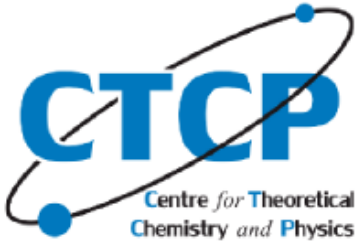
Benchmark Calculations of Atomic Properties of Elements 112 to 122

A. Borschevsky, V. Pershina, E. Eliav, and U. Kaldor



Properties under study:

- Ionization potential
- Electron affinity
- Polarizability

Motivation:

- Fundamental knowledge: relativistic effects, structure of the periodic table, etc.
- Link to chemical/physical properties: reactivity, electronegativity, adsorption enthalpy…

Methods

- Relativity
- Electron correlation
- Basis sets

Relativity

Classical example: gold atom (eV)

			NR	DC	Expt.
IP	$5d^{10}6s$	$^2S_{1/2}$	7.06	9.21	9.23
EE	$5d^9 6s^2$	$^2D_{3/2}$	5.30	2.66	2.66
	$5d^9 6s^2$	$^2D_{5/2}$	5.30	1.12	1.14
	$5d^{10}6p_{1/2}$	$^2P_{1/2}$	3.31	4.72	4.63
	$5d^{10}6p_{3/2}$	$^2P_{3/2}$	3.31	5.18	5.11
EA	$5d^{10}6s^2$	$^1S_0$	1.28	2.29	2.31

- strong stabilization and contraction of the *s* orbitals
- stabilization of the $p_{1/2}$ orbitals
- destabilization and expansion of the $p_{3/2}$, *d* orbitals

For SHE:

1. $^2S \rightarrow {}^2D_{5/2}$ transition (eV)[1]

	Cu	Ag	Au	E111
NR	1.39	3.75	5.30	5.43
DCB	1.39	3.75	1.15	-2.95

Ground state of element 111 is **$6d^9 7s^2$ $^2D_{5/2}$**
NR calculations yield **$6d^{10}7s$** ^{2}S, same as the other coinage metals

2. Electron affinity of 118[2]

Predicted electron affinity of element 118 is **0.056** eV, NR calculations give no electron affinity

[1] Eliav et al, Phys. Rev. Lett. **73**, 3203 (1994)
[2] I. Goidenko, PRA **67**, 020102 (2003)

Relativity

Classical example: gold atom (eV)

			NR	DC	Expt.
IP	$5d^{10}6s$	$^2S_{1/2}$	7.06	9.21	9.23
EE	$5d^96s^2$	$^2D_{3/2}$	5.30	2.66	2.66
	$5d^96s^2$	^2D	5.30	1.12	1.14

- strong stabilization and contraction of the *s* orbitals
- stabilization of the $p_{1/2}$ orbitals
- destabilization and expansion of the

Any investigation of the structure, spectroscopy and chemistry of SHE must include relativity from the start; threating it as a perturbation is inadequate

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Predicted electron affinity of element 118 is **0.056** eV, NR calculations give no electron affinity

Ground state of element 111 is $6d^97s^2\ ^2D_{5/2}$
NR calculations yield $6d^{10}7s\ ^2S$, same as the other coinage metals

[1]Eliav et al, Phys. Rev. Lett. **73**, 3203 (1994)
[2] I. Goidenko, PRA **67**, 020102 (2003)

Relativity

- 4-c Dirac-Coulomb-Breit Hamiltonian:

$$H_{\mathrm{DCB}} = \sum_i h_D(i) + \sum_{i<j} (1/r_{ij} + B_{ij}),$$

$$h_D(i) = c\alpha_i \cdot \mathrm{p}_i + c^2 \beta_i + V_{nuc}(i)$$

- $\boldsymbol{\alpha_i}$, $\boldsymbol{\beta_i}$ - four dimensional Dirac matrices
- V_{nuc}- nuclear attraction operator (finite nucleus model)
- $B_{ij} = -\frac{1}{2r_{ij}}\left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + (\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})/r_{ij}^2\right]$, Breit term

correct up to the order of α^2, higher order corrections (QED) are possible

- 4 component wave functions: $\Psi = \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix}$

Electron correlation

Correlation (explicit electronic interaction) is important for both light and heavy systems, and for all properties

- **Ionization potentials**

	DF	MP2	CCSD	CCSD(T)	Exp.
I	9.663	10.028	10.362	10.436	10.451
At	8.437	9.213	9.241	9.317	-
117	6.619	7.692	7.554	7.650	-

- **Electron affinities**

Element 118: without correlation: EA<0

with correlation EA=0.056 eV

- **Polarizabilities**

	DF	MP2	CCSD	CCSD(T)	Exp.
Hg	44.90	27.47	35.31	34.14	33.9 (0.3)
112	29.46	25.11	27.66	27.64	-

Correlation methods

Some correlation methods:

- Configuration interaction (CI): Full CI/CISD
- Multiconfigurational Dirac-Fock (MCDF)
- Perturbation methods (MP2, CASPT2)
- **Coupled cluster (CC) method**

Most powerful (yet most computationally expensive) approach.

$$\Psi = \exp(S)\Psi_0 = \left(1 + S + \frac{S^2}{2!} + \cdots\right)\Psi_0$$

S is the excitation operator (usually truncated at S_2):

$$S = S_1 + S_2 + \cdots + S_N;\ S_1 = \sum_{ia} s_i^a a_a^\dagger a_i;\ S_2 = \sum_{ijab} s_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

CC equations:

$$\text{CCSD: } \Psi_{\text{CCSD}} = \exp(S_1 + S_2)|\Phi_0\rangle.$$

$$\langle\Phi_0|(H - E_{\text{CCSD}})\exp(S_1 + S_2)|\Phi_0\rangle = 0$$

Correlation methods

Some correlation methods:

- Configuration interaction (CI): Full CI/CISD
- Multiconfigurational Dirac-Fock (MCDF)
- Perturbation methods (MP2, CASPT2)
- **Coupled cluster (CC) method**

- Highly accurate
- Equivalent to infinite order perturbation expansion
- Size extensive (energy scales linearly with num. of electrons)
- Fulfils the separability condition

$$S = S_1 + S_2 + \cdots + S_N;\ \ S_1 = \sum_{ia} s_i^a a_a^\dagger a_i;\ \ S_2 = \sum_{ijab} s_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

Coupled cluster methods

CCSD(T) - relativistic single reference coupled cluster

Closed shell systems/systems with one dominant configuration

Open shell systems, transition energies, bond dissociation: multireference coupled cluster

FSCCSD - Fock space coupled cluster

- open shell systems
- many transition energies in a single calculation
- very high accuracy
- limitations:

1. two valence holes/two valence particles only: **application to systems with more valence particles is in development, E. Eliav, Tel Aviv group**
2. convergence difficulties limit the size of the mode space: **Intermediate Hamiltonian (IH) approach**

Intermediate Hamiltonian approach (IH)

Developed in the Tel Aviv group, three variants: **IH1**, **MSIH** and **XIH.**

Allows for use of extremely large model spaces, while avoiding convergence difficulties. **Benchmark accuracy often requires very large model spaces.**

Ionization potential of Ra with XIHFCC (exp. IP=5.278 eV)

Model space	IP (eV)	Error (eV)
8*s*7*p*6*d*	5.380	0.102
8*s*9*s*7*p*8*p*6*d*7*d*5*f*	5.332	0.054
8-11*s*7-10*p*6-9*d*5-6*f*5*g*	5.313	0.035
8-14*s*7-11*p*6-10*d*5-7*f*5-6*g*	5.300	0.022
8-15*s*7-12*p*6-10*d*5-8*f*5-6*g*4*h*	5.284	0.006
8-15*s*7-12*p*6-11*d*5-9*f*5-6*g*4*h*	5.282	0.0037

Same accuracy can be expected for the obtained IP of element 120 (5.888 eV)

Basis sets

- **Faegri dual family basis sets**

K. Faegri, Theor. Chem. Acc. **105** 252 (2001)

- **Universal basis set of Malli**

Malli *et al,* PRA **47**, 143 (1993)

Software

- Tel Aviv atomic computational package

E. Eliav, U. Kaldor, and Y. Ishikawa

- DIRAC08/DIRAC10 computational package

DIRAC, a relativistic ab initio electronic structure program, release DIRAC08 (2008)/release DIRAC10 (2010)

Basis sets

- **Faegri dual family basis sets**

K. Faegri, Theor. Chem. Acc. **10**

- **Universal basis set of M**

Malli *et al,* PRA **47**, 143 (1993)

- Augmented by high *l* functions (up to *l*=6)
- Extended to convergence

Software

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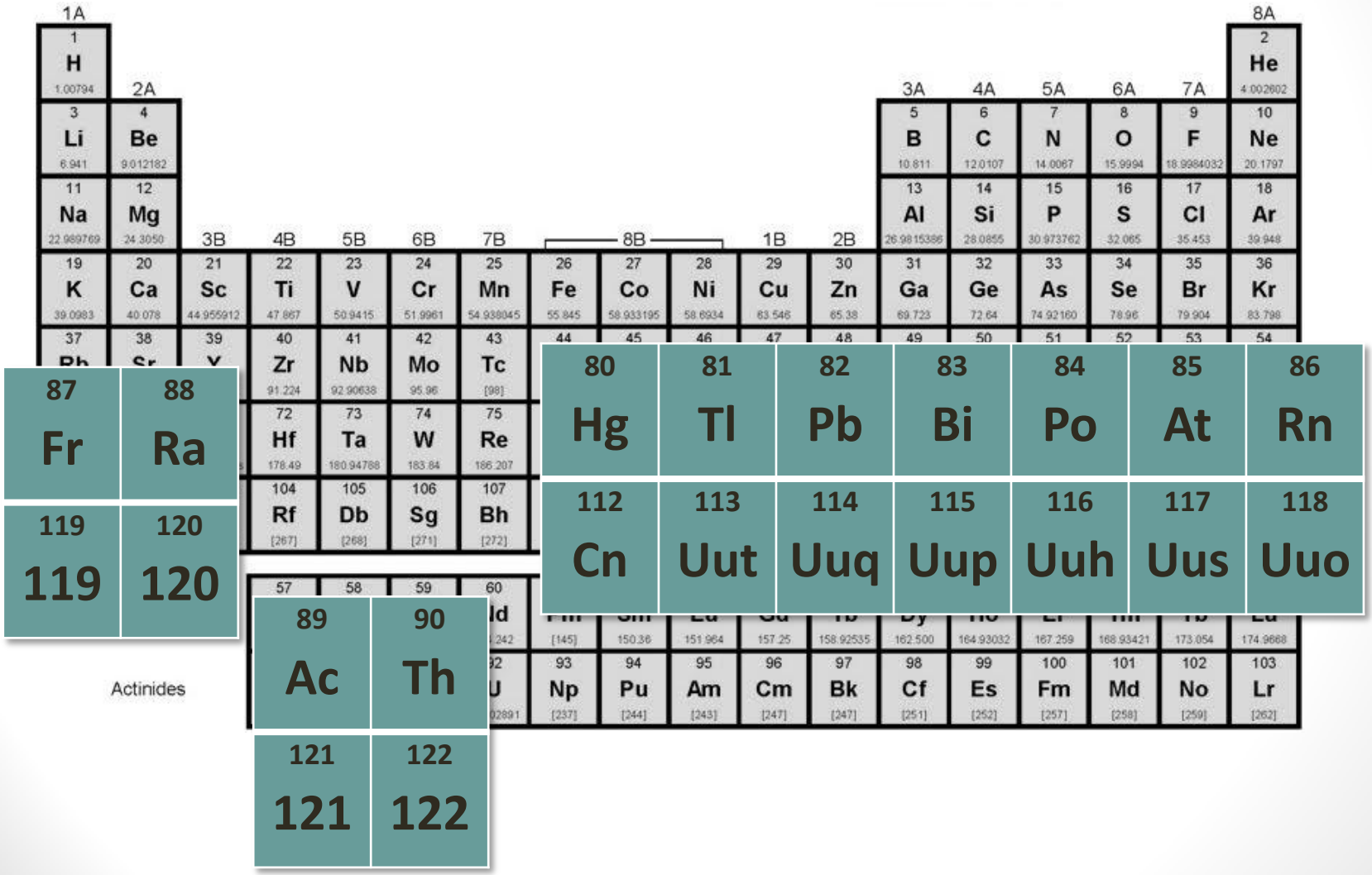
Atoms of interest:



Results

- Ionization potentials
- Electron affinities
- Polarizabilities

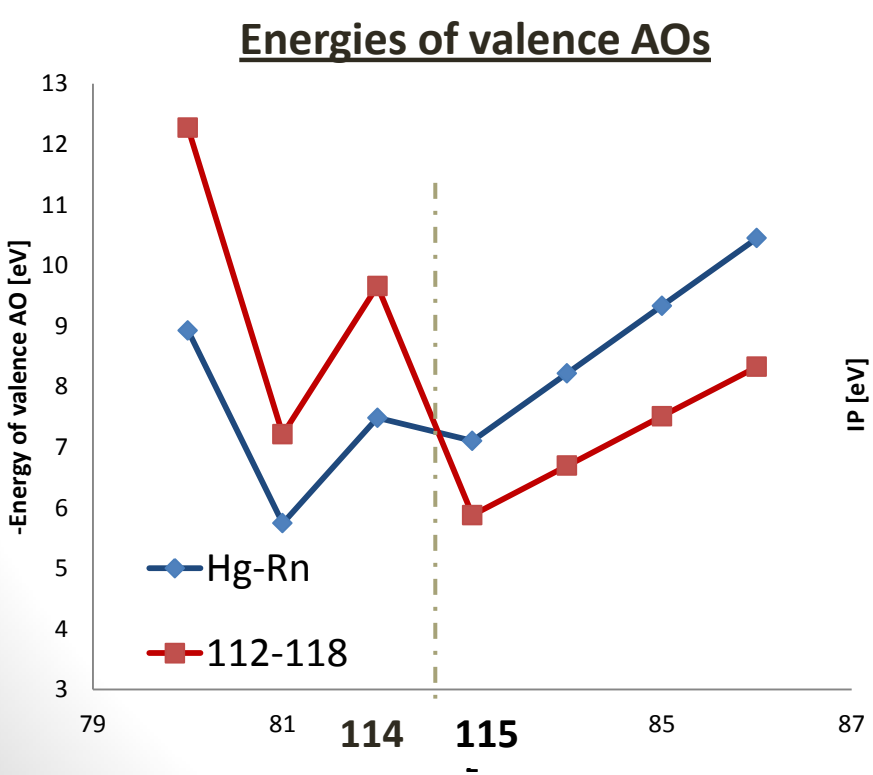
Ionization potentials – 7*p* elements

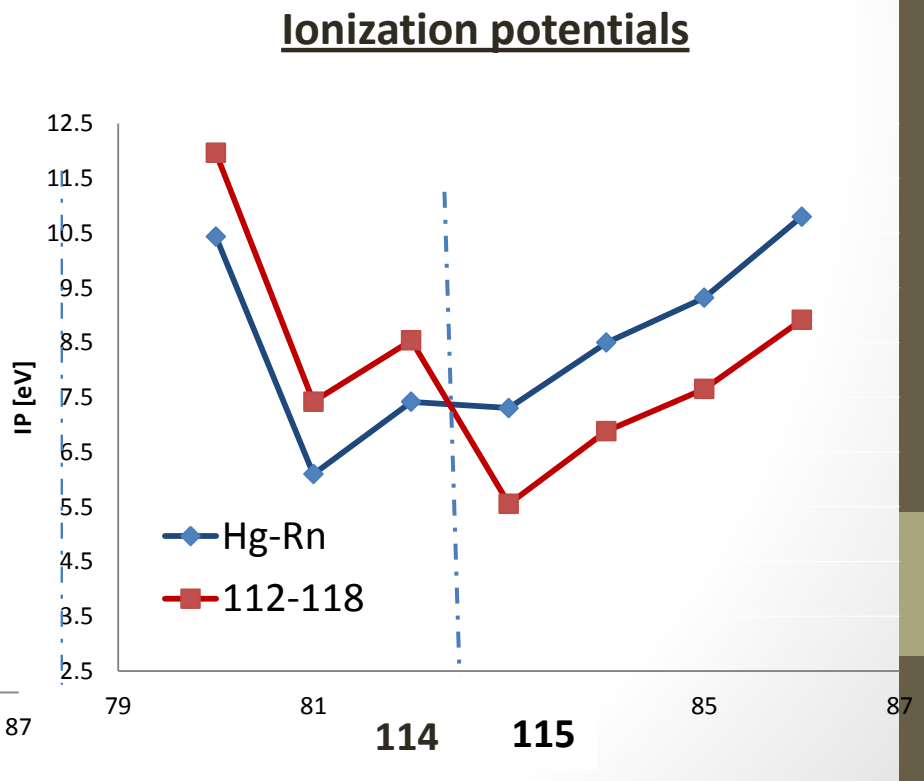
	Hg	Tl	Pb	Bi	Po	At	Rn
IHFSCC	10.455[1]	6.096	7.349[2]	7.304	8.499	9.317	10.799
Other calc.	10.39[3] ECP-CCSD(T)		7.044[4] MCDF			9.35[5] MCDF	10.482[3] ECP-CCSD(T)
IP exp. (eV)	10.438	6.108	7.417	7.286	8.414	-	10.749
	Cn	**113**	**114**	**115**	**116**	**117**	**118**
IHFSCC (eV)	11.970[1]	7.420	8.539[2]	5.553	6.881	7.650	8.914
Other calc.	11.68[3] ECP-CCSD(T)	7.4[7] DF	8.286[4] MCDF	5.5[6] DF	7.5[6] DF	7.64[5] MCDF	8.6423[3] ECP-CCSD(T)

[1] E. Eliav *et al.*, PRA **52**, 2765 (1995)
[2] A. Landau *et al.*, JCP **114**, 2977 (2001)
[3] C. Nash, JPC A **109**, 3493 (2005)
[4] Y.J. Yu *et al.*, JCP **128**, 124316 (2008)
[5] Z. Chang *et al.*, JPC A **114**, 13388 (2010)
[6] B. Fricke, Struct. Bonding **21**, 89 (1975)
[7] Keller *et al.*, JPC **74**, 1127 (1970)

Ionization potentials – 7*p* elements

	Hg	Tl	Pb	Bi	Po	At	Rn
IHFSCC	10.455[1]	6.096	7.349[2]	7.304	8.499	9.317	10.799
	Cn	**113**	**114**	**115**	**116**	**117**	**118**
IHFSCC (eV)	11.970[1]	7.306	8.539[2]	5.553	6.881	7.650	8.914

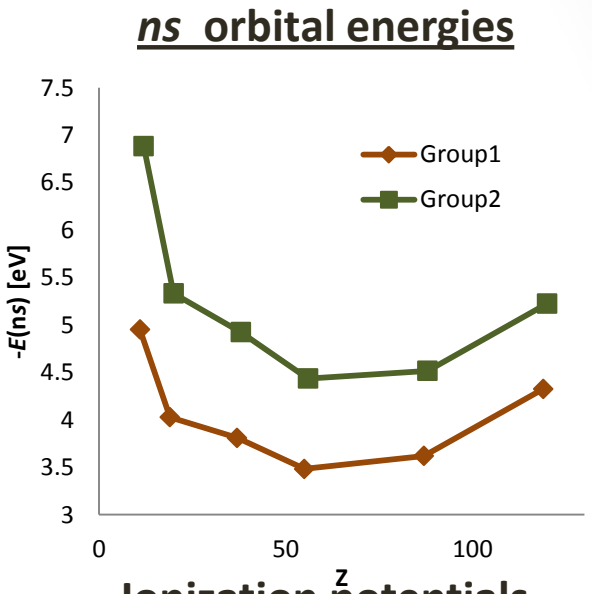


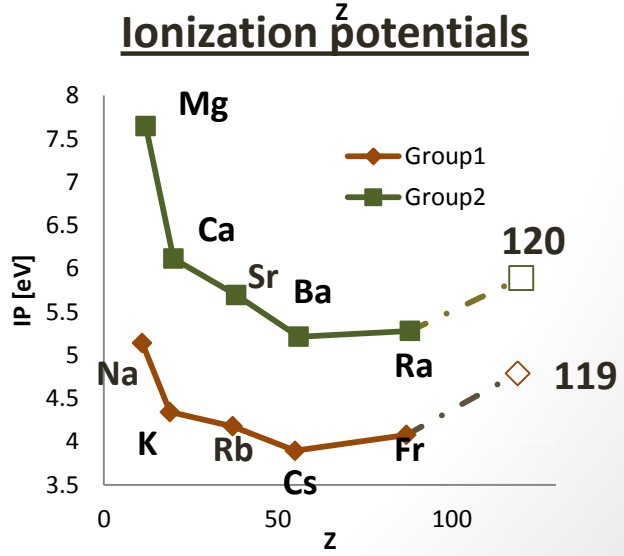


Ionization potentials – 8*s* elements

	Fr	Ra
IHFSCC	4.077[1]	5.282
DK+CCSD(T)	4.038[2]	
IP exp. (eV)	4.073	5.278
	119	**120**
IP calc (eV)	4.788[1]	5.888
DK+CCSD(T)	4.713[2]	6.0 (**DF**)[3]

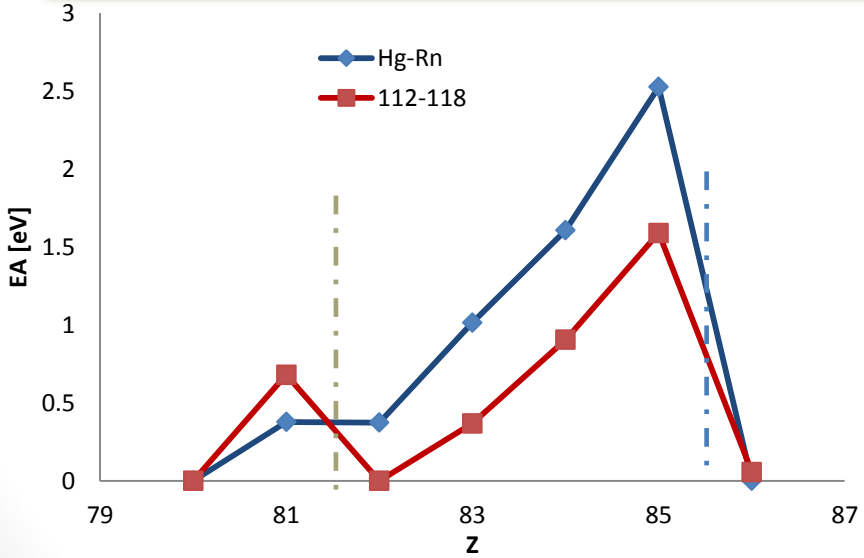
[1] E. Eliav *et al.*, Chem. Phys. **311**, 163 (2005)
[2] I. Lim *et al.*, JCP **122**, 104103 (2005)
[3] B. Fricke, Struct. Bonding **21**, 89 (1975)





Electron affinities – 7*p* and 8*s* elements

	Hg	Tl	Pb	Bi	Po	At	Rn
IHFSCC (eV)	-	0.410[1]	0.373	1.015	1.608	2.527	-
EA exp. (eV)	-	0.377	0.364	0.942	1.9 (3)	2.38[2] (**MCDF**)	-
	Cn	**113**	**114**	**115**	**116**	**117**	**118**
IHFSCC (eV)	-	0.680[1]	-	0.368	0.905	1.589	0.056[3]
						1.45[2] (**MCDF**)	



	Fr	Ra
IP calc (eV)	0.491[4]	0.100
IP exp. (eV)	0.492	
	119	**120**
IP calc (eV)	0.663[4]	0.052

[1] E. Eliav *et al*, PRA **53**, 3926 (1996)
[2] Z. Chang *et al.*, JPC A **114**, 13388 (2010)
[3] I. Goidenko, PRA **67**, 020102 (2003)
[4] A. Landau *et al.* JCP **115**, 2389 (2001)

Elements 121 and 122

	Ac	Th
Ground state	$7s^2$**$6d_{3/2}$**	**$6d^2$**$7s^2$
IP (eV)	5.17 ($7s^2$)	6.307 (**$6d^27s$**)
EA (eV)	0.345 ($7s^2$**$6d7p$**)	-
	121	**122**
Ground state	$8s^2$**$8p_{1/2}$**	$8s^2$**$7d_{3/2}8p_{1/2}$**
IP (eV)	4.447 ($8s^2$)	5.595 (**$8s^27d_{3/2}$**)
EA (eV)	0.569 ($8s^2$**$7p^2_{1/2}$**)	-

[1] E. Eliav, S. Shmulyian, U. Kaldor, and Y. Ishikawa, J. Chem. Phys. **109**, 3954 (1998)

[2] E. Eliav, A. Landau, Y. Ishikawa, and U. Kaldor, J. Phys. B **35**, 1693 (2002)

Polarizabilities

Finite field approach

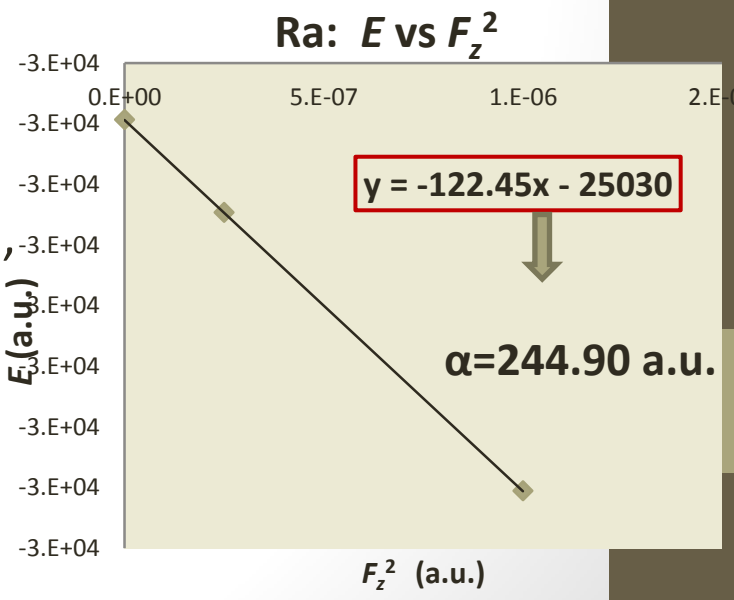
- Electric dipole polarizability (α): a measure of the distortion of the charge distribution by an external electric field. For a uniform electric field acting in the *z* direction (F_z),

$$\alpha = -\frac{\partial^2 E(F_z)}{\partial F_z}$$

- For an atom in an external electric field,

$$E(F_z) = E(0) + F_z \left.\frac{\partial E(F_z)}{\partial F_z}\right|_{F_z=0} + \frac{1}{2} F_z^2 \left.\frac{\partial E^2(F_z)}{\partial^2 F_z}\right|_{F_z=0} + \ldots$$

- Calculate the energy $E(F_z)$ of the ground state of the atom for different values of external field, (F_z=0.0, 0.0005, 0,001 a.u.)
- Obtain derivative with respect to F_z^2 (**a**) by numerical differentiation
- Polarizability: **α=-2·a**



Polarizabilities – 7*p* and 8*s* elements

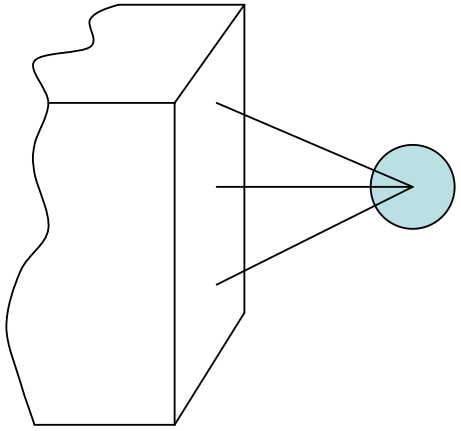
	Hg	Tl	Pb	Bi	Po	At	Rn
This work (a.u)	34.15	52.3	46.96	47.36	43.57	42.37	35.04
α other calc. (a.u)	34.42[1] **PP+CCSD(T)**	51.6[2] **4C+CI**	47.71[3] **RCCSD(T)**	48.6[4] **DK+CASPT2**	46.8[5] **DF**	43.14[6] **2C+CI**	28.61[7]
α exp. (a.u.)	33.9 (0.3)	51(7)	47.1 (7)				
	Cn	**113**	**114**	**115**	**116**	**117**	**118**
This work (a.u.)	27.64	29.9	30.6	73.69	72.00	71.43	46.3
α other calc.	25.8[1] **PP+CCSD(T)**		31.98[3] **RCCSD(T)**				52.4[7] **ECP-CCSD(T)**

[1] M. Seth *et al*., JCP **106**, 3623 (1997)
[2] T. Fleig, PRA **72**, 0526506 (2005)
[3] Thierfelder *et al*., PRA **78**, 052506 (2008)
[4] B. O. Roos *et al,* JPC **108**, 2851 (2004)
[5] V. Kellö and A. J. Sadlej, Theor. Chim. Acta **83**, 351 (1992)
[6] T. Fleig and A. J. Sadlej, PRA **65**, 032506 (2002)
[7] C. Nash, JPC A **109**, 3493 (2005)
[8] I. Lim *et al.,* JCP **122**, 104103 (2005)
[9] I. Lim and P. Schwerdtfeger, PRA **70** 062501 (2004)

	Fr	Ra
α this work [a.u.]	**in progress**	244.90
α **PP/DK+CCSD(T)**	315.2[8]	246.2[9]
	119	**120**
α this work [a.u.]	**in progress**	168.15
α **DK+CCSD(T)**	163.8[8]	

Adsorption on inert surfaces:

Weak interactions: ad-atom - slab model



$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{\alpha_{at}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{at}}\right)x^3} \approx -\Delta H_{ads}$$

E(x)-dispersion interaction energy

IP_{slab} - ionization potentials of the surface material

ε - the dielectric constant of the surface material

IP_{at} - ionization potentials of the adsorbed atom

α_{at} –polarizability of the adsorbed atom

x - the adatom-surface distance (approximated by R_{vdW} of the adsorbed species)

Exp. values

Calc. values

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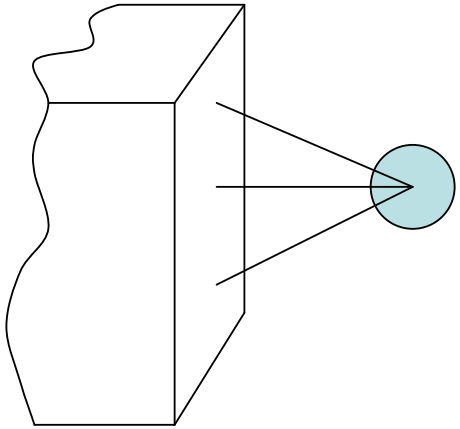

$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{\alpha_{at}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{at}}\right)x^3} \approx -\Delta H_{ads}$$

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x - the adatom-surface distance (approximated by R_{vdW} of the adsorbed species)

Exp. values

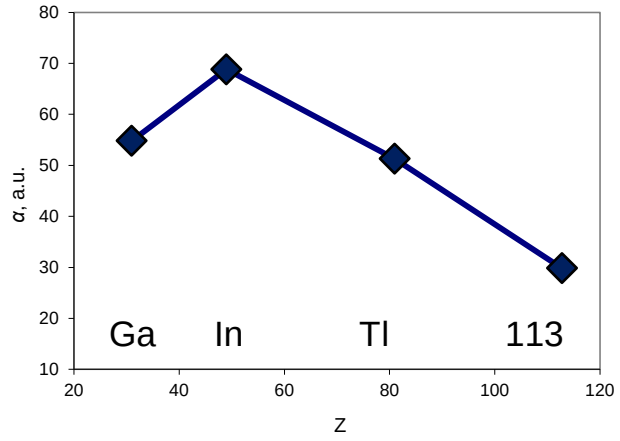
Calc. values

Example: adsorption of Tl and 113 on Teflon and PE

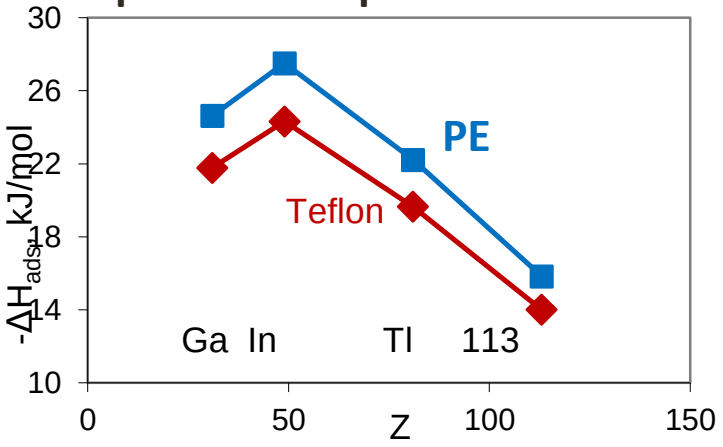
	α [a.u.]	IP [eV]	R_{vdW} [Å]	ΔH_{ads} (Teflon) [kJ/mol]	ΔH_{ads} (PE) [kJ/mol]
Al	45.89	5.986	1.89	17.28	19.54
Ga	54.80	5.999	1.87	21.78	24.63
In	68.83	5.786	1.93	24.32	27.51
Tl	51.3	6.108	1.90	19.65	22.22
113	29.85	7.306	1.84	14.00	15.83

	Teflon	PE
ε	2.04	2.26
IP_{slab} [eV]	10.12	9.7

Polarizabilities of Ga to 113



Adsorption enthalpies of Ga to 113



Summary

- Methods: **4-c Dirac-Coulomb-Breit Hamiltonian**
  Fock space CC
  Intermediate Hamiltonian
  Large, converged basis sets
- Powerful computational tool kit, tailored for superheavy systems
- Benchmark calculations for elements 112 to 122, and lighter homologues
- Excellent agreement with available experiment; same accuracy is expected for SHE

Collaboration:

- A. Borschevsky – Centre for Theoretical Chemistry and Physics, Massey University, Auckland, New Zealand (at the moment visiting researcher at HIM)
- Valeria Pershina- GSI, Darmstadt, Germany
- Ephraim Eliav and Uzi Kaldor – Tel Aviv University, Israel

Many thanks to the Helmholtz-Institute Mainz for the visiting scientist grant

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Thank you for your attention!

Many thanks to the Helmholtz-Institute Mainz for the visiting scientist grant