Fully relativistic *ab initio* studies of superheavy elements

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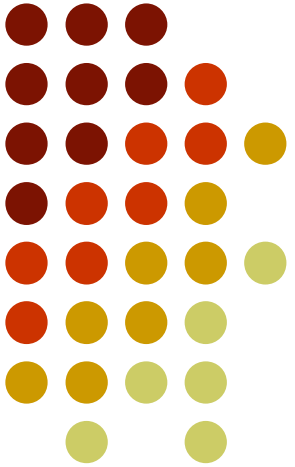


Reliable Calculations must take into account:

- Relativity
- Correlation

Relativity

Dirac-Coulomb-Breit Hamiltonian:

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

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

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

- **α** 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:

$$\phi_{n\kappa} = \begin{pmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{pmatrix}$$

LARGE

small

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

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

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

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

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

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

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

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:

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

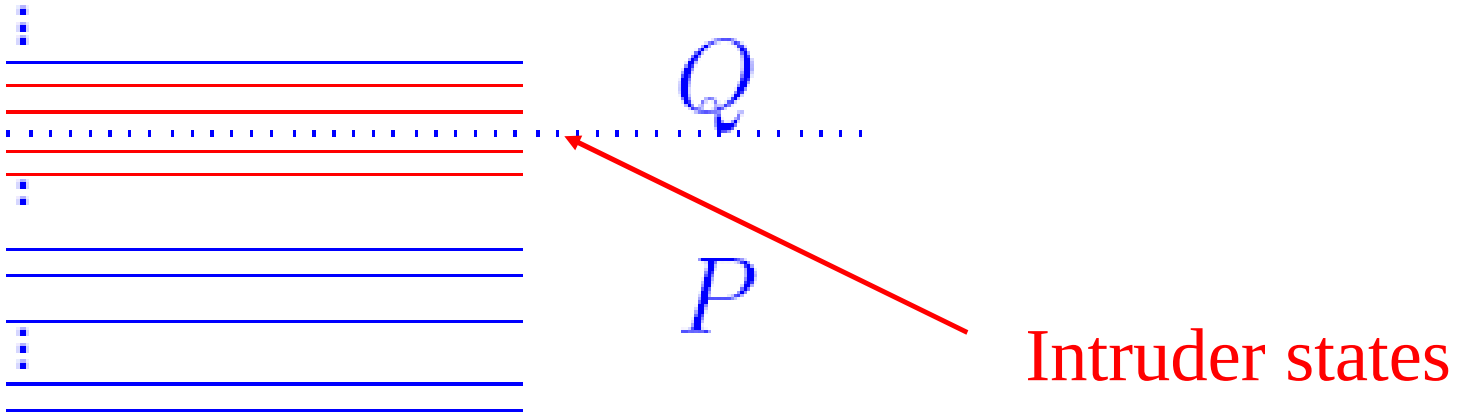
$$Q[\Omega, H_0]P = Q(V\Omega - \Omega H_{\text{eff}})_{\text{linked}} P$$

Fock space CC:

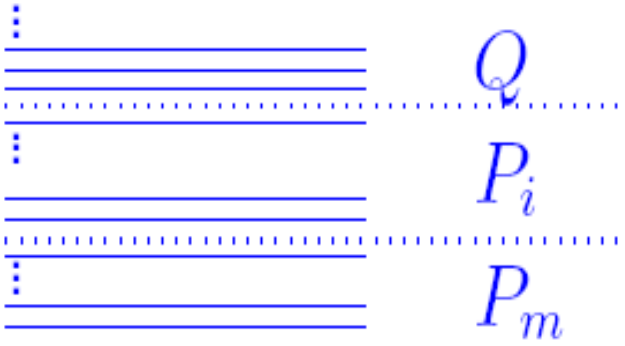
- One of the most powerful and accurate methods
- A large number of energies obtained in a single calculation
- Limitation: convergence difficulties

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)



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

$$H_I = PH\Omega P$$

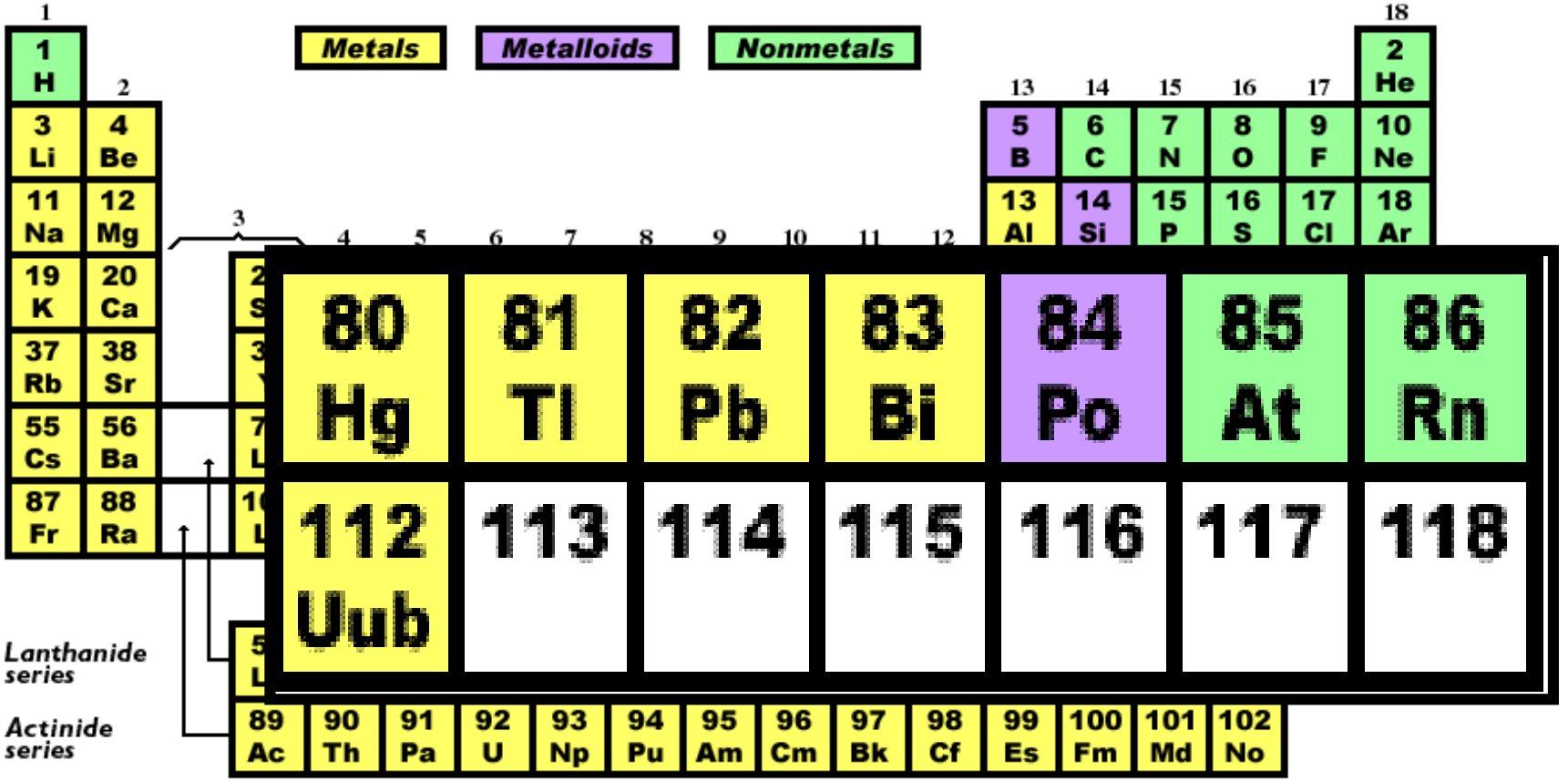
$$H_I P|\Psi_m\rangle = E_m P|\Psi_m\rangle$$

Freedom in evaluation of the problematic QSP_i matrix elements

Applications

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

Polarizabilities of the 7*p* elements



Adsorption model

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

Polarizability of the adsorbed atom

$IP_{slab/at}$ - 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:

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

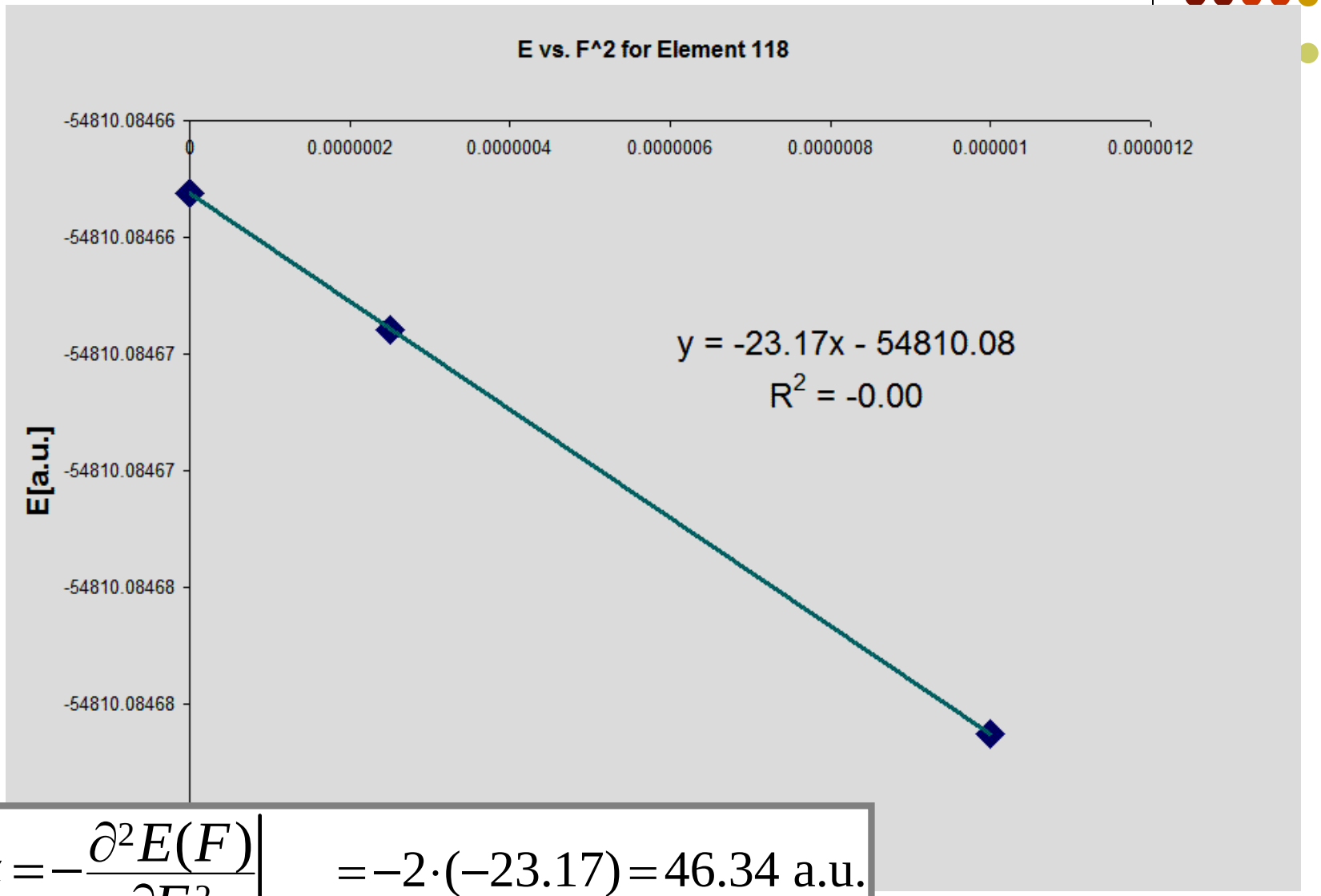
Energy of an atom in a static uniform electric field:

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

Obtaining the polarizability

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

- 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

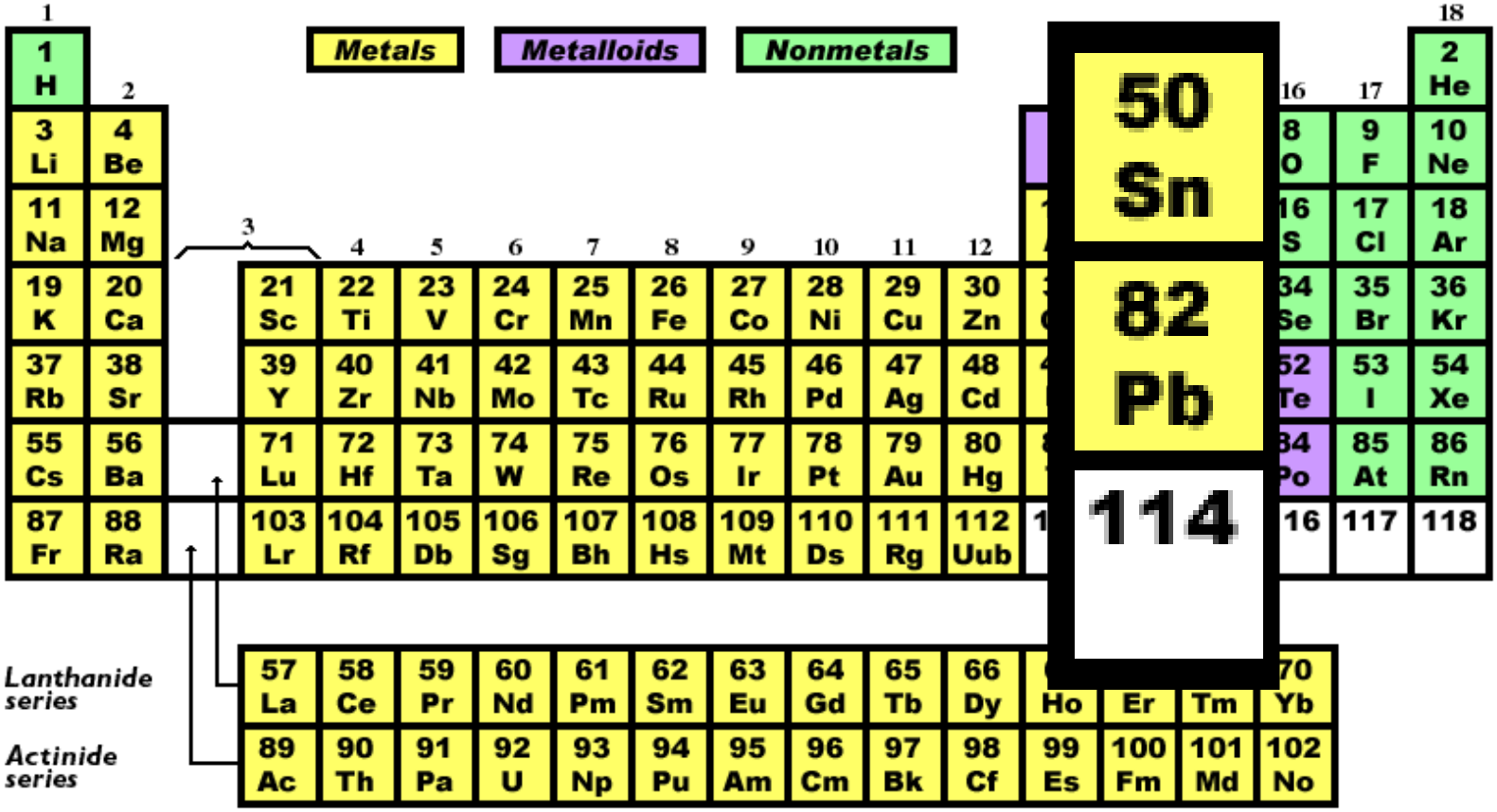
	Hg	Tl	Pb	Rn
α [a.u.]	34.2	51.3	46.9	35.0
Exp.		**51(7)**		
	E112	**E113**	**E114**	**E118**
α [a.u.]	27.6	29.9	30.6	46.3

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



Calculations

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

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

- **Mixed sector intermediate Hamiltonian CC**

Sn: [Kr]$4d^{10}5s^2 5p^2_{1/2}$ → Sn^- $(5p^2_{1/2}5p_{3/2})$

Pb: [Xi] $5d^{10}4f^{14}\,6s^2 6p^2_{1/2}$ → Pb^- $(6p^2_{1/2}6p_{3/2})$

E114: [Rn]$5d^{10}4f^{14}\,6s^2 7p^2_{1/2}$ → $\mathrm{E114}^-$ $(7p^2_{1/2}7p_{3/2})$

- **Large basis sets**

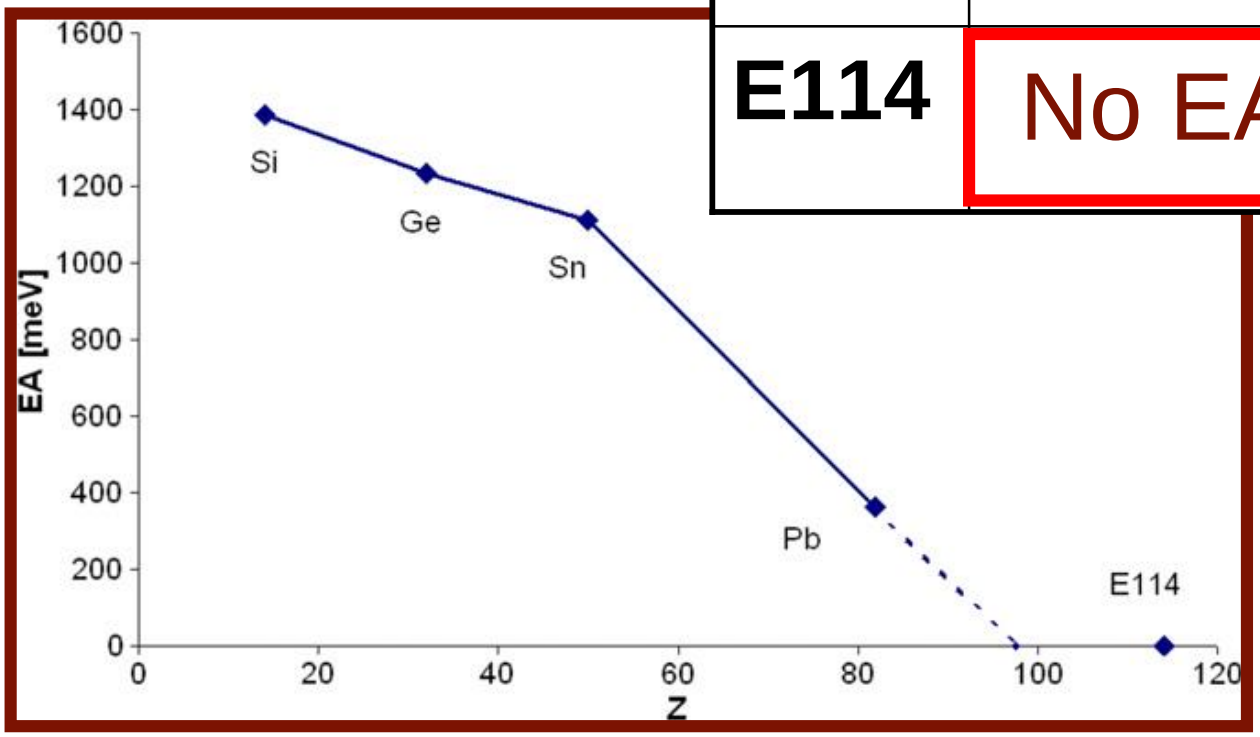
Sn	35*s*29*p*24*d*20*f*15*g*9*h*4*i*
Pb	37*s*31*p*26*d*21*f*16*g*11*h*6*i*
E114	37*s*31*p*26*d*21*f*16*g*11*h*6*i*

- **Model spaces**

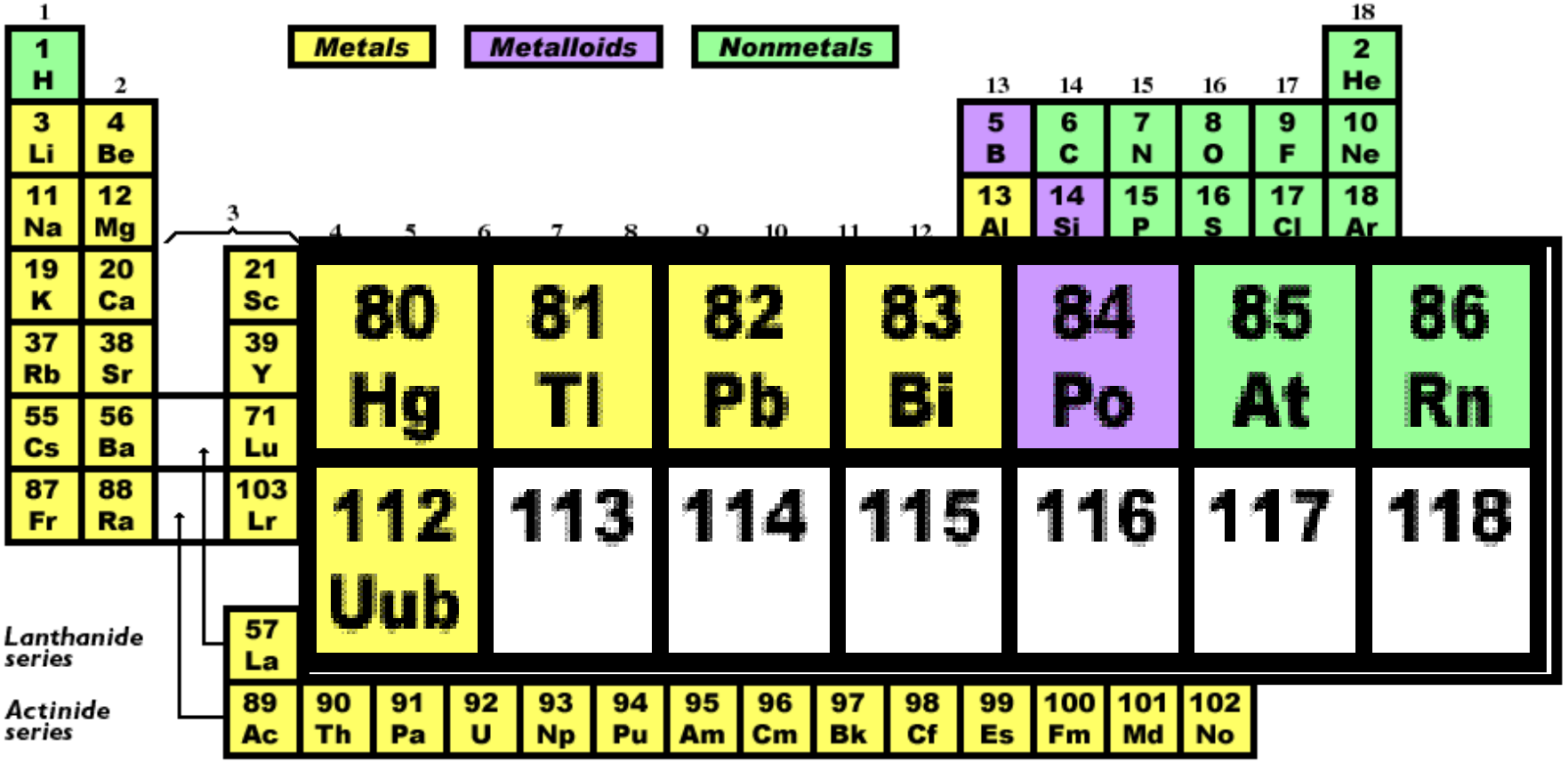
Sn	6-11*s*5$p_{3/2}$6-8*p*5-7*d*4-6*f*5*g*
Pb	7-12*s*6$p_{3/2}$7-10*p*6-8*d*5-6*f*5*g*
E114	8-13*s*7$p_{3/2}$8-10*p*7-10*d*6-7*f*5*g*

Results

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



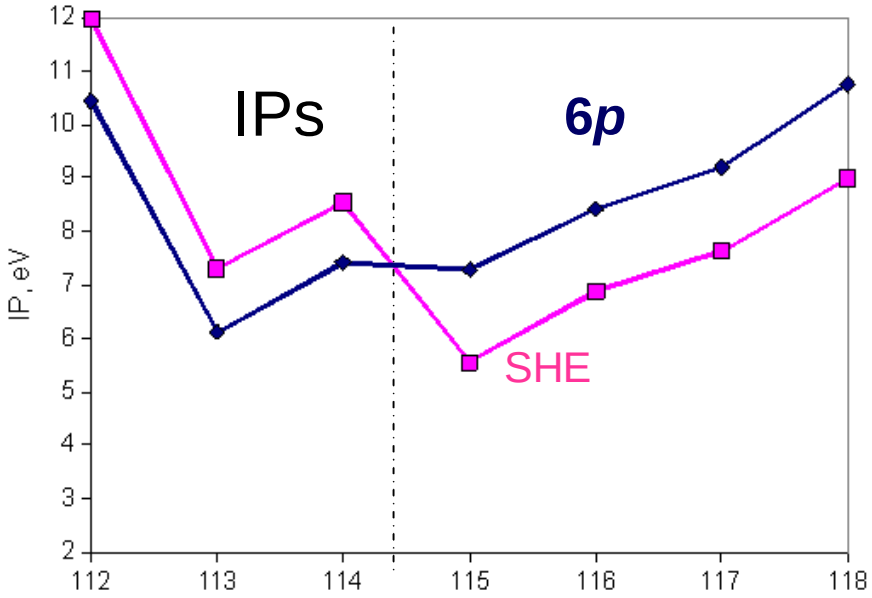
Ionization Potentials and Electron Affinities of 7*p* elements

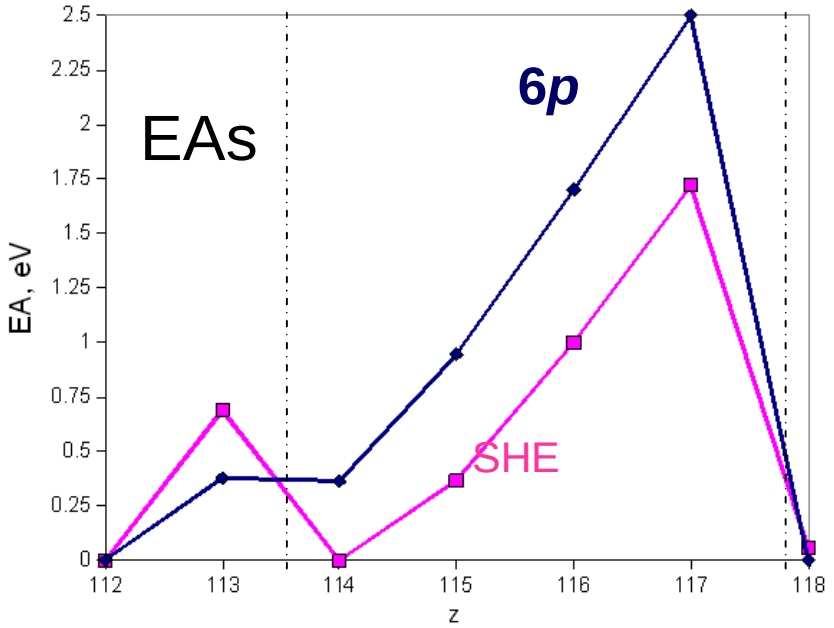


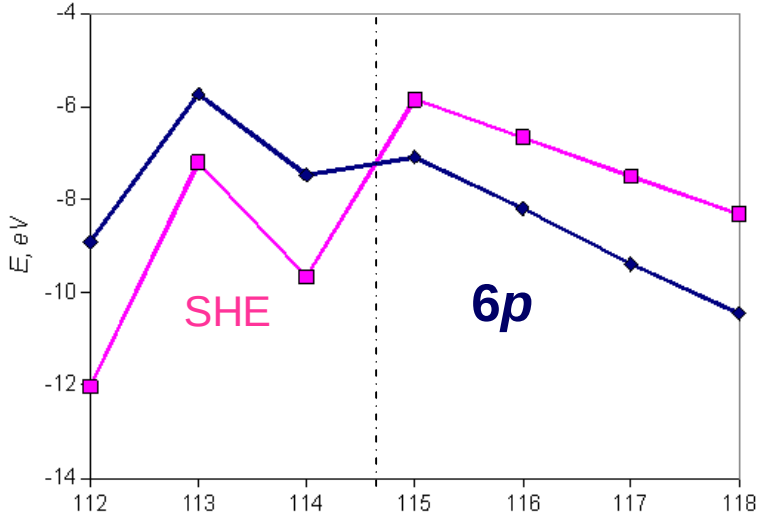
	Hg	Tl	Pb	Bi	Po	At	Rn
IP	10.445	6.096	7.349	7.295	**8.499**	**9.430**	10.833
$IP_{exp.}$	10.438	6.110	7.415	7.285	8.414	-	10.749
EA	0	0.41	**0.363**	1.008	-	**2.525**	0
$EA_{exp.}$	0	0.378	0.364	0.946		-	0
	E112	**E113**	**E114**	**E115**	**E116**	**E117**	**E118**
IP	11.97	7.306	8.539	5.553	**6.881***	**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 7*p* elements and their 6*p* homologues



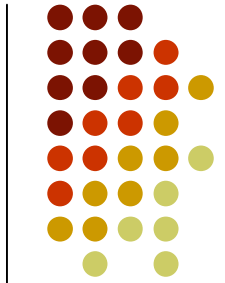




Binding energies

- 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!