

# **Influence of spin-dependent interactions on chemical bonding in superheavy element compounds: E112 (eka-Hg) versus Hg**

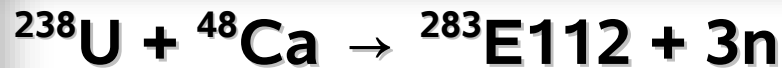
**Andrei Zaitsevskii  
Nikolai Mosyagin  
Anatoly Titov  
Elena Rykova**

- **Petersburg Nuclear Physics Institute, Gatchina**
- **Photochemistry Center RAS, Moscow**
- **Chemical Dept., Moscow State University**
- **HEPTI, RRC “Kurchatov Institute”, Moscow**

# E112: general

superheavy element from the “island of stability”

$^{283}\text{E112}$  ( $t_{1/2}=4\text{s}$ ,  $\alpha$ -decay to  $^{279}\text{E110}$ )



(FLNR, Dubna, Oganessian et al, 199, 2004)

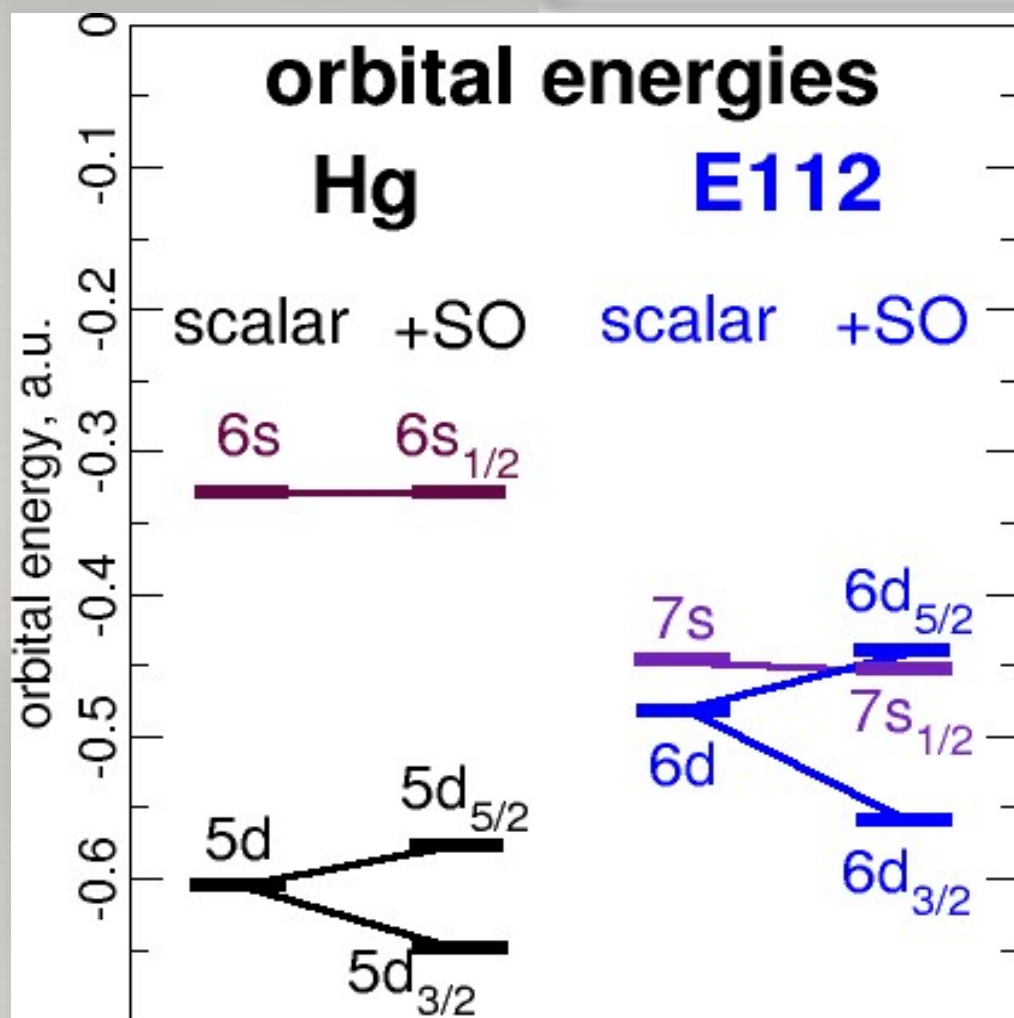


(FLNR, Dmitriev et al.; E112 detected by thermochromatography on gold surface)

## closed-shell atom

- . old hypothesis on rare-gas like behavior (Pitzer, 1975)
- . exptl & computational evidences for certain similarities with Hg rather than with Rn
  - e.g. good adsorption on gold

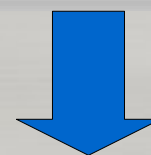
# E112: general



strong 7s contraction

large spin-orbit splittings

7s- $6d_{5/2}$  quasidegeneracy



difficulties for molecular  
electronic structure calculations

spin-orbit-free  
(scalar relativistic) treatment  
is not a good starting point

6d strongly involved in bonding  
spatial localization  $\sim 6s, 6p$   
→ at least 18-20 electrons  
should be correlated

**lowest excitation energy**

Hg: 4.7 eV E112: 3.6 eV

( $6s-6p_{1/2}$ ) ( $6d_{5/2}-7p_{1/2}$ )

## systems studied

HgH vs **E112H**  
Hg<sub>2</sub> vs **E112<sub>2</sub>**  
HgAu vs **E112Au**

s-s interactions

σ-like bond

importance of magnetic interactions is not evident

# basic models: shape-consistent semilocal RECP for small atomic cores generalized RECP (GRECP)

**inner core** replaced by RECP

**outer-core** and **valence** electrons

**(n-1)s (n-1)p (n-1)d ns** (20 for Hg, E112, 19 for Au)  
are treated explicitly

**atomic semilocal RECP**  $\sum_{jl} w_{jl}(r) P_{jl}$

extracted from *valence* solutions of atomic relativistic problem

**GRECP: semilocal RECP** +  $\sum_{jln}^{outer\ core} w'_{jln} P_{jln}$

different semilocal RECPs for outer-core and other (valence etc) orbitals

**basic models:  
shape-consistent semilocal RECP for small  
atomic cores  
generalized RECP (GRECP)**

**extracted from atomic  
Dirac-Fock-Breit solutions**

**Breit and finite-nuclei  
effects incorporated**

**scalar & spin-dependent  
(SO) relativistic effects  
reside in effective 1-e  
potentials**

**kinetic energy & e-e  
interactions as in non-rel  
hamiltonian -> quasi-non-  
relativistic methods usable**

**readily split into  
spin-averaged part and  
effective SO interactions**

**spin-orbit-free analog  
is well and simply defined**

**“chemical accuracy” for  
ground and low-lying  
excited states**

# outer core + valence shell correlation treatment

## relativistic Fock-space coupled clusters - RCCSD

(+ estimates for higher amplitudes from spin-orbit CI, h.e.)

spin-restricted closed-shell reference

very simple (up to 1p) model spaces

SD: poor treatment of 1p (target!) valence sectors

basis set limitations

RCC (Eliav & Kaldor)

## spin-orbit DFT (SO DFT)

fully unrestricted optimization of two-component 1-el spinors

equal-footing treatment of scalar and SO terms

in some cases single det recovers effects of “restricted  
configuration” mixing

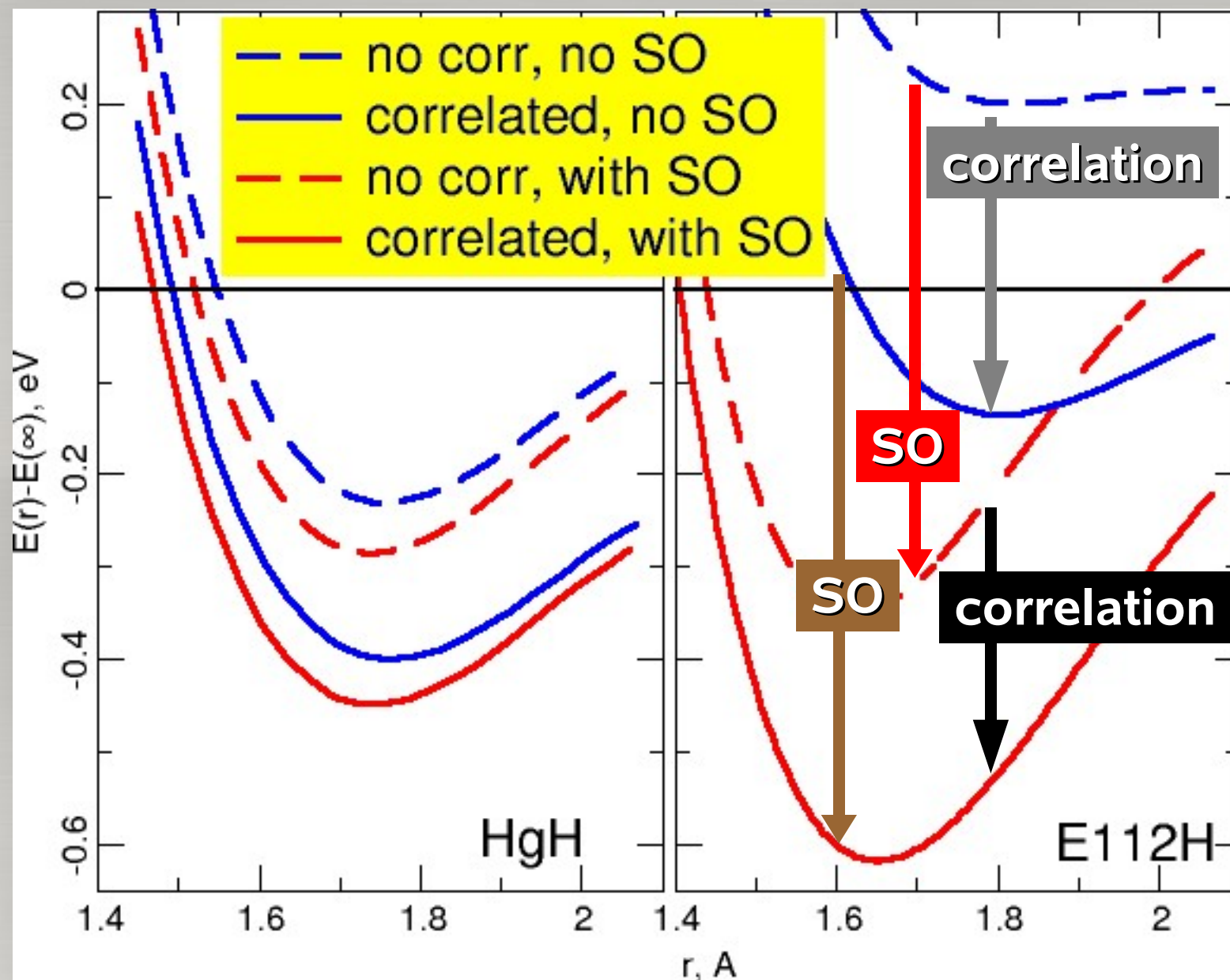
NWChem 4.x

## coupled clusters with UHF reference - UCCSD(T)

for spin-free problem only!

Gaussian 03

# ground-state potential curves: HgH vs E112H



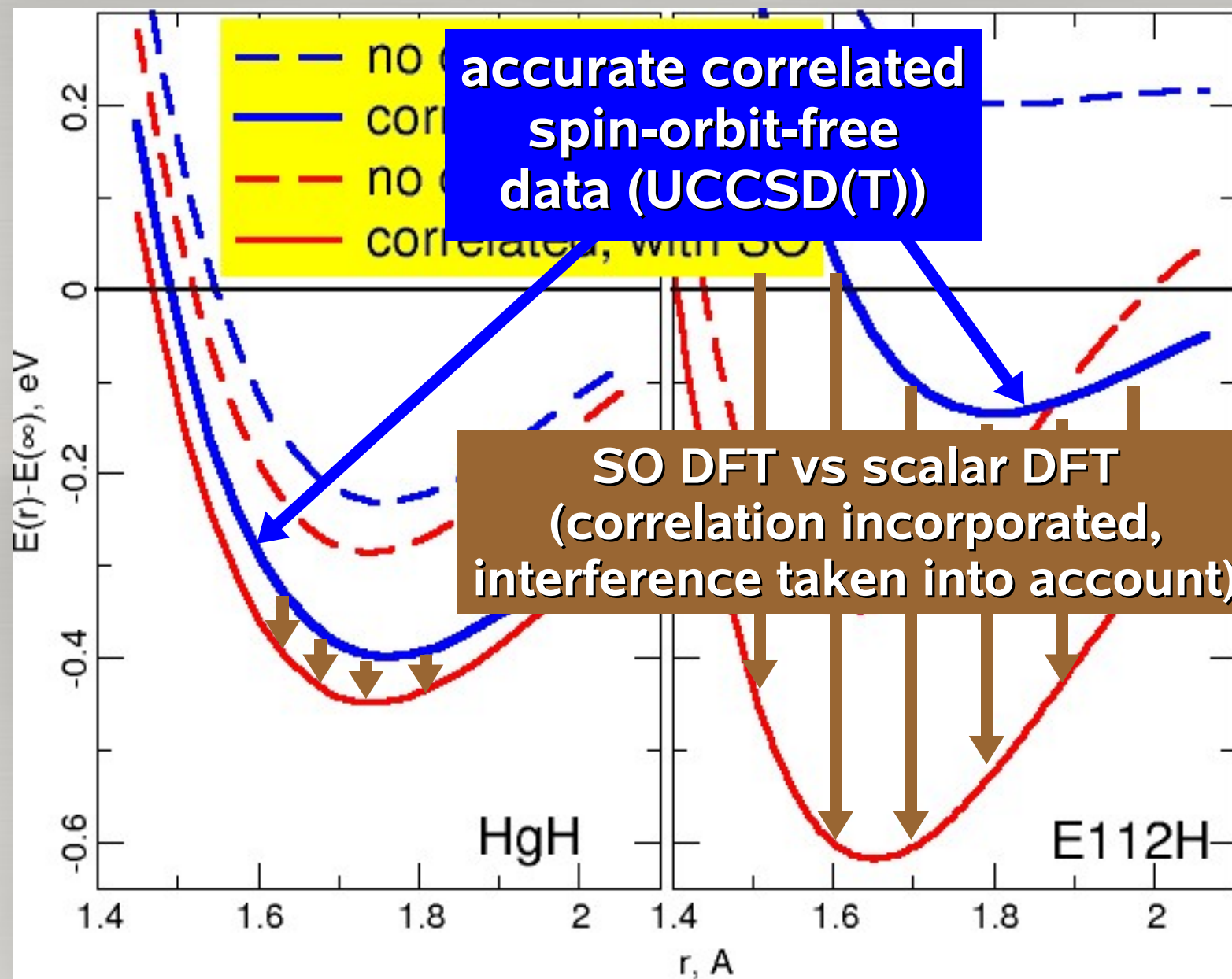
interference:

**SO**  $\neq$  **SO**

**correlation**  
 $\neq$

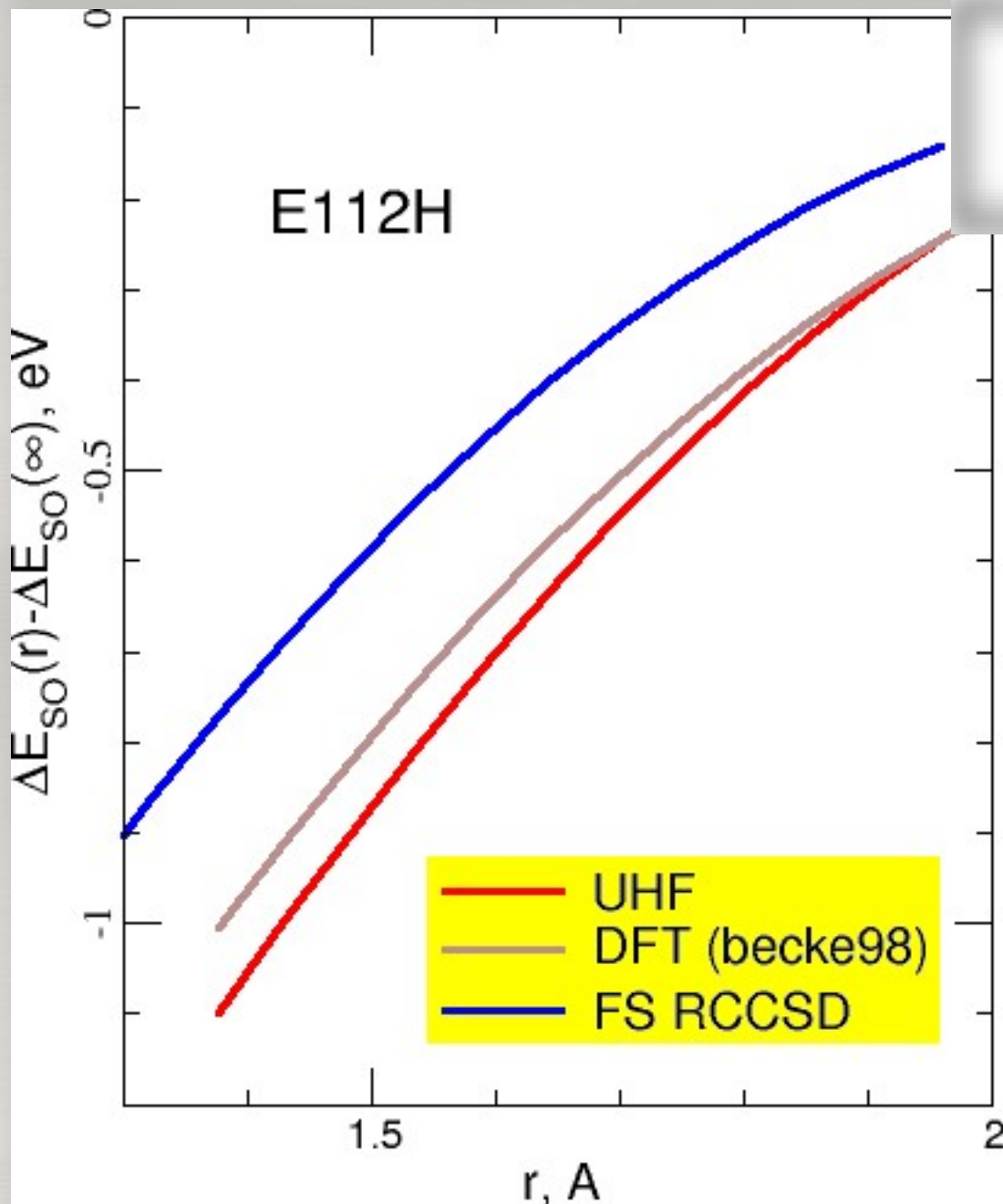
**correlation**

# ground-state potential curves: HgH vs E112H



$$\Delta E_{so}(r)$$
$$-\Delta E_{so}(\infty)$$

# spin-orbit contribution to E112-H interaction energy



more significant at small r:  
strong spin-orbit stabilization

difference between  
**FS RCCSD** and **DFT**:  
**FS RCCSD**  
strong basis set effects  
SO-free closed-shell  
vacuum  
roughly approximate  
treatment of target sector  
no d-holes in model space

**DFT**:  
one-det nature  
approximate  
exchange-corr  
functional

# HgH vs E112H: bond energies & lengths

diss. energy, eV  
HgH      **E112H**

bond length, Å  
HgH      **E112H**

*spin-orbit-free*

FS CCSD

**-0.03**

**1.74**

UCCSD(T)

0.40

**0.13**

1.75

**1.80**

*spin-orbit included*

FS RCCSD + h.e.

0.41

**0.42**

1.74

**1.66**

UCCSD(T) + SO

0.45

**0.62**

1.73

**1.64**

SO DFT (becke98)

0.45

**0.62**

1.74

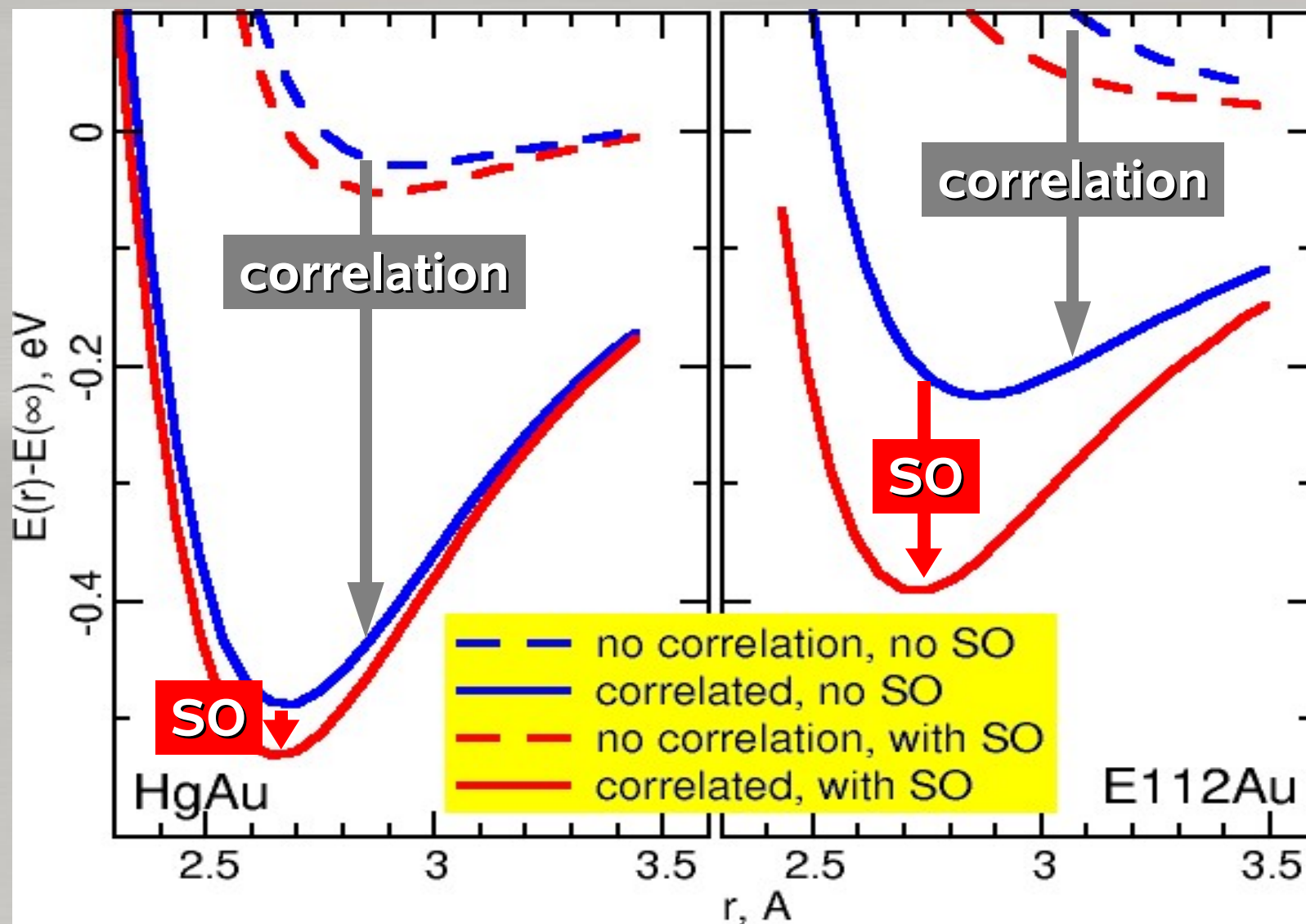
**1.65**

**exptl**

0.46

1.74

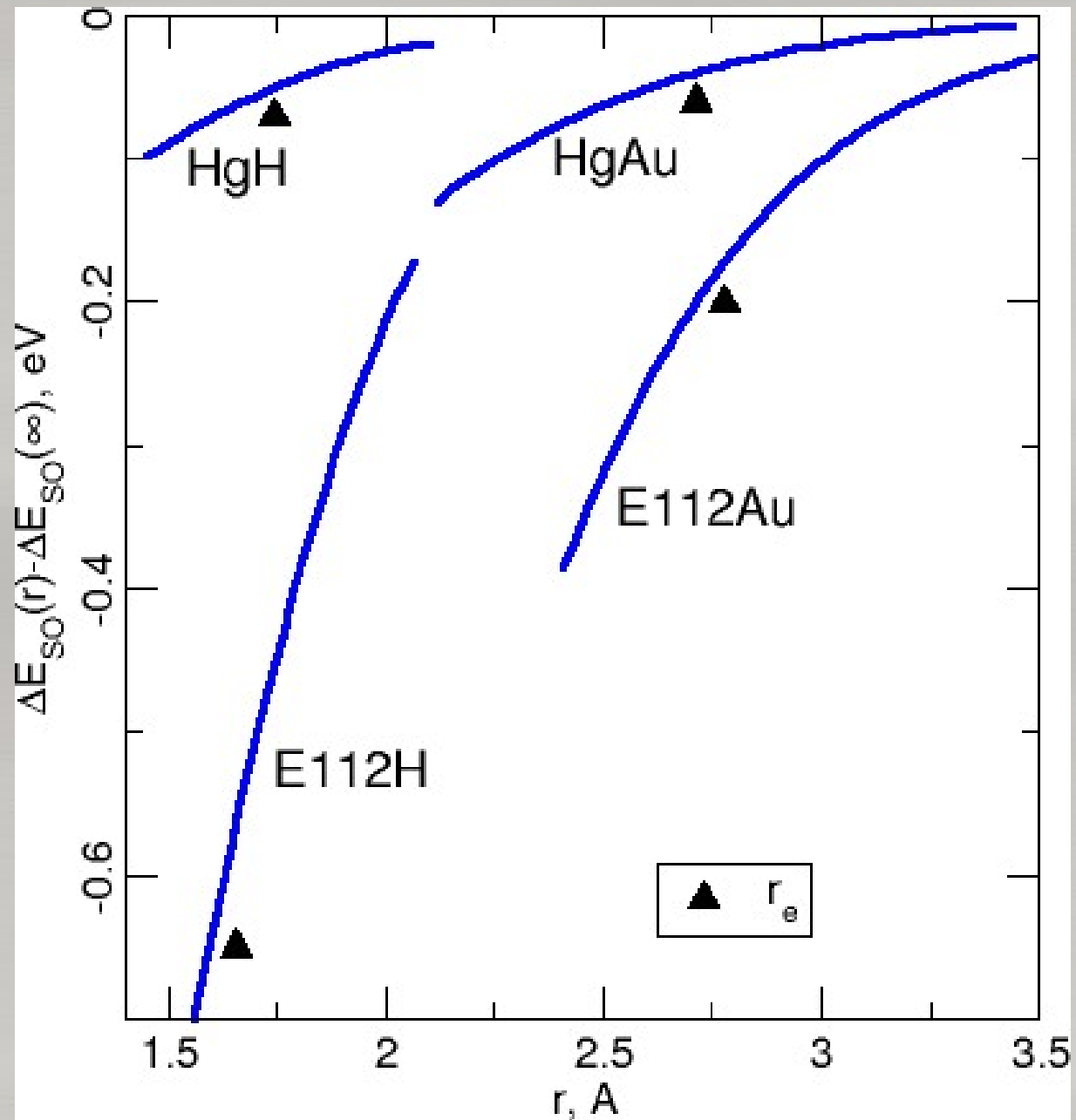
# ground-state potential curves: HgAu vs E112Au



# HgAu vs E112Au: bond energies & lengths

	diss. energy, eV		bond length, Å	
	HgAu	E112Au	HgAu	E112Au
<i>spin-orbit-free</i>				
UCCSD(T)	0.49	0.22	2.67	2.87
<i>spin-orbit included</i>				
SO DFT (Becke 98)	0.51	0.36	2.71	2.77
UCCSD(T) + SO	0.53	0.39	2.65	2.73
<i>4-component relativistic DFT (Sarpe-Tudoran et al., 2002-2004)</i>				
4-comp RDFT (GGA)	0.55	0.41		
4-comp RDFT (GGA)	0.50	0.27	2.67	2.73
4-comp RDFT (LDA)	1.03	0.93	2.59	2.65


# spin-orbit contributions to interaction energies



# Hg<sub>2</sub> vs E112<sub>2</sub>: bond energies & lengths

	diss. energy, eV		bond length, Å	
	Hg <sub>2</sub>	E112 <sub>2</sub>	Hg <sub>2</sub>	E112 <sub>2</sub>
<i>spin-orbit-free</i>				
CCSD(T)	0.041	0.038	3.79	3.88
<i>spin-orbit included</i>				
CCSD(T) + SO	0.043	0.053	3.74	3.65
exptl	0.045		3.66	
<i>4-component relativistic DFT (Anton et al., 2005) with two different GGA functionals</i>				
4-comp RDFT (b88p86)	0.009	0.039	3.63	3.45
4-comp RDFT (pw91)	0.048	0.080	3.55	3.39

# conclusions

- spin-orbit stabilization is essential for the description of E112-X “s-s-type” bonding  
(SO contributions  $\sim 1/2$  E112-Au binding energy  
70-80% of E112-H binding energy)
  - E112H is more stable than HgH,  
E112<sub>2</sub> is more stable than Hg<sub>2</sub>,  
stability of E112Au is comparable to that of HgAu  
(E112Au bond energy  $\sim 3/4$  HgAu bond energy)
- 
- certain similarity between E112 and Hg interactions with gold exists

see poster “Spin-orbit DFT simulation of eka-Hg interactions with Au clusters”, E.Rykova *et al.*

## websites

<http://kintech.ru/rel/>  
<http://qchem.pnpi.spb.ru/>

## acknowledgement

**computer facilities: Kinetic Technologies Ltd**

**research support by  
russian foundation for basic research  
grants n° 06 03 32346 & 06 03 33060**