

Fully relativistic *ab initio* studies of superheavy elements

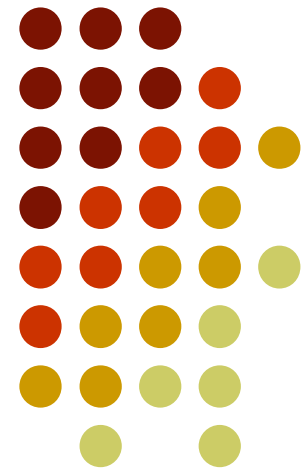


Anastasia Borschevsky

Valeria Pershina

Uzi Kaldor

Ephraim Eliav



Reliable Calculations must take into account:



- **Relativity**
- **Correlation**

Relativity





Dirac-Coulomb-Breit Hamiltonian:

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

$$h_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V_{\text{nuc}}$$

$$\boldsymbol{\alpha} = \begin{pmatrix} 0_2 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0_2 \end{pmatrix}, \quad \beta = \begin{pmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{pmatrix}$$

- $\boldsymbol{\alpha}$ and β are the four-dimensional Dirac matrices
 - V_{nuc} is the nuclear attraction operator
- *finite nucleus model is used, charge described by a Gaussian distribution/uniformly charged sphere



DF spinors:

$$\phi_{n\kappa} = \begin{pmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{pmatrix} \begin{matrix} \leftarrow \text{LARGE} \\ \leftarrow \text{small} \end{matrix}$$

$$(|\kappa| = j + 1/2)$$

DF equation:

$$F_{\kappa} \phi_{n\kappa} = \varepsilon_{n\kappa} \phi_{n\kappa}$$

$$F(x) = h_d(x) + \sum_j^N \int \frac{\phi_j^*(x')(1 - P_{ij})\phi_j^*(x')}{|r - r'|} dx'$$

Correlation





Coupled Cluster Method

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

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

Excitation amplitudes s_i^a and s_{ij}^{ab} needed. Obtained by projecting Schrödinger equation unto Φ_i^a and Φ_{ij}^{ab} .

$$\langle \Phi_i^a | (H - E_{\text{CCSD}}) (1 + S_1 + S_2 + \frac{1}{2} S_1^2 + S_1 S_2 + \frac{1}{3!} S_1^3) | \Phi_0 \rangle = 0,$$

$$\langle \Phi_{ij}^{ab} | (H - E_{\text{CCSD}}) (1 + S_1 + S_2 + \frac{1}{2} S_1^2 + S_1 S_2 + \frac{1}{3!} S_1^3 + \frac{1}{2} S_1^2 + \frac{1}{2} S_1^2 S_2 + \frac{1}{4!} S_1^4) | \Phi_0 \rangle = 0.$$

Result – coupled nonlinear equations for s_i^a and s_{ij}^{ab} . Very large systems of equations, solved iteratively.



Multireference CC

- Divide the function space into a small model space P (containing the important functions) and a complementary (“virtual”) space Q , $P+Q=1$.
- Diagonalize the effective Hamiltonian:

$$H_{\text{eff}} = PH\Omega P \quad \Omega = \{\exp(S)\}$$

$$Q[\Omega, H_0]P = Q(V\Omega - \Omega H_{\text{eff}})_{\text{linked}}P$$

Fock space CC:

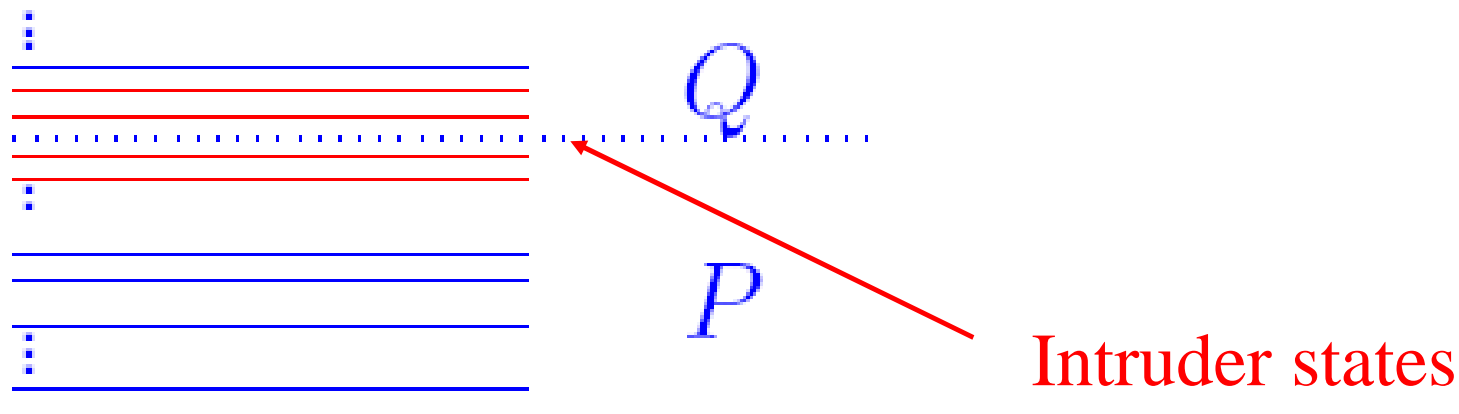


- One of the most powerful and accurate methods
- A large number of energies obtained in a single calculation
- Limitation: convergence difficulties

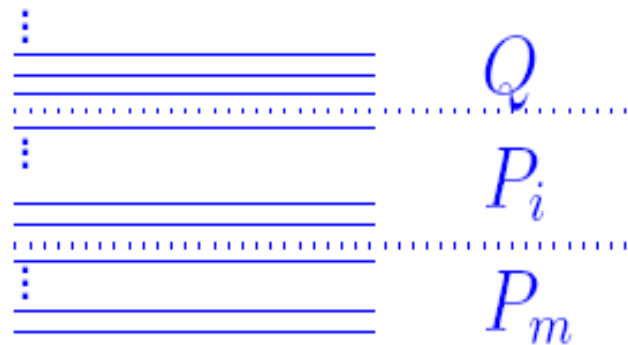


Convergence difficulties

- Large model space P provides better description of the states of interest
- Convergence is enhanced if P and Q are well separated in energy and weakly interacting



Intermediate Hamiltonian Method (IH)



$$P_m + P_i = P, \quad P + Q = 1$$

$$H_I = PH\Omega P$$

$$H_I P|\Psi_m\rangle = E_m P|\Psi_m\rangle$$

Freedom in evaluation of the problematic QSP_i matrix elements

Applications



- Polarizabilities of the $7p$ elements
- Electron affinities of group 14 elements
- Ionization potentials and electron affinities of the $7p$ elements

Polarizabilities of the 7p elements



		Metals										Metalloids		Nonmetals			
1																	18
1	2											13	14	15	16	17	2
H	He											B	C	N	O	F	Ne
3	4											13	14	15	16	17	18
Li	Be											Al	Si	P	S	Cl	Ar
11	12																
Na	Mg																
19	20																
K	Ca																
37	38																
Rb	Sr																
55	56																
Cs	Ba																
87	88																
Fr	Ra																
Lanthanide series																	
Actinide series																	
		80	81	82	83	84	85	86									
		Hg	Tl	Pb	Bi	Po	At	Rn									
		112	113	114	115	116	117	118									
		Uub															
		89	90	91	92	93	94	95	96	97	98	99	100	101	102		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

Adsorption model



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

Polarizability of the adsorbed atom

$\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{at}} \right)$

$IP_{slab/at}$ - the ionization potentials of the surface material and the adsorbed atom

ε - the dielectric constant of the surface

x - ad-atom distance, approximated by R_{vdW} of the adsorbed element.



Polarizability:

$$\alpha = - \left. \frac{\partial^2 E(F)}{\partial F^2} \right|_{F=0}$$

Energy of an atom in a static uniform electric field:

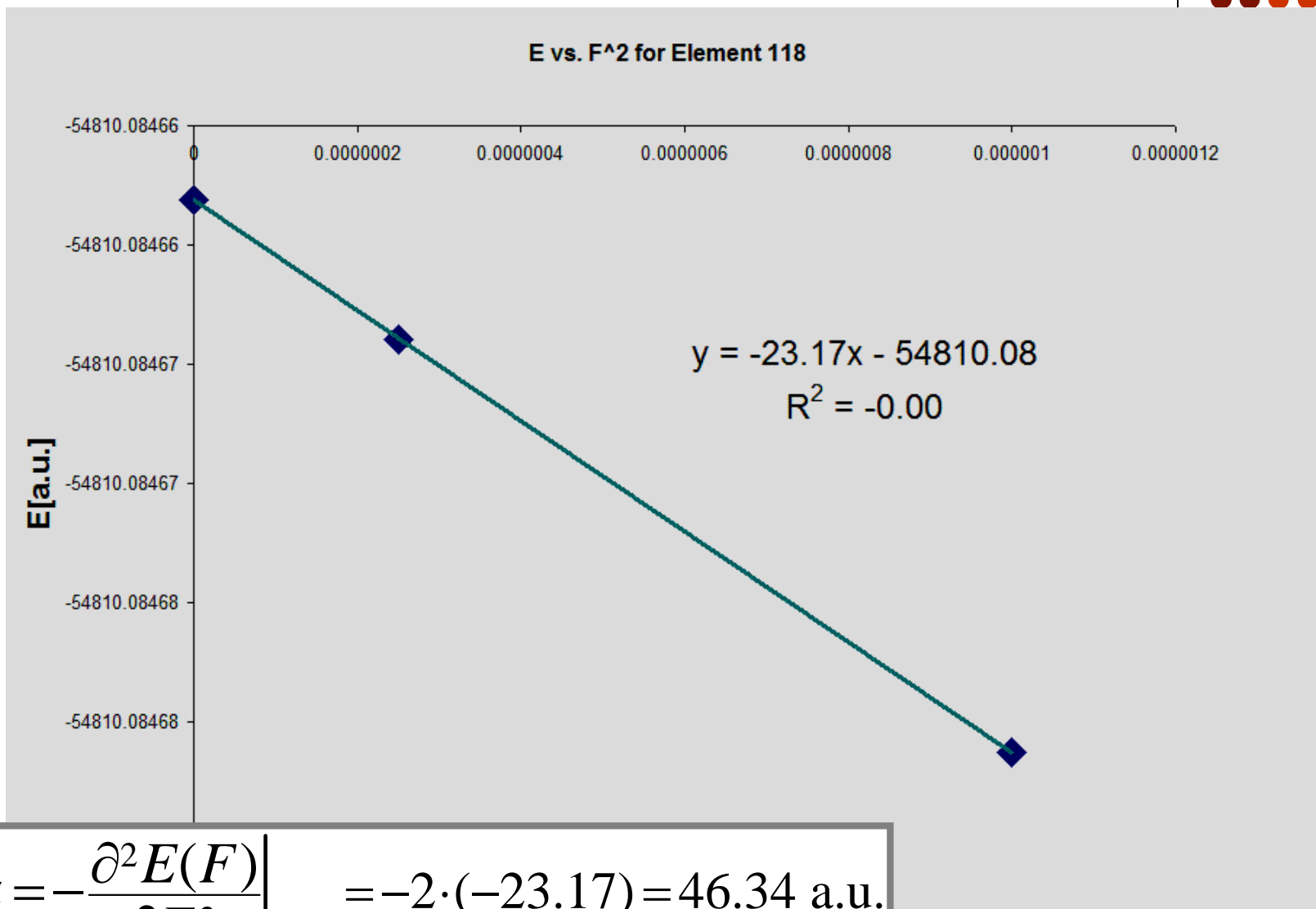
$$E(F) = E(0) + F \cdot \left. \frac{\partial E(F)}{\partial F} \right|_{F=0} + \frac{1}{2} F^2 \cdot \left. \frac{\partial^2 E}{\partial F^2} \right|_{F=0} + \dots$$

Obtaining the polarizability



$$E(F) = E(0) + \frac{1}{2} F^2 \cdot \left. \frac{\partial^2 E}{\partial F^2} \right|_{F=0} + \dots \square E(0) - \frac{1}{2} \alpha F^2$$

- Calculate the energy for different values of the external field
- Plot the energies $E(F)$ as a function of F^2
- Obtain the derivative by numerical differentiation



$$\alpha = -\left. \frac{\partial^2 E(F)}{\partial F^2} \right|_{F=0} = -2 \cdot (-23.17) = 46.34 \text{ a.u.}$$

Energy calculations



Relativistic effects:

4 component Dirac-Coulomb Hamiltonian:

$$H_{DC} = \sum_i h_D(i) + \sum_{i<j} \frac{1}{r_{ij}}$$

$$h_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V_{nuc}$$

- **Dirac08 package was used**



Electron correlation

- For closed shell elements- single reference CCSD(T)
- Open shell elements- Fock space CC

Basis sets

- $26s24p18d13f5g2h$

Results



	Hg	Tl	Pb	Rn
α [a.u.]	34.2	51.3	46.9	35.0
Exp.		51(7)		
	E112	E113	E114	E118
α [a.u.]	27.6	29.9	30.6	46.3

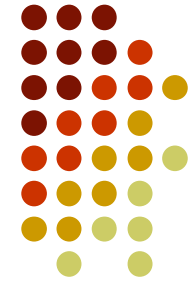
Results



	Hg	Tl	Pb	Rn
α [a.u.]	34.2	51.3	46.9	35.0
Exp.		51(7)	47(7)*	
	E112	E113	E114	E118
α [a.u.]	27.6	29.9	30.6	46.3

* Phys. Rev. A **78**, 05250 (2008)

Electron affinities of group 14 elements



		Metals										Metalloids		Nonmetals			
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be														8 O	9 F	10 Ne
11 Na	12 Mg														16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Nh	114	115 Mh	116	117	118
Lanthanide series		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
Actinide series		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

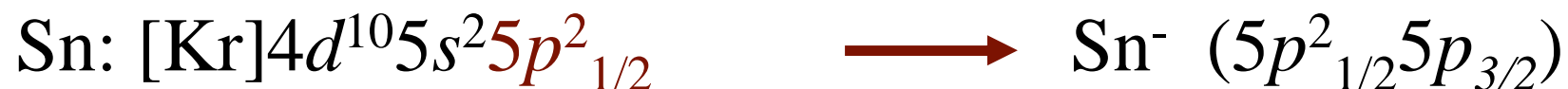
Calculations



- **4-component Dirac-Coulomb-Breit Hamiltonian**

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

- **Mixed sector intermediate Hamiltonian CC**



- **Large basis sets**

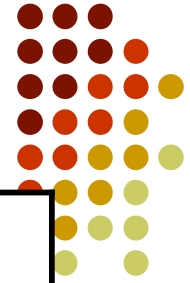
Sn	$35s29p24d20f15g9h4i$
Pb	$37s31p26d21f16g11h6i$
E114	$37s31p26d21f16g11h6i$



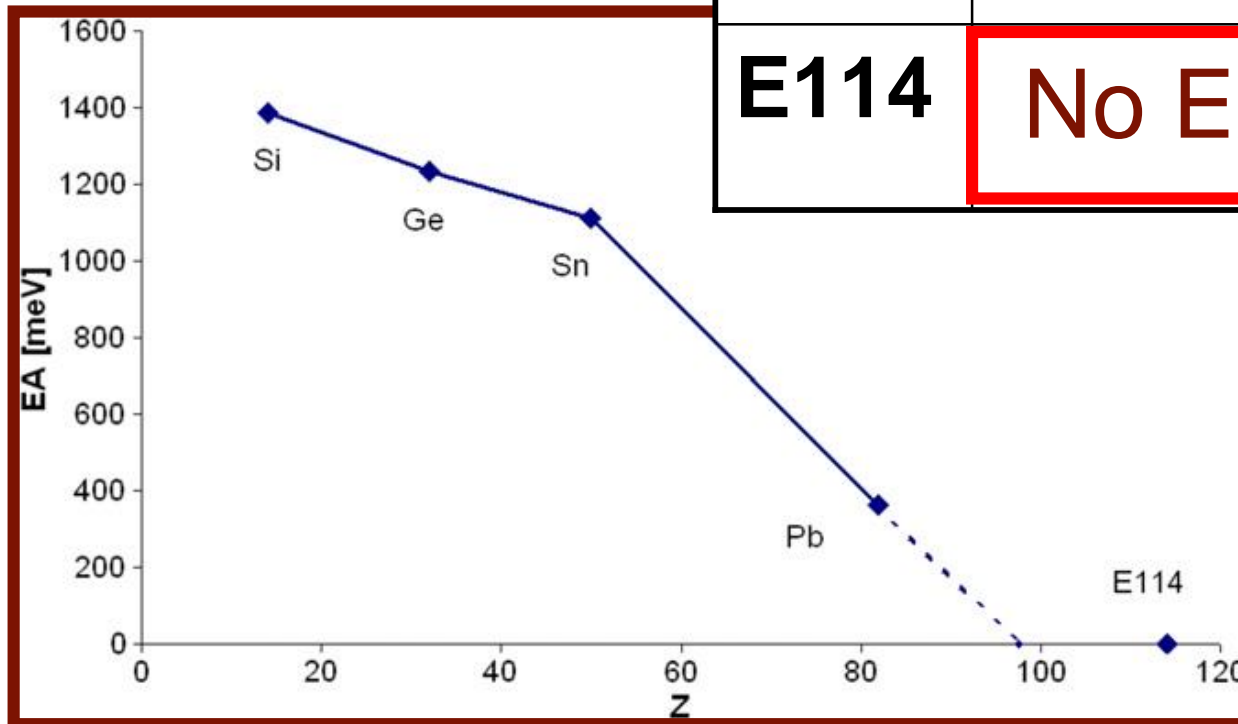
- **Model spaces**

Sn	$6-11s5p_{3/2}6-8p5-7d4-6f5g$
Pb	$7-12s6p_{3/2}7-10p6-8d5-6f5g$
E114	$8-13s7p_{3/2}8-10p7-10d6-7f5g$

Results



	EA [meV]	EA exp.
Sn	1072	1112
Pb	363	364
E114	No EA	



Ionization Potentials and Electron Affinities of 7p elements



1												13 14 15 16 17						18
Metals		Metalloids										Nonmetals						
1 H	2 He											5 B	6 C	7 N	8 O	9 F	10 Ne	
3 Li	4 Be											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
11 Na	12 Mg	3 Sc	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	80	81	82	83	84	85	86									
37 Rb	38 Sr	39 Y	Hg	Tl	Pb	Bi	Po	At	Rn									
55 Cs	56 Ba	71 Lu																
87 Fr	88 Ra	103 Lr	112	113	114	115	116	117	118									
		57 La	Uub															
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No			

Lanthanide series

Actinide series

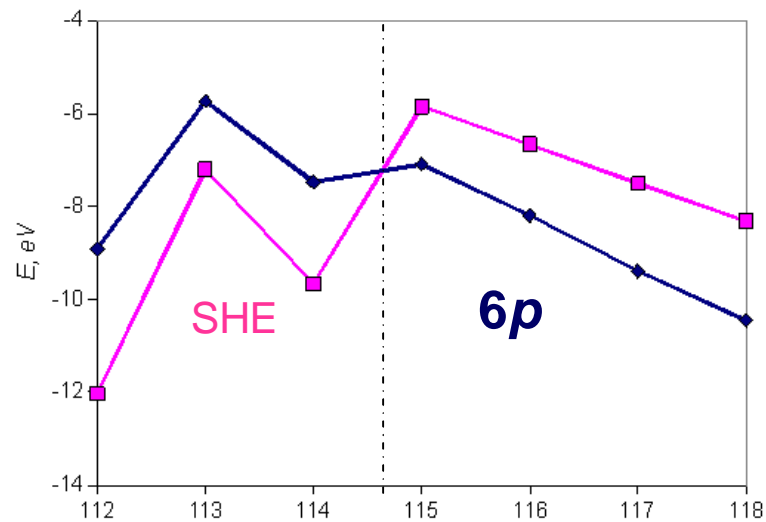
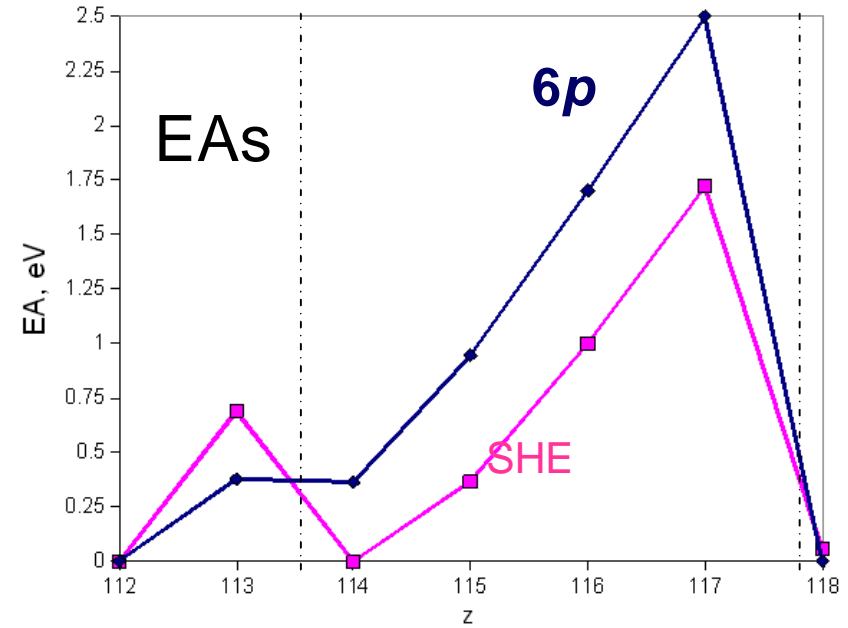
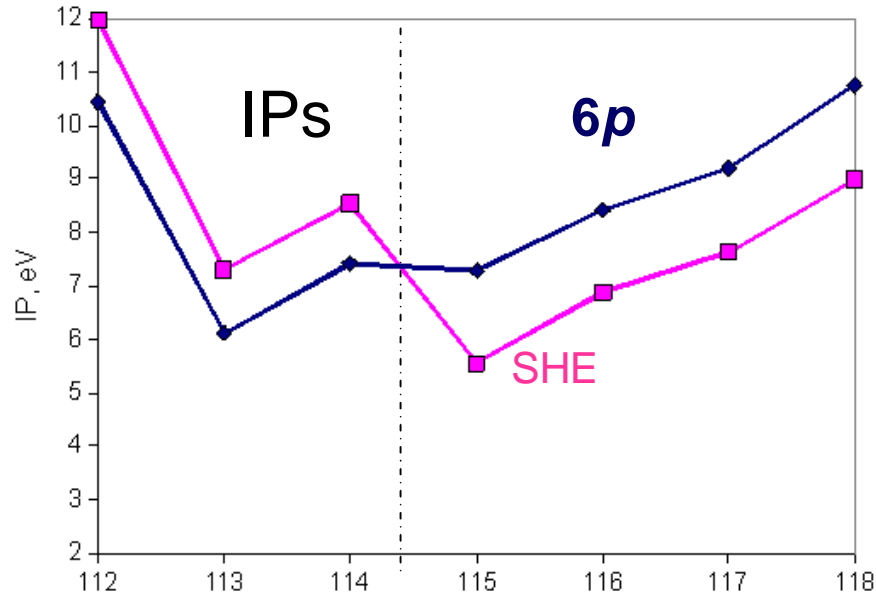
	Hg	Tl	Pb	Bi	Po	At	Rn
IP	10.445	6.096	7.349	7.295	8.499	9.430	10.833
IP _{exp.}	10.438	6.110	7.415	7.285	8.414	-	10.749
EA	0	0.41	0.363	1.008	-	2.525	0
EA _{exp.}	0	0.378	0.364	0.946		-	0
	E112	E113	E114	E115	E116	E117	E118
IP	11.97	7.306	8.539	5.553	6.881*	7.626*	8.984
EA	0	0.69	0	0.366		1.719	0.056

***Previous calculations:** (B. Fricke, Structure and Bonding **21**, 89 (1975))

IP(E116): 7.5 eV

IP(E117): 7.7 eV

Ionization Potentials and Electron Affinities of 7p elements and their 6p homologues



Binding energies



- 4-c Dirac-Coulomb-Breit Hamiltonian
- Fock space coupled cluster method
- Intermediate Hamiltonian approach



Benchmark calculations of properties of superheavy elements



**Thank you for your
attention!**