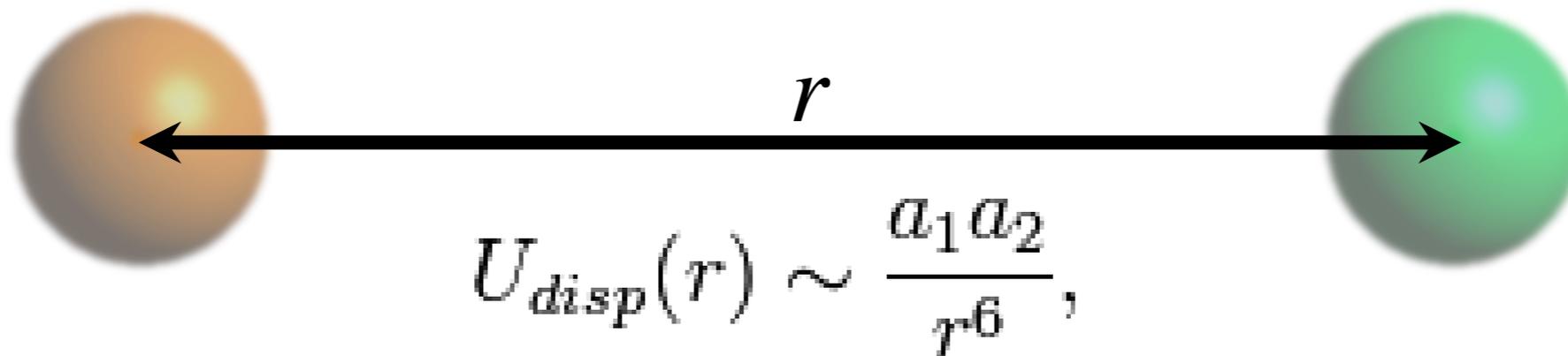
The only adatom – Au surface distance is varied; the Au-Au distances are experimental.

## Results:

- E113-Au<sub>n</sub>: RDFT is in a reasonable agreement with CCSD(T), CBS+SO
- Cn-Au<sub>n</sub>: wrong trend of RDFT results: underestimate seriously the binding energy

# Correlation contributions to interaction energy of non-overlapping subsystems of electrons (London interaction)

interaction of neutral non-polar separated many-electron systems “instantaneous dipole – instantaneous dipole”  
effect of electron correlation of different subsystems

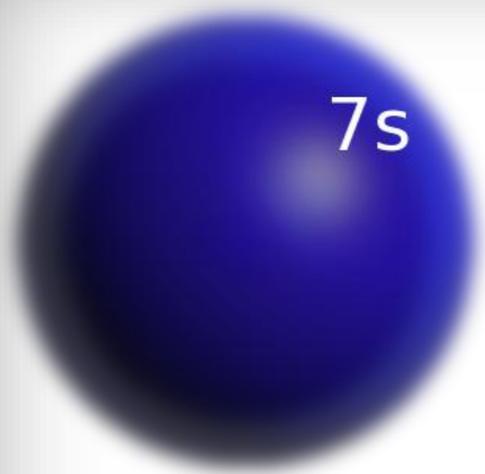


**is not** determined by the distribution of the charge density of free subsystems (as electrostatic, e.g., dipole-dipole int-n)  
**is not** associated with a significant change in the charge density of subsystems (as induction one)

**is not described  
by simple DFT models**

$$E_{XC} = \int E_{xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \dots] d\mathbf{r}$$

# Correlation contributions to interaction energy of non-overlapping subsystems of electrons (London interaction)



**Cn:**

**6d is well polarizable but more compact than 7s**

**Au:**

**5d is more compact than 6s**

**when forming Au-Cn bond the filled d-shells are almost not overlapping**

**interaction  $5d^{10}$  Au -  $6d^{10}$  Cn**

**is like London (dispersion) attraction of *aurophilic* type**

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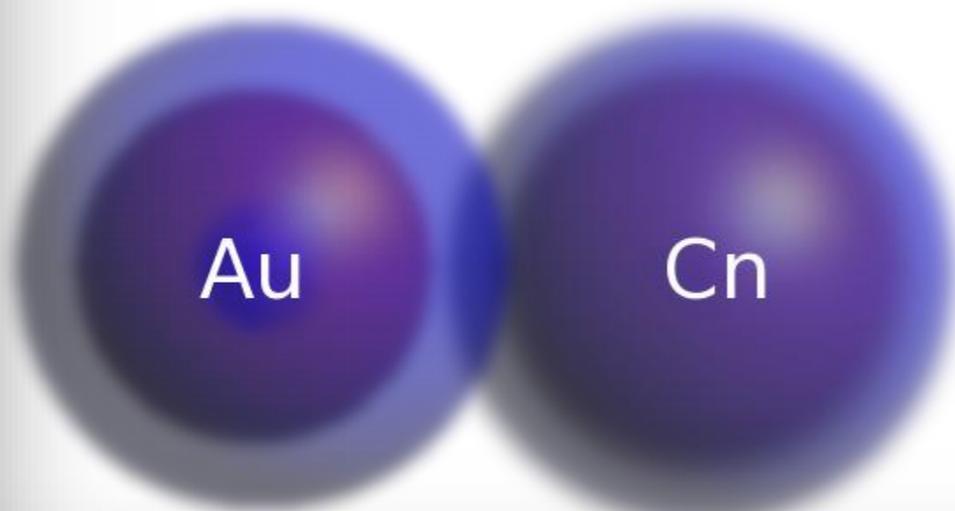
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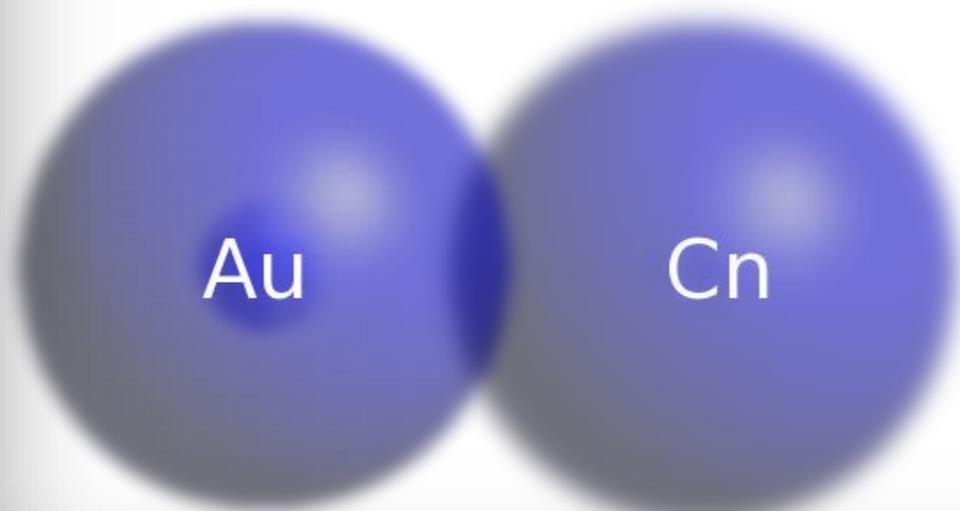
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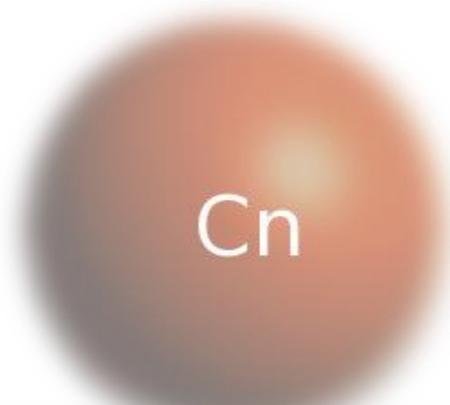
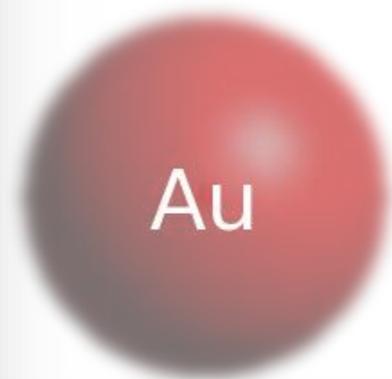
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**when forming Au-Cn bond the filled d-shells are almost not overlapping**

**interaction  $5d^{10}$  Au -  $6d^{10}$  Cn**

**is like London (dispersion) attraction of *aurophilic* type**



**not described by simple DFT models**

# Modeling of adsorption complexes E113 etc. / Au<sub>n</sub>

- It is necessary to start from *ab initio* studies of small **but not diatomic** systems and then choose appropriate exchange-correlation functional

- ⊙ solution of many-electron problem: two-component ***unrestricted non-collinear relativistic DFT*** (RDFT)

[van Wüllen, Z.Phys.Chem. **224**, 413 (2010)]

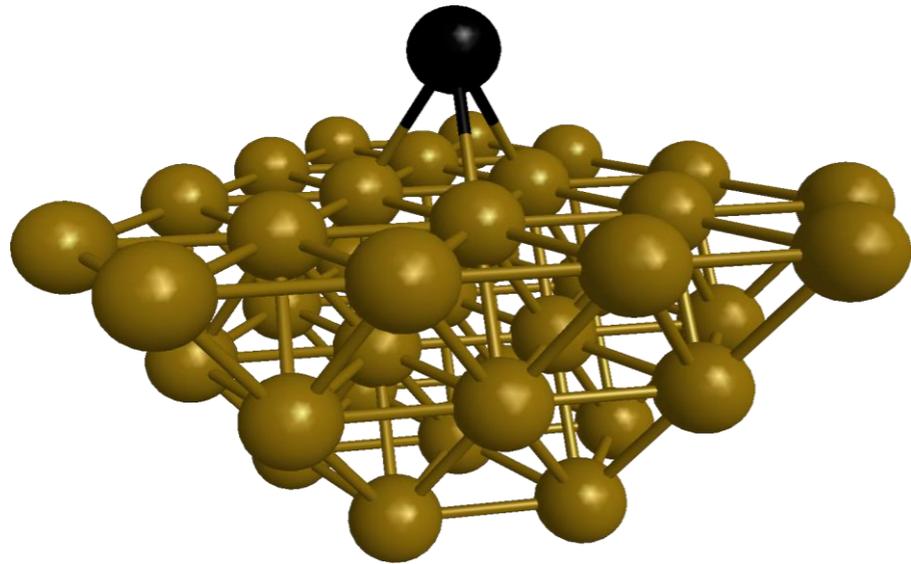
- ⊙ basis sets optimized for large differences of one-electron states  $nl_{l+1/2}$  &  $nl_{l-1/2}$

in practice, close to ***the complete basis sets limit***

- ⊙ Au clusters **up to 37 atoms** (~ limit on the cluster size)

- ⊙ If necessary, applying ***ab initio* corrections** (Cn/Au, Hg/Au)

# Large cluster models: E113 etc. / Au: RDFT

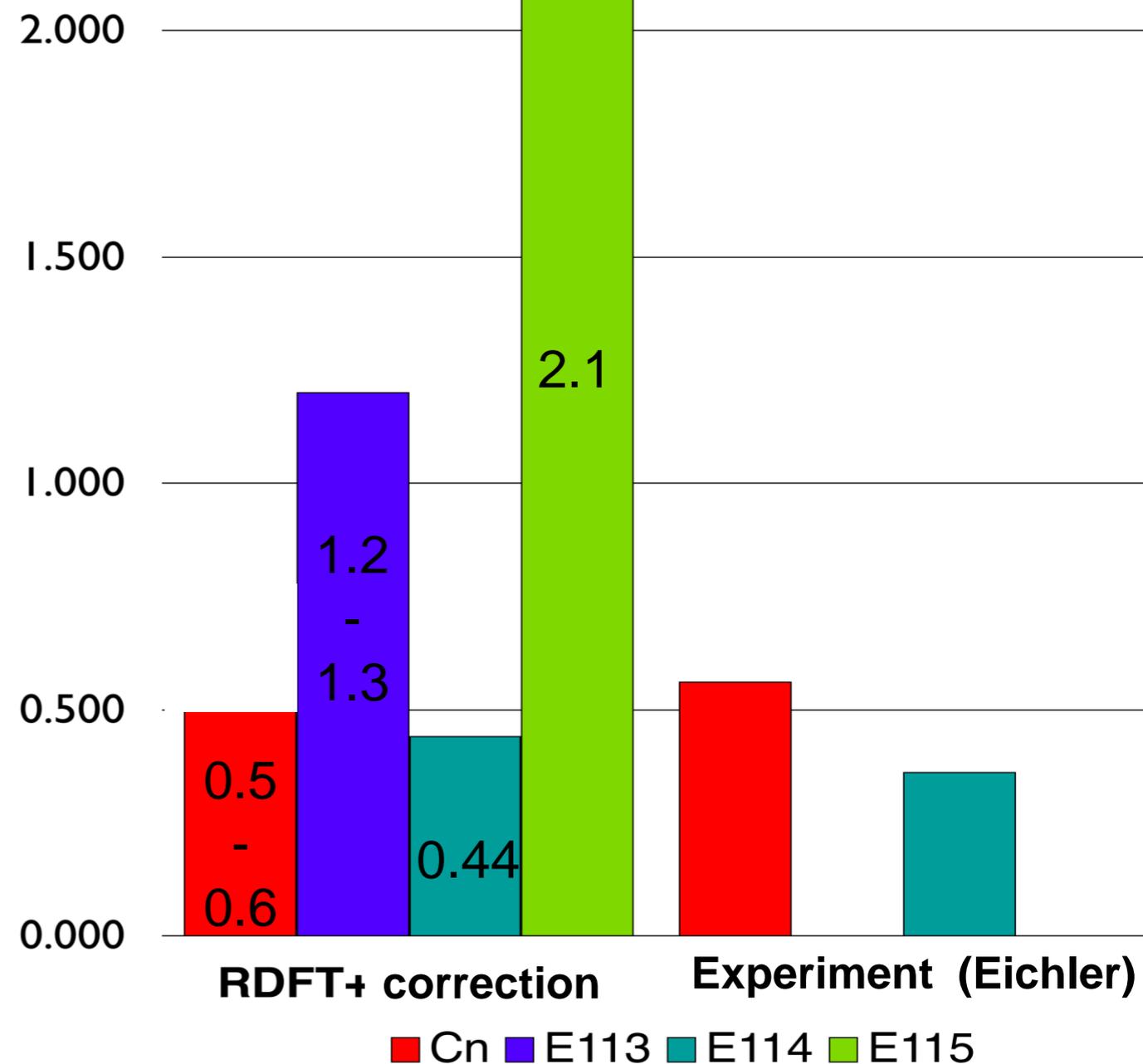


- complex113-Au<sub>37</sub> :  
position of E113 is over the Au-atom in second and third layer of surface (111)

- quite close binding energies for both positions and functionals:  
Becke – Perdew & PBE0

ca. 1.2 eV

adsorption energy on Au, eV



# Some conclusions

- **Cn** is “more or less” homologue of Hg;
- **E113** is **doubtful** homologue of Tl: notably less stable bonding with Au, completely due to magnetic interactions; significant contributions of filled 6d to bond; ??? *transition-like element* ???
- **E114** is **only** “formal” homologue of Pb;
- **E115** is a **good** homologue of Bi;
- **E113 & E114** form an *unique* “ultra-short” subperiod.

Supported by

RFBR grant N 09-03-00655-a

- <http://rel.kintechlab.com/>; <http://www.qchem.pnpi.spb.ru/>

**Thank you for attention!**



# *What is required for accurate relativistic calculation?*

Choosing a suitable *methods for calculating the electronic structure* taking account of the required accuracy of properties, complexity of the system (number of atoms and electrons, features of the valence structure, types of atoms: *s*-, *p*-, *d*- or *f*-elements, etc.), acceptable computational cost :

method of accounting for *electron correlation*  
(fixing the subset of correlated electrons);

optimal *effective Hamiltonian* (relativistic, scalar-relativistic=without SO) and related *one-electron basis set* (choosing / generation for each atom treated)

# Correlation methods

- *Coupled-clusters (CC)*

Relativistic coupled-clusters with single and double excitations (RCCSD)

[U.Kaldor, E.Eliav, A. Landau, *Tel-Aviv Uni.*, Israel;  
N.S. Mosyagin *et al.*, JCP , 115, 2007 (2001)]

scalar-relativistic (without SO) CCSDT (srCCSDT) to use large basis sets:  
within CFOUR package [[www.cfour.de](http://www.cfour.de)];  
multi-reference CC code by M.Kállay (MRCC)

- the most advanced approach now; allows one to achieve *the best accuracy* for relatively small systems with simple valence structure. There are many different single- and multi-reference developments, combined ones including CI & many-body perturbation theory.

## Effective Hamiltonian:

Relativistic pseudopotential (GRECP or Generalized PP):  
A.V. Titov & N.S. Mosyagin, IJQC **71**, 359 (1999); N.S.  
Mosyagin *et al.*, Int.Rev.At.Mol.Phys. **1**, 63 (2010).

Restoration of electronic structure in heavy-atom cores:  
A.V. Titov *et al.*, PTCP **B15**, 253 (2006).

Basis Sets: GC-basis: N.S. Mosyagin *et al.*, JPB **33**, 667 (2000).

# *Dirac-Coulomb (4-comp.) vs. pseudopotential (2-comp.)*

**Spectroscopic constants for low-lying excited state  $^2\Pi_{3/2}$  of HgH.**

<b>Year: Method</b>	<b><math>R_e(\text{\AA})</math></b>	<b><math>w_e(\text{cm}^{-1})</math></b>	<b><math>T_e(\text{cm}^{-1})</math></b>
<b>1993: Stuttgart PP / MR-CI</b>	<b>1.610</b>	<b>1930</b>	<b>28714</b>
<b>1996: shape-consistent PP / MRD-CI</b>	<b>1.615</b>	<b>2033</b>	<b>28490</b>
<b>2001: Generalized PP / RCC-SDT</b>	<b>1.579</b>	<b>2083</b>	<b>28275</b>
<b>2001: Dirac-Coulomb / RCC-SD(T)</b>	<b>1.594</b>	<b>2005</b>	<b>28122</b>
<b>1950-1988: Experiment</b>	<b>1.580</b>	<b>2079</b>	<b>28270</b>
	<b><math>\pm 0.001</math></b>	<b><math>\pm 12</math></b>	<b><math>\pm 14</math></b>

PP : relativistic pseudopotential;

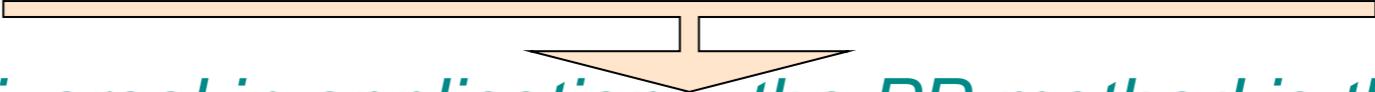
MR-CI: multi-reference configuration interaction;

RCC-SD: relativistic coupled cluster with single and double excitations.

# *What makes the core pseudopotential (PP)?*

Reduces the electronic structure calculation to an explicit treatment of only valence electrons:

- exclusion of chemically inactive (core) electrons from the calculation, while maintaining a sufficiently accurate description of the electronic structure and interactions in the valence region;
- providing Pauli orthogonality with respect to the occupied (explicitly excluded) core states, i.e., prevent the “collapse” of valence electrons into core;
- efficient treatment of relativistic effects (scalar -relativistic , spin-orbit , **Breit**);
- smoothing the pseudospinors to minimize atomic basis set size and computational cost depending on the task.



*Being universal in applications, the PP method is the most flexible approach for calculating the electronic structures.*

# *Concluding remarks*

computational accuracy can be higher than experimental; the properties which cannot be obtained experimentally to-date can be evaluated with good accuracy, that is important for many (fundamental) experiments;

good prospects for further improvement of accuracy with accounting for correlation and relativistic effects, the application field can be extended on more complicated systems, other properties and processes;

the pseudopotential method (+ electronic structure restoration in atomic cores for studying core properties) is the most efficient, prospective and universal approach for calculating not only polyatomic systems but even for diatomic ones when relativistic effects are important;

though there is no universal scheme to uniquely select a method for correlation treatment, reasonable recommendations can be formulated;

pseudopotentials and basis sets are accessible by internet.