Calculations of the electron affinity of polonium at the CCSD(T) level

LISA Academic Day – 16/06/2022

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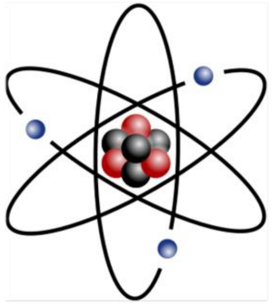
Research projects

university of groningen



- Calculation of the **electron affinity of polonium** with the single reference **CCSD(T)** approach
  - Influence of **the basis set parameters**: cardinality, augmentation, correlating functions
  - Influence of the **method** used : DHF, CCSD(T), CCSDT(Q)…
  - Influence of the size of the **correlating space**
  - Estimation of the **uncertainty**
  - **QED effects**
  - Submit for publication – collaboration with Miranda Nichols (ESR 06)
- **Field shift** calculation for a transition in **gold** with single reference **CCSD(T)** approach
  - Similar investigations
- Calculation of the **mass shift** for a transition in **gold** with **CI+MBPT** approach

DIRAC program and
Tel Aviv Package

- Determination of the **atomic factors** for several transitions in **fluorine** with **CI+MBPT** approach
- Calculation of hyperfine structure and isotope shifts in plutonium

AMBiT program

— Work in progress

Training - Teaching activities

- Workshops & courses at the University of Groningen
  - **Literature** review
  - **English** conversation for academics
  - **Project** management
  - Scientific **writing**
  - Efficient **communication** in Academia
  - Scientific **integrity**
  - **Computer** infrastructure management
  - **Dutch** A0-A1

…

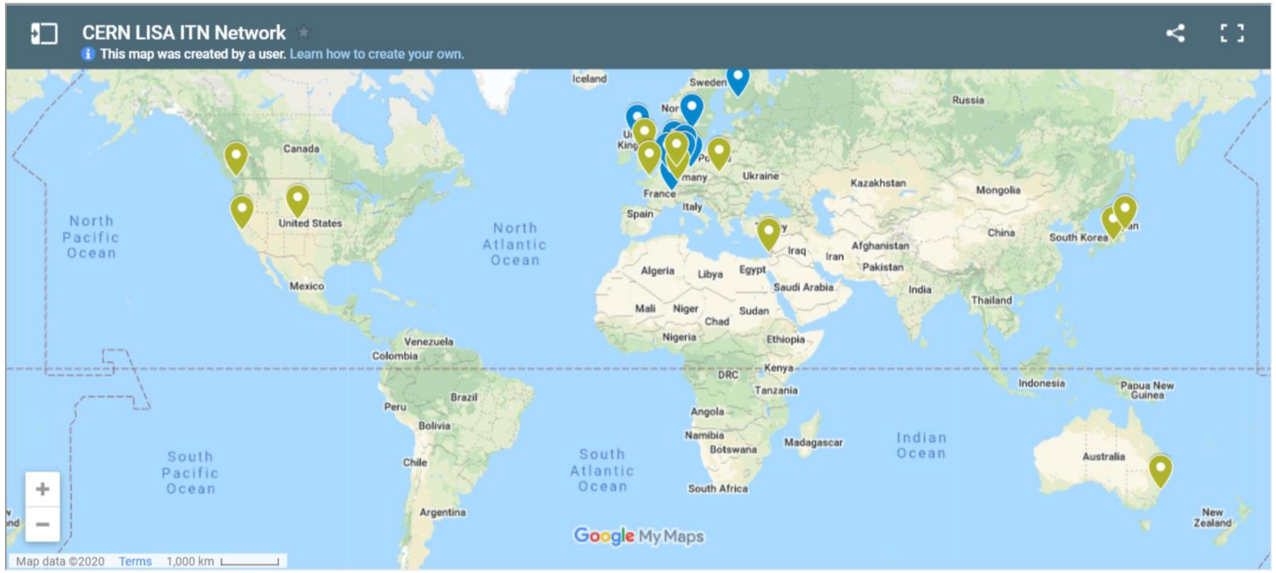
- Teaching assistant for 3rd year bachelor students: **Material Design – Theoretical Methods**
  - Tutorials
  - Computer labs
  - Grading

Scientific motivation

The last electron affinity to measure in the 6 first rows of the p block

Framework: the LISA project

- **L**aser **I**onization and **S**pectroscopy of **A**ctinides
- **15** PhD students
- **3** years
- Research scope:
  - Fundamental understanding of the **atomic structure**
  - Societal applications: targeted **cancer therapy** and **radioecology**
- https://lisa-itn.web.cern.ch/


CERN LISA ITN Network

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ESR 01


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ESR 10


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Darcy van Eerten
ESR 12


Helena Escudero
ESR 13


Raphaël Crosa-Rossa

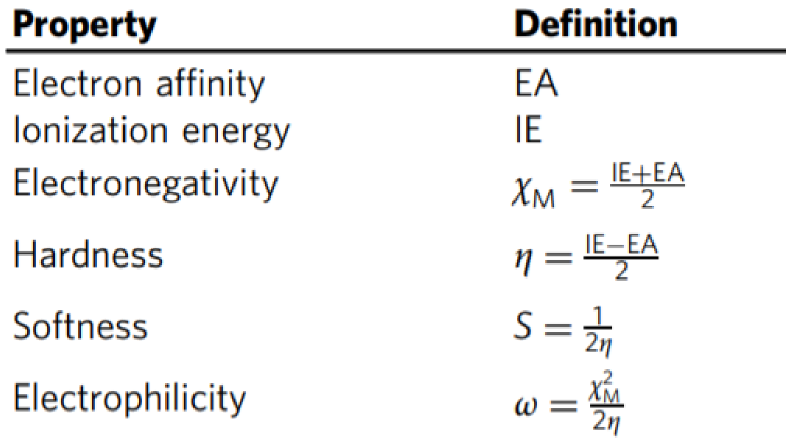

Mitzi Urquiza
ESR 15

Electron affinity (EA) of Polonium

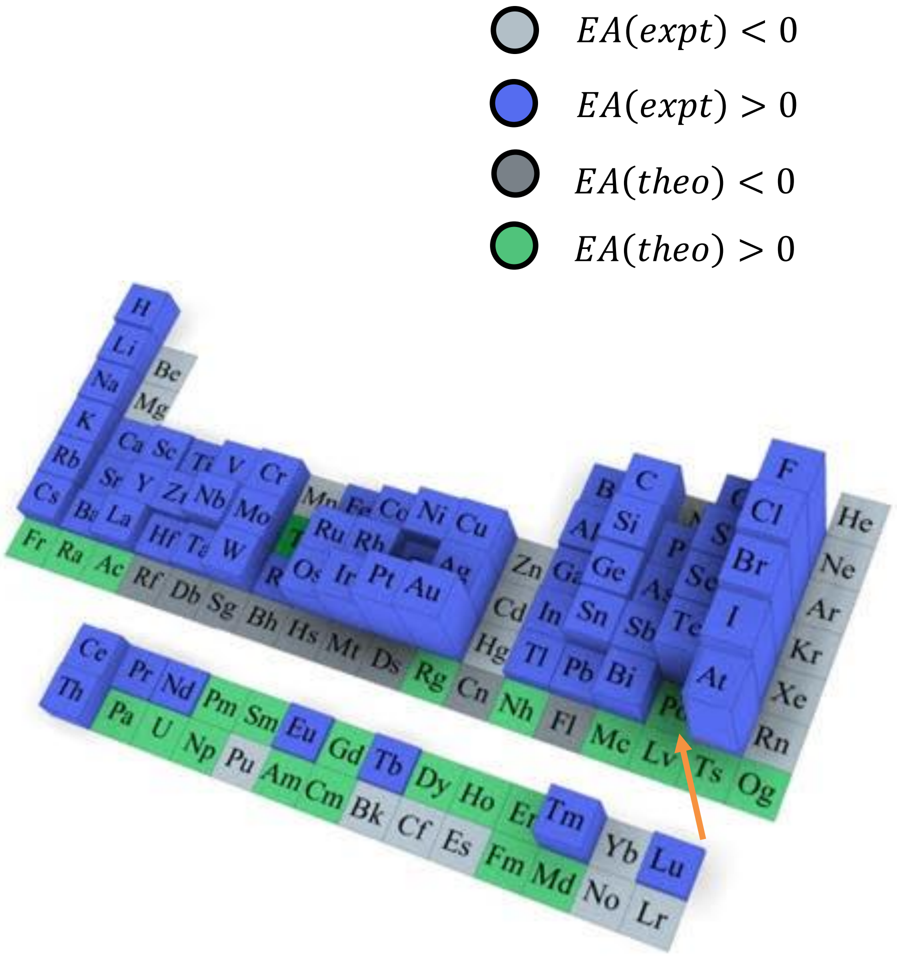
- **Definitions:**

$$Po(g) + e^- \rightarrow Po^-(g) \qquad EA = E(Po,g) - E(Po^-)$$

- IP and EA gives access to **fundamental physicochemical properties**:



Property	Definition
Electron affinity	EA
Ionization energy	IE
Electronegativity	$\chi_M = \frac{IE+EA}{2}$
Hardness	$\eta = \frac{IE-EA}{2}$
Softness	$S = \frac{1}{2\eta}$
Electrophilicity	$\omega = \frac{\chi_M^2}{2\eta}$



Figures Adapted from Leimbach, D., Karls, J., Guo, Y. *et al.* The electron affinity of astatine. *Nat Commun* **11,** 3824 (2020). https://doi.org/10.1038/s41467-020-17599-2

Previous work and collaboration

- The electron affinity of Po will be **measured** in the near future at **ISOLDE** (Miranda Nichols, ESR 06, based in **Gothenburg** (Sweden)
- The EA will be measured by **laser photodetachment**
- **Previously**, the electron affinity have been **calculated** by Borschevsky *et al*, and other research teams, but a **higher accuracy** is expected with the present calculations

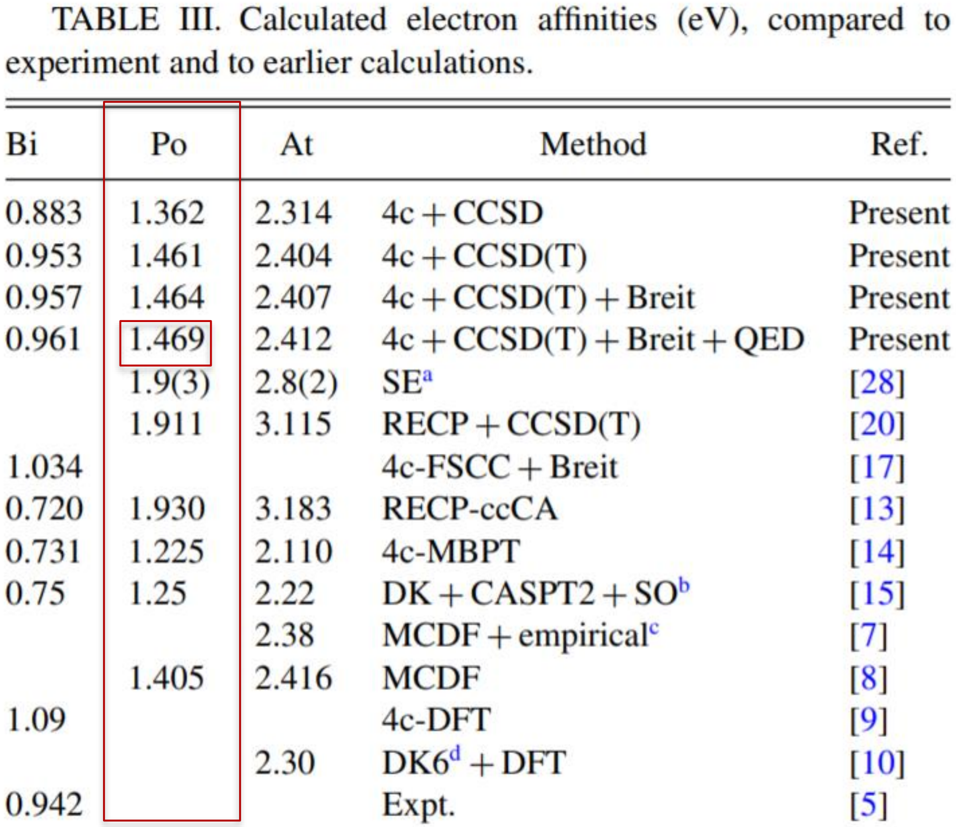


TABLE III. Calculated electron affinities (eV), compared to experiment and to earlier calculations.

Bi	Po	At	Method	Ref.
0.883	1.362	2.314	4c + CCSD	Present
0.953	1.461	2.404	4c + CCSD(T)	Present
0.957	1.464	2.407	4c + CCSD(T) + Breit	Present
0.961	1.469	2.412	4c + CCSD(T) + Breit + QED	Present
	1.9(3)	2.8(2)	SE[a]	[28]
	1.911	3.115	RECP + CCSD(T)	[20]
1.034			4c-FSCC + Breit	[17]
0.720	1.930	3.183	RECP-ccCA	[13]
0.731	1.225	2.110	4c-MBPT	[14]
0.75	1.25	2.22	DK + CASPT2 + SO[b]	[15]
		2.38	MCDF + empirical[c]	[7]
	1.405	2.416	MCDF	[8]
1.09			4c-DFT	[9]
		2.30	DK6[d] + DFT	[10]
0.942			Expt.	[5]

Borschevsky, A., Pasteka, L. F., Pershina, V., Eliav, E., & Kaldor, U. (2015). Ionization potentials and electron affinities of the superheavy elements 115-117 and their sixth-row homologues Bi, Po, and At. Physical Review A, 91(2)

Leimbach, D., Karls, J., Guo, Y. *et al.* The electron affinity of astatine. *Nat Commun* **11,** 3824 (2020). https://doi.org/10.1038/s41467-020-17599-2

Method

The relativistic single reference coupled cluster approach

Relativistic coupled cluster approach

- **Born-Oppenheimer** approximation
- **Dirac-Schrödinger** equation
- **Hartree-Fock** method

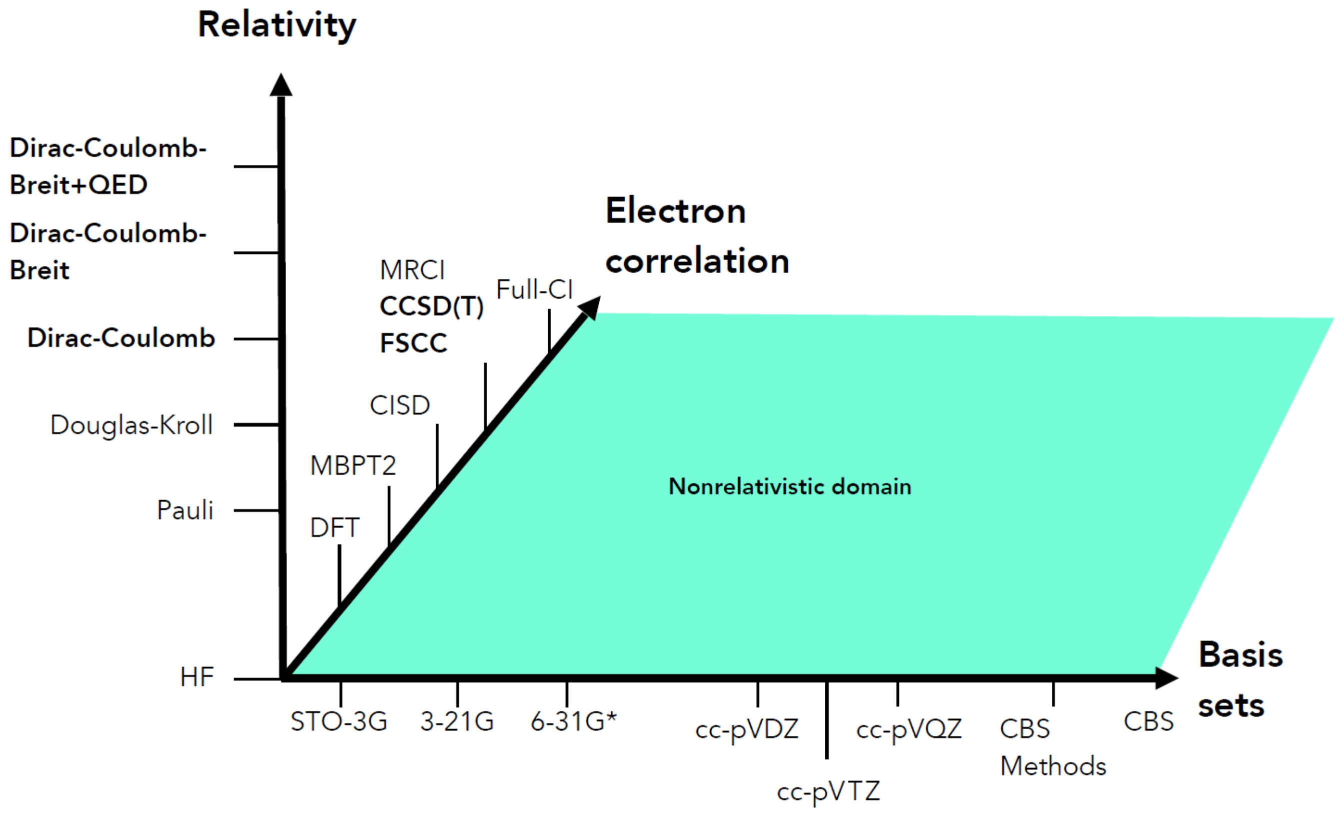
$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_i(\mathbf{x}_1) & \psi_j(\mathbf{x}_1) & \ldots & \psi_k(\mathbf{x}_1) \\ \psi_i(\mathbf{x}_2) & \psi_j(\mathbf{x}_2) & \ldots & \psi_k(\mathbf{x}_2) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_i(\mathbf{x}_N) & \psi_j(\mathbf{x}_N) & \ldots & \psi_k(\mathbf{x}_N) \end{vmatrix}$$

- Electron **correlation**: include (single, double,…) excitations
- Treatment with an **exponential ansatz**

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}} |\Phi_0\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N$$

Method, Hamiltonian and Basis Sets



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

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

What can we play with?

- **Method**: DHF, CCSD, CCSD(T), CCSDT(Q),…
- **Basis set**
  - **Cardinality**: Double, Triple, Quadruple Zeta
  - Number of **correlating functions**: valence (v), core-valence (cv) or all electrons (ae)
  - Single, double,… **diffuse** functions

- Number of **correlated electrons** and **virtual cut-off**

- 2 components and non-relativistic **Hamiltonians**

Basis sets: definition

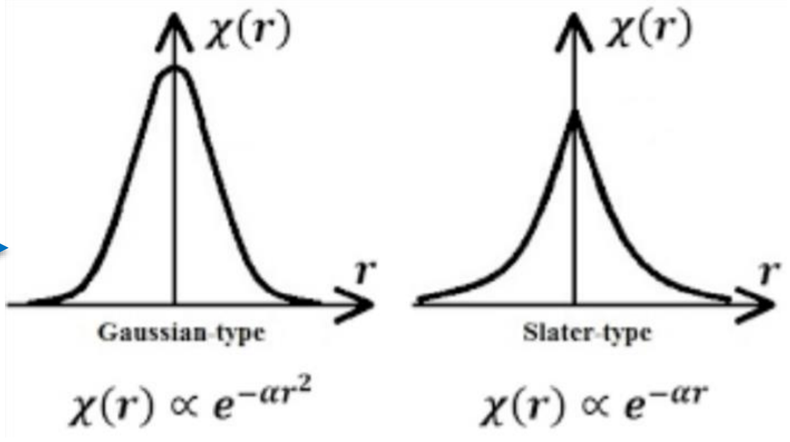
- Atomic orbitals described as a **linear combination** of basis functions

$$\psi_k = \sum_s c_{ks}\phi_s$$

- **Expression** of the functions:

$$\phi_{nlm}(r,\theta,\phi) = R_n(r)Y_{lm}(\theta,\phi)$$

- Radial part described with **Slater** (STO) or **Gaussian** (GTO) functions



Gaussian functions

$$\chi_{\zeta,n,l,m}(r,\theta,\varphi) = NY_{l,m}(\theta,\varphi)r^{2n-2-l}e^{-\zeta r^{2}}$$

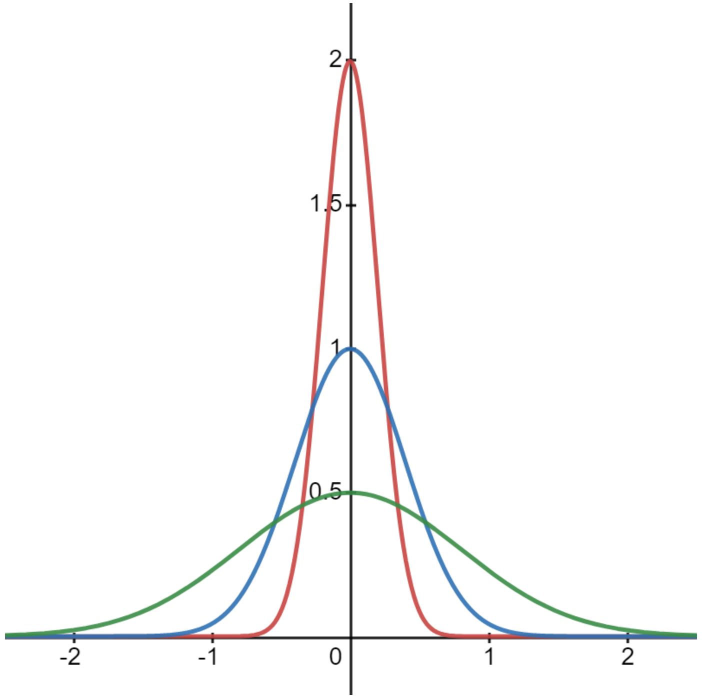


Figure 4: Gaussian functions with different exponents

Parameters

- **Cardinality**: number of functions describing each atomic orbital:

Double zeta	2 functions
Triple zeta	3 functions
Quadruple zeta	4 functions

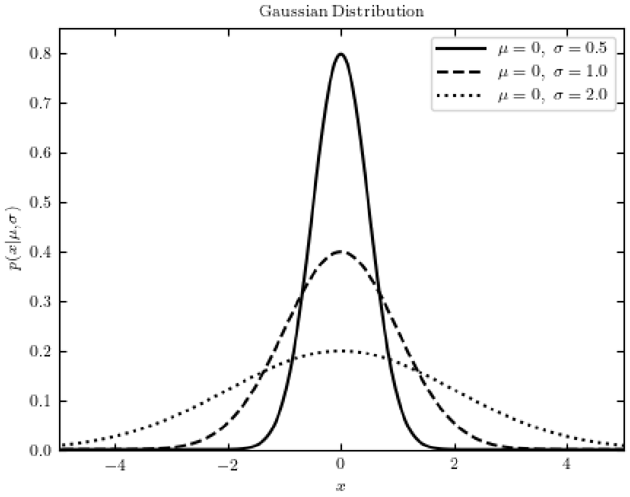
…

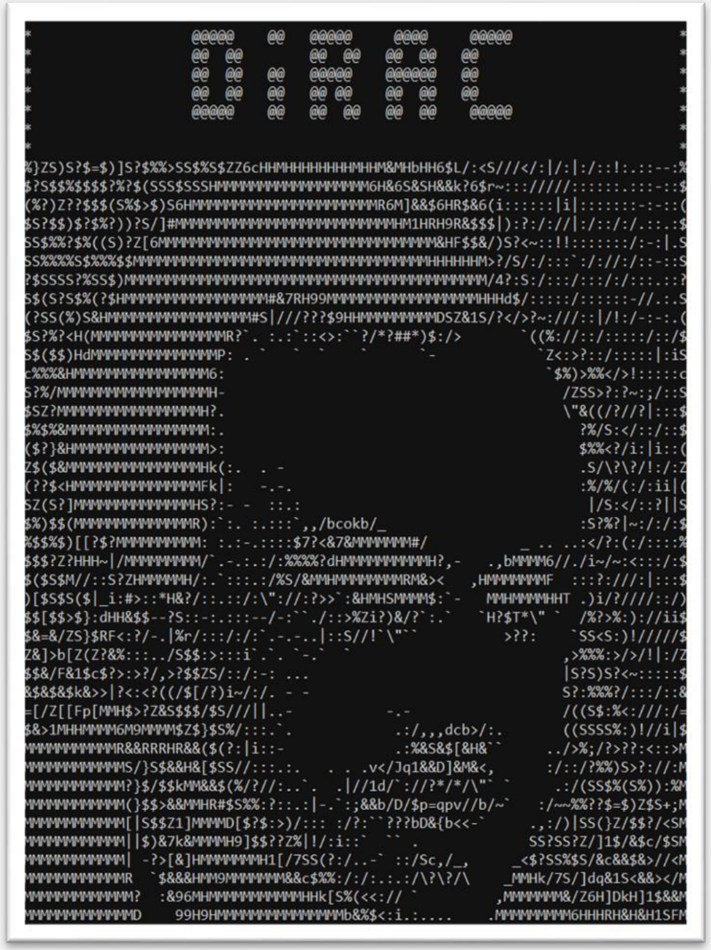
- Number of **correlation optimized functions**: valence (v), core-valence (cv), all electrons (ae)

- Additional **diffuse** functions:

s-aug	1 layer of diffuse functions
d-aug	2 layers of diffuse functions

…

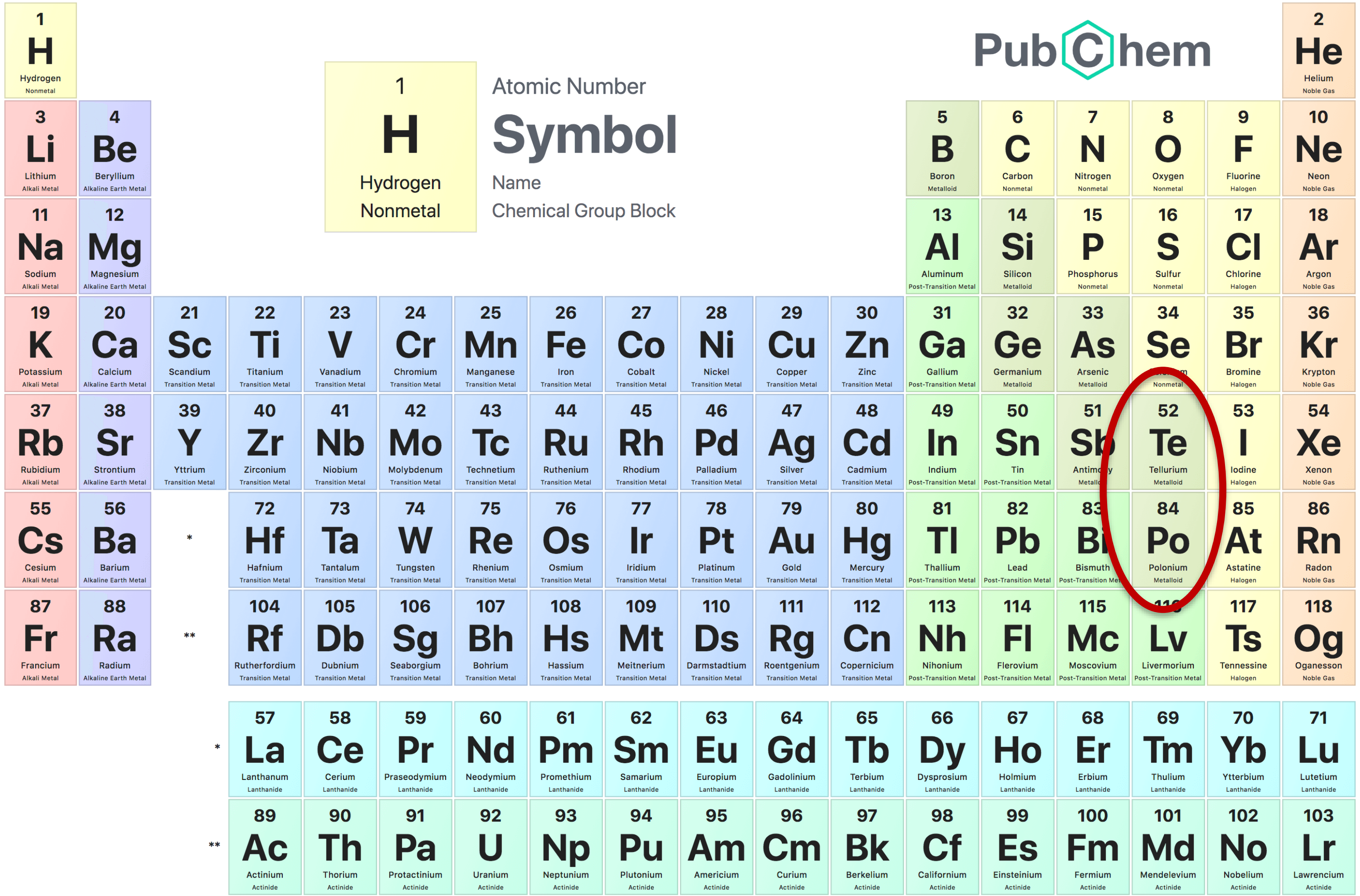




Preliminary results

Tellurium and Polonium

PERIODIC TABLE OF ELEMENTS



PubChem

1
H
Hydrogen
Nonmetal

Atomic Number
Symbol
Name
Chemical Group Block

1 H Hydrogen Nonmetal																	2 He Helium Noble Gas
3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth Metal											5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth Metal											13 Al Aluminum Post-Transition Metal	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth Metal	21 Sc Scandium Transition Metal	22 Ti Titanium Transition Metal	23 V Vanadium Transition Metal	24 Cr Chromium Transition Metal	25 Mn Manganese Transition Metal	26 Fe Iron Transition Metal	27 Co Cobalt Transition Metal	28 Ni Nickel Transition Metal	29 Cu Copper Transition Metal	30 Zn Zinc Transition Metal	31 Ga Gallium Post-Transition Metal	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas
37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth Metal	39 Y Yttrium Transition Metal	40 Zr Zirconium Transition Metal	41 Nb Niobium Transition Metal	42 Mo Molybdenum Transition Metal	43 Tc Technetium Transition Metal	44 Ru Ruthenium Transition Metal	45 Rh Rhodium Transition Metal	46 Pd Palladium Transition Metal	47 Ag Silver Transition Metal	48 Cd Cadmium Transition Metal	49 In Indium Post-Transition Metal	50 Sn Tin Post-Transition Metal	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas
55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth Metal	*	72 Hf Hafnium Transition Metal	73 Ta Tantalum Transition Metal	74 W Tungsten Transition Metal	75 Re Rhenium Transition Metal	76 Os Osmium Transition Metal	77 Ir Iridium Transition Metal	78 Pt Platinum Transition Metal	79 Au Gold Transition Metal	80 Hg Mercury Transition Metal	81 Tl Thallium Post-Transition Metal	82 Pb Lead Post-Transition Metal	83 Bi Bismuth Post-Transition Metal	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas
87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth Metal	**	104 Rf Rutherfordium Transition Metal	105 Db Dubnium Transition Metal	106 Sg Seaborgium Transition Metal	107 Bh Bohrium Transition Metal	108 Hs Hassium Transition Metal	109 Mt Meitnerium Transition Metal	110 Ds Darmstadtium Transition Metal	111 Rg Roentgenium Transition Metal	112 Cn Copernicium Transition Metal	113 Nh Nihonium Post-Transition Metal	114 Fl Flerovium Post-Transition Metal	115 Mc Moscovium Post-Transition Metal	116 Lv Livermorium Post-Transition Metal	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
		*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide
		**	89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide

Te: effect of the method used

v2z

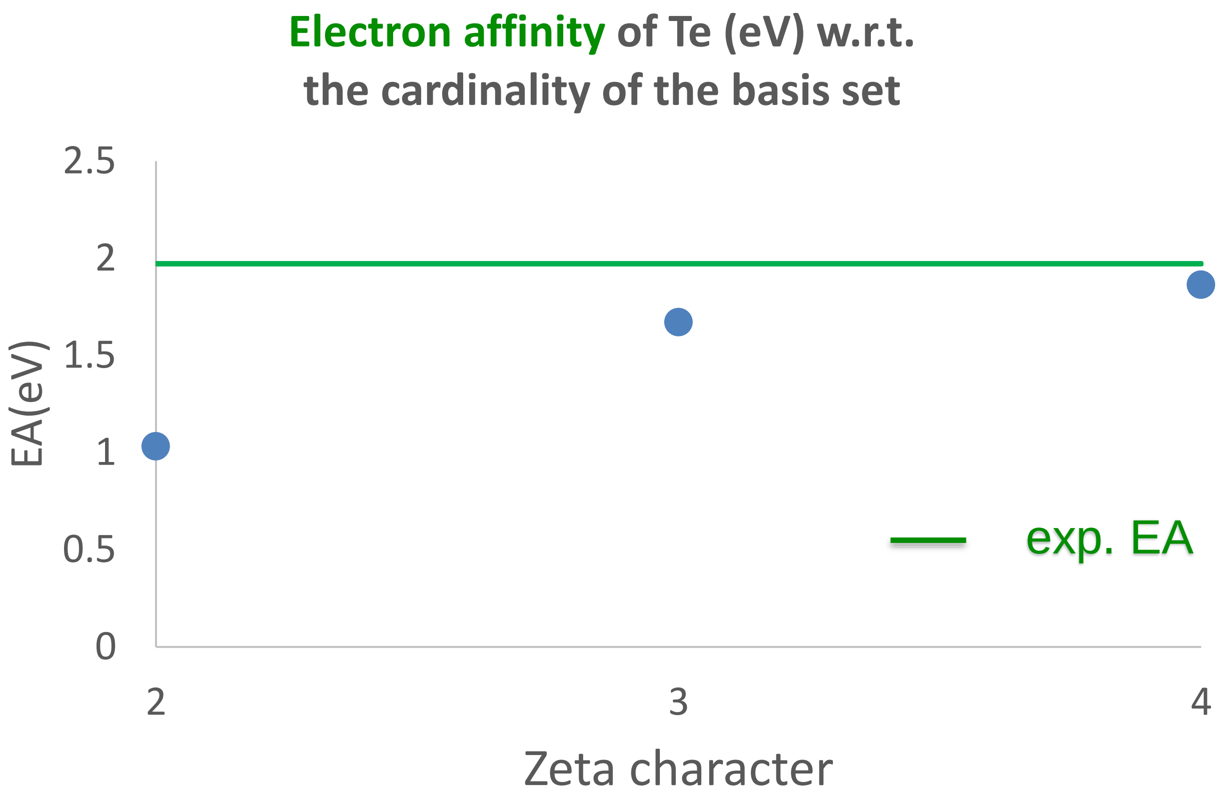
Method	EA(eV)	ΔEA(eV)
DHF	1.314	**0**
CCSD(T)	1.033	**-0.281**
Exp.	1.971	

v4z

Method	EA (eV)	ΔEA(eV)
DHF	1.680	**0**
CCSD(T)	1.863	**+0.183**
Exp.	1.971	

- **Correlation** has a very large impact on the electron affinity
- The CC method improves the results for a **sufficiently large basis set**

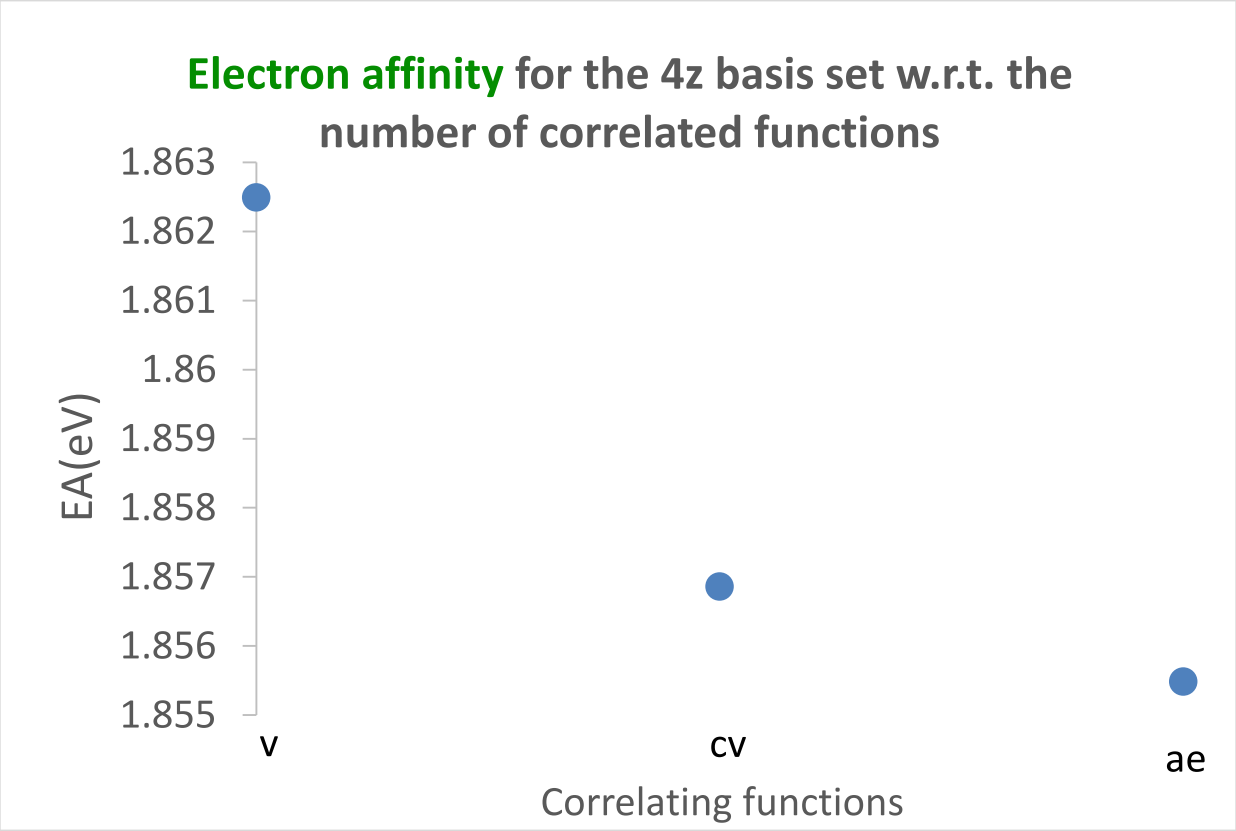
Te: effect of the cardinality of the basis set



- **Large effect** of the zeta character for the **electron affinity**: **4z** character necessary to obtain the desired meV accuracy

Correlating space: -1200au to 1200au

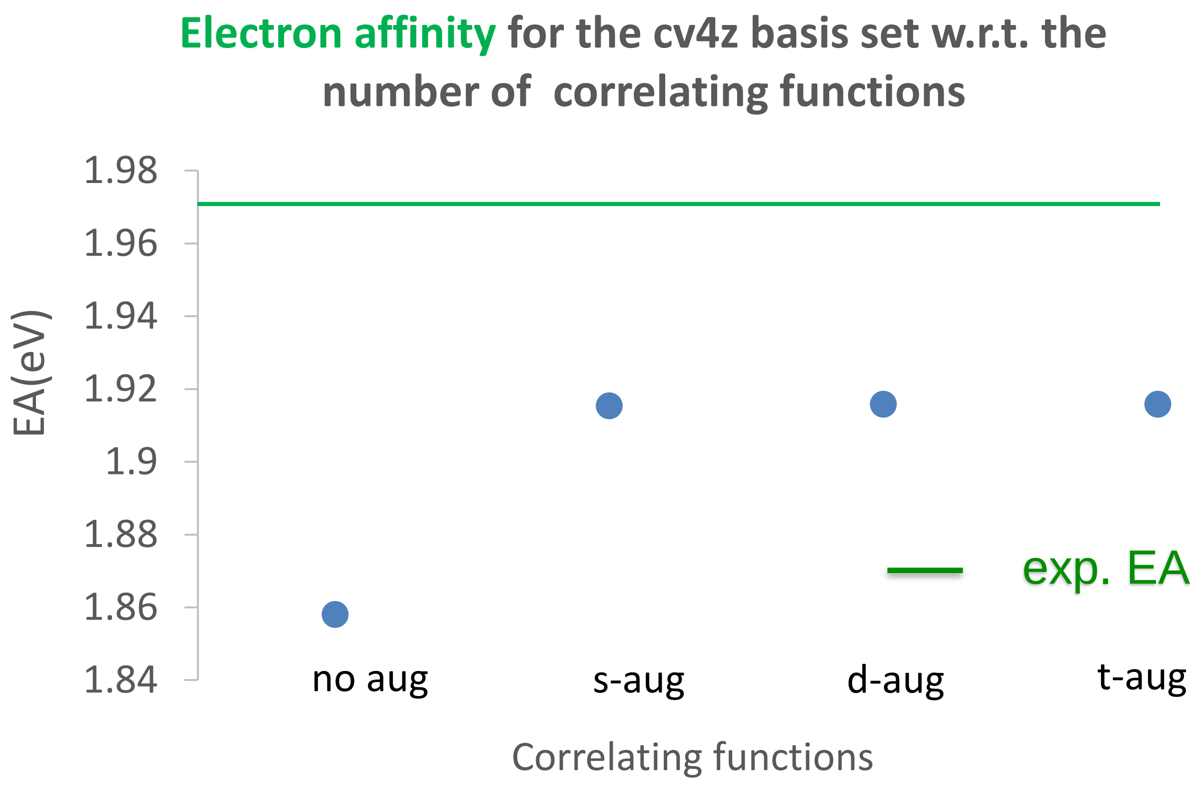
Te: number of correlating functions v, cv, ae



- The inclusion of **core-valence** basis functions improves the accuracy. **All-electron** functions have a slight effect (2meV)

Correlating space: -1200au to 500au

Te: Effect of additional diffuse functions



- The inclusion of 2 layers of **diffuse functions** reduces the error by half

Correlating space: -1200au to 1200au

Te: Number of correlated electrons and virtual cut-off

Number of correlated electrons	Virtual cut-off(au)	EA (eV)	ΔEA(eV)
24	30	1.918	**0**
52	50	1.917	**-0.001**
52	1200	1.917	**0**
52	3000	1.917	**0**
	Exp.	1.971	

- Correlating a larger space has a **very small effect** on the calculated EA: ~ **1 meV** for the EA

Basis set: s-aug-cv4z

Po: effect of the method used

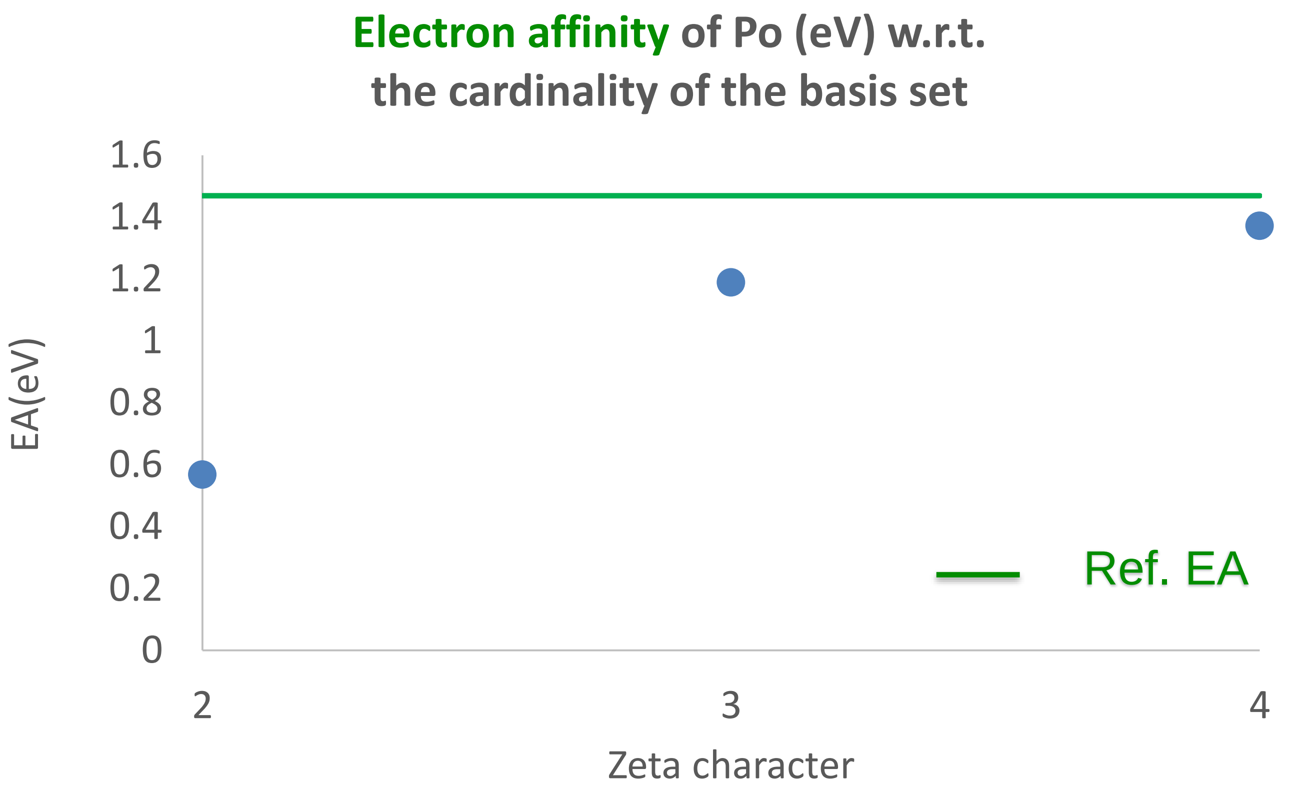
v4z

Method	EA (eV)	ΔEA(eV)
DHF	1.695	0
CCSD(T)	1.372	-0.323
4C+CCSD(T)+ QED + Breit*	1.469	

- **Same conclusions** as for tellurium

*Borschevsky, A., Pasteka, L. F., Pershina, V., Eliav, E., & Kaldor, U. (2015). Ionization potentials and electron affinities of the superheavy elements 115-117 and their sixth-row homologues Bi, Po, and At. Physical Review A, 91(2)

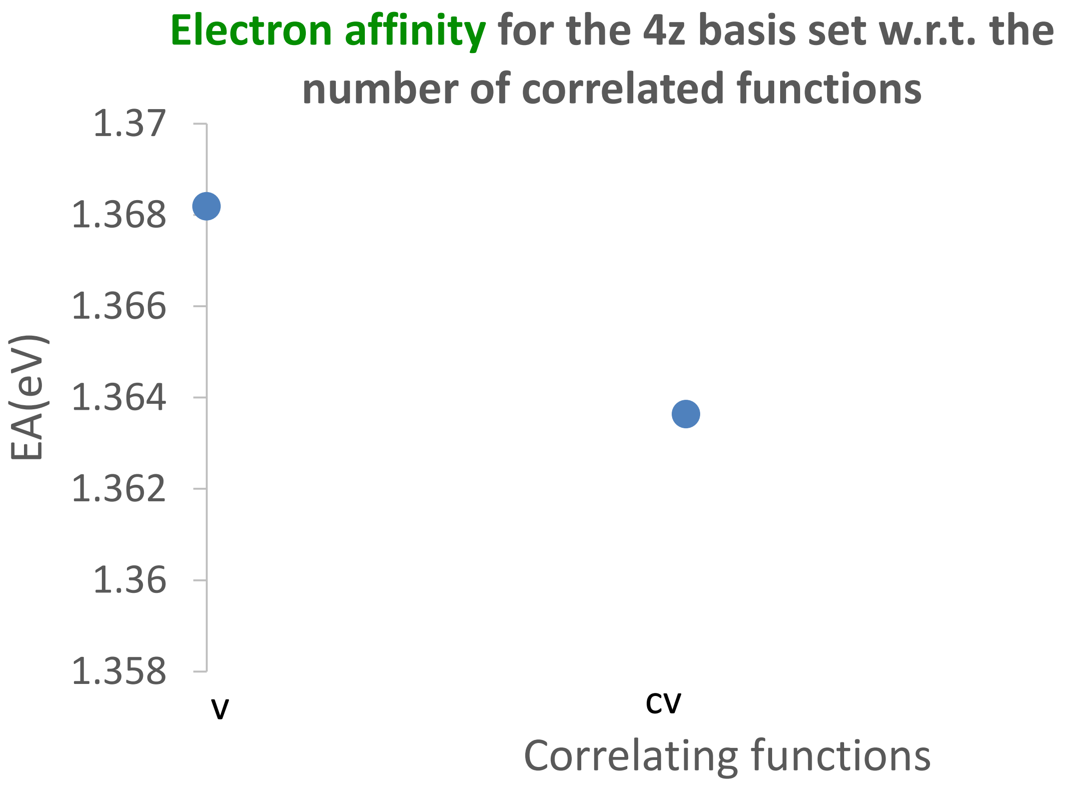
Po: effect of the cardinality of the basis set



- Same conclusions, with even a **larger effect** than for tellurium

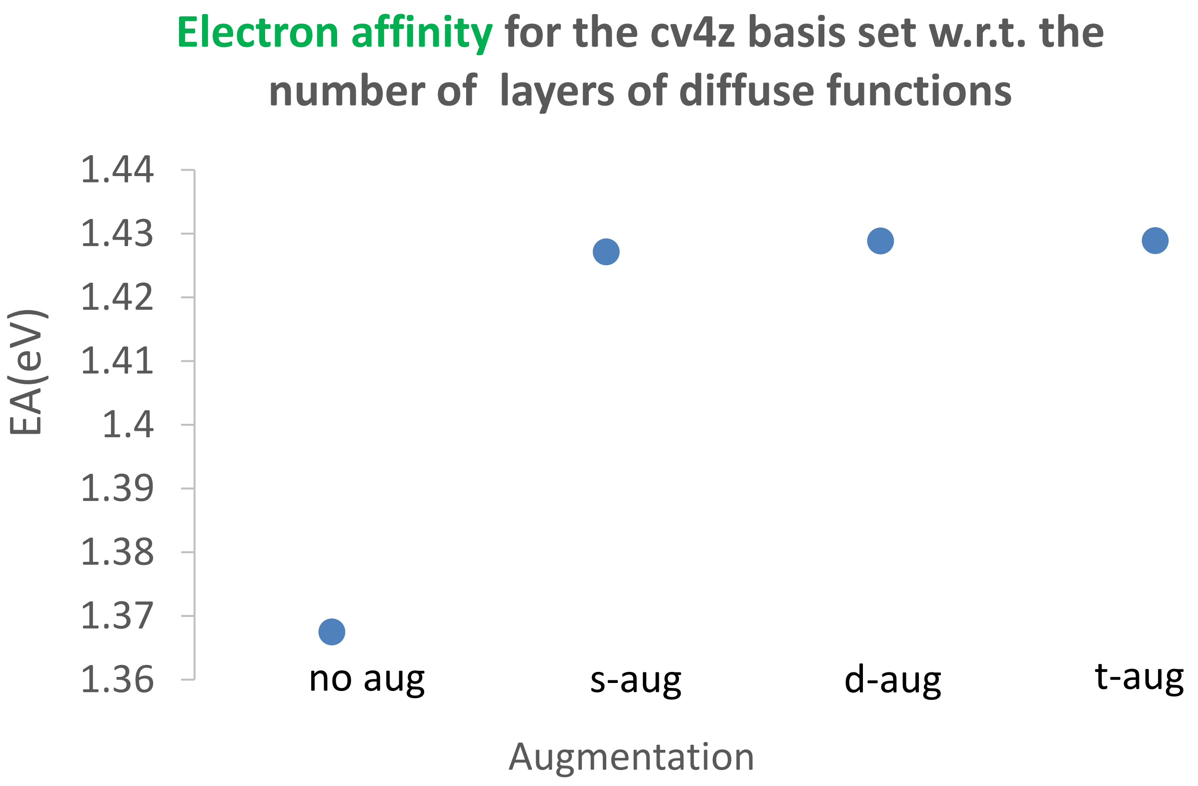
Correlating space: -1200au to 1200au

Po: number of correlating functions v, cv, ae



- **Similar conclusions** than for tellurium with a **stronger effect**

Po: Effect of additional diffuse functions



- Larger effect than for tellurium: **double augmentation** improves the accuracy

Correlating space: -1200au to 1200au

Po: Number of correlated electrons and virtual cut-off

Number of correlated electrons	Virtual cut-off(au)	EA (eV)	ΔEA(eV)
48	30	1.427	0
80	300	1.424	-0.003
84	50	1.424	0
84	3500	1.424	0
4C+CCSD+ QED + Breit*		1.469	

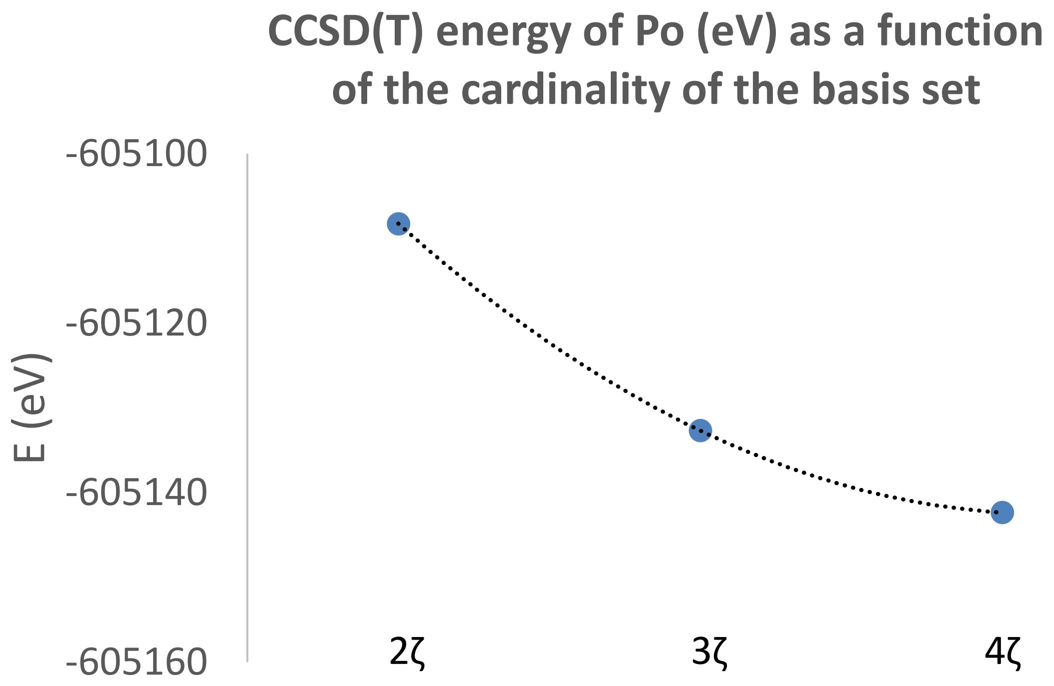
- **Small** but **larger effect** than for tellurium.

Basis set: s-aug-cv4z

Extrapolation to the CBS limit

- The “true” energy of the system corresponds to an **infinite number** of basis functions, impossible in practice
- To approach this number, we **extrapolate** our results
- This is done w.r.t. the **cardinality** of the basis set, major source of uncertainty

$$E(n) = E_{cbs} + \frac{A}{n^3}$$



Vasilyev, V. (2017). Online complete basis set limit extrapolation calculator. *Computational and Theoretical Chemistry*, *1115*, 1-3.

Final tables – basis set

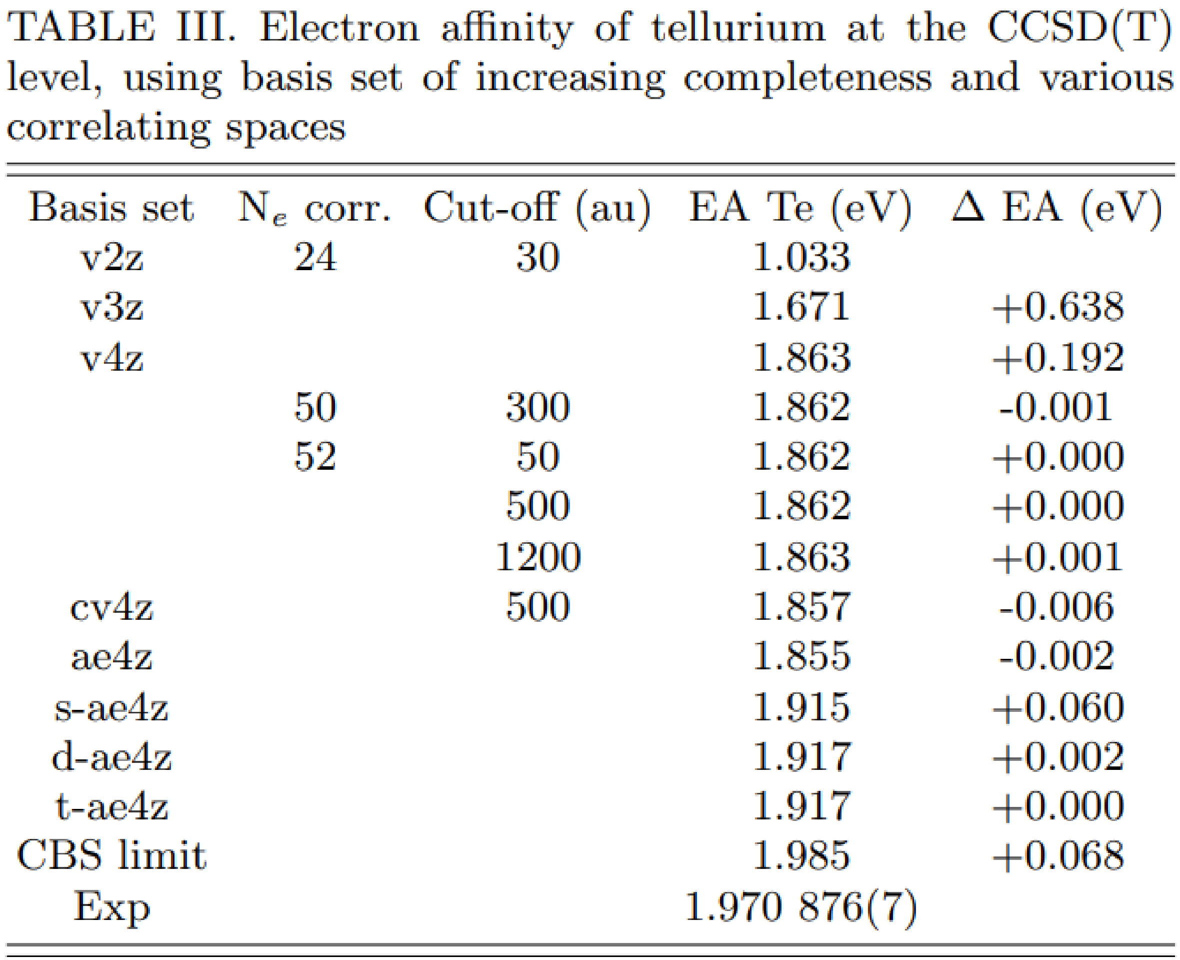


TABLE III. Electron affinity of tellurium at the CCSD(T) level, using basis set of increasing completeness and various correlating spaces

Basis set	N_e corr.	Cut-off (au)	EA Te (eV)	Δ EA (eV)
v2z	24	30	1.033	
v3z			1.671	+0.638
v4z			1.863	+0.192
	50	300	1.862	-0.001
	52	50	1.862	+0.000
		500	1.862	+0.000
		1200	1.863	+0.001
cv4z		500	1.857	-0.006
ae4z			1.855	-0.002
s-ae4z			1.915	+0.060
d-ae4z			1.917	+0.002
t-ae4z			1.917	+0.000
CBS limit			1.985	+0.068
Exp			1.970 876(7)	

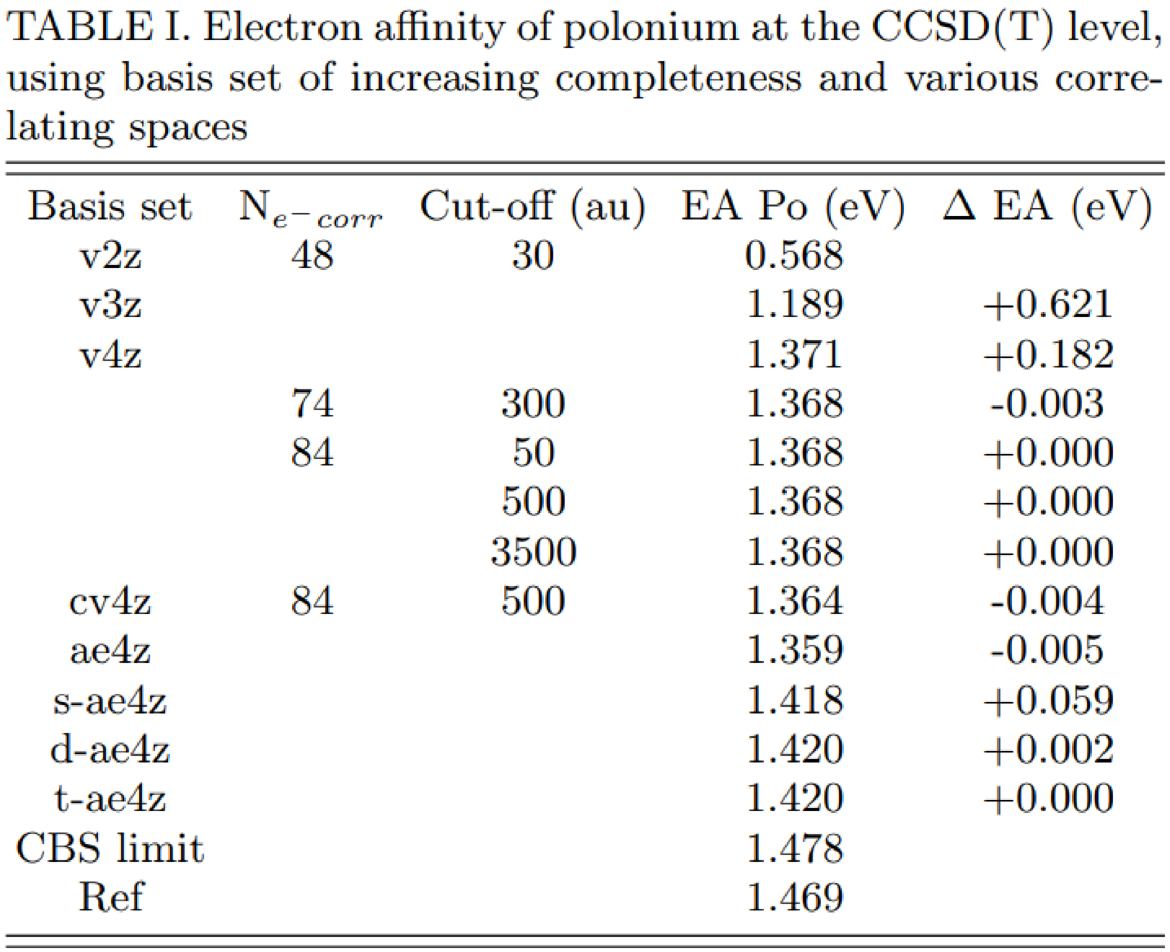


TABLE I. Electron affinity of polonium at the CCSD(T) level, using basis set of increasing completeness and various correlating spaces

Basis set	N_{e-corr}	Cut-off (au)	EA Po (eV)	Δ EA (eV)
v2z	48	30	0.568	
v3z			1.189	+0.621
v4z			1.371	+0.182
	74	300	1.368	-0.003
	84	50	1.368	+0.000
		500	1.368	+0.000
		3500	1.368	+0.000
cv4z	84	500	1.364	-0.004
ae4z			1.359	-0.005
s-ae4z			1.418	+0.059
d-ae4z			1.420	+0.002
t-ae4z			1.420	+0.000
CBS limit			1.478	
Ref			1.469	

Final tables – Method

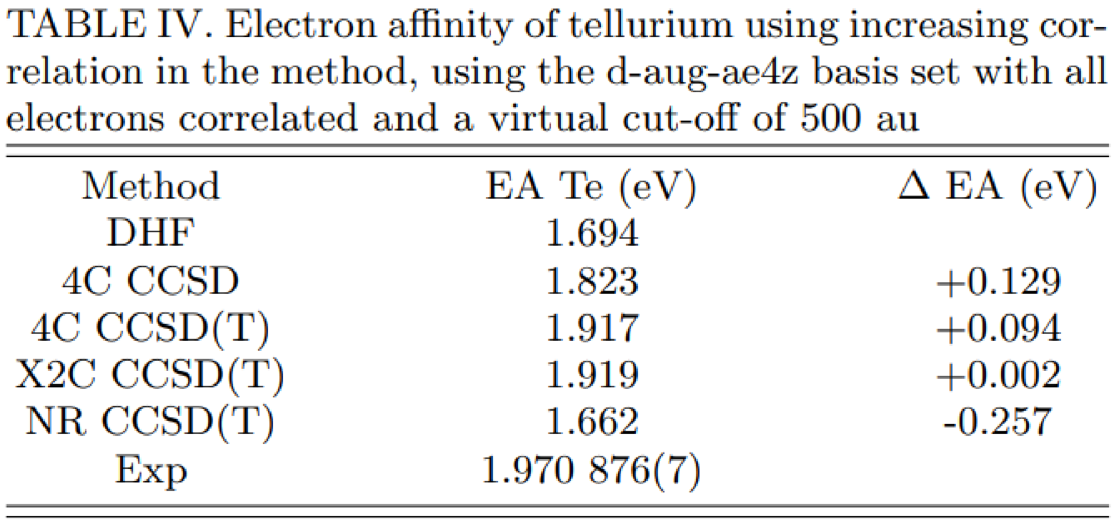


TABLE IV. Electron affinity of tellurium using increasing correlation in the method, using the d-aug-ae4z basis set with all electrons correlated and a virtual cut-off of 500 au

Method	EA Te (eV)	Δ EA (eV)
DHF	1.694	
4C CCSD	1.823	+0.129
4C CCSD(T)	1.917	+0.094
X2C CCSD(T)	1.919	+0.002
NR CCSD(T)	1.662	-0.257
Exp	1.970 876(7)	

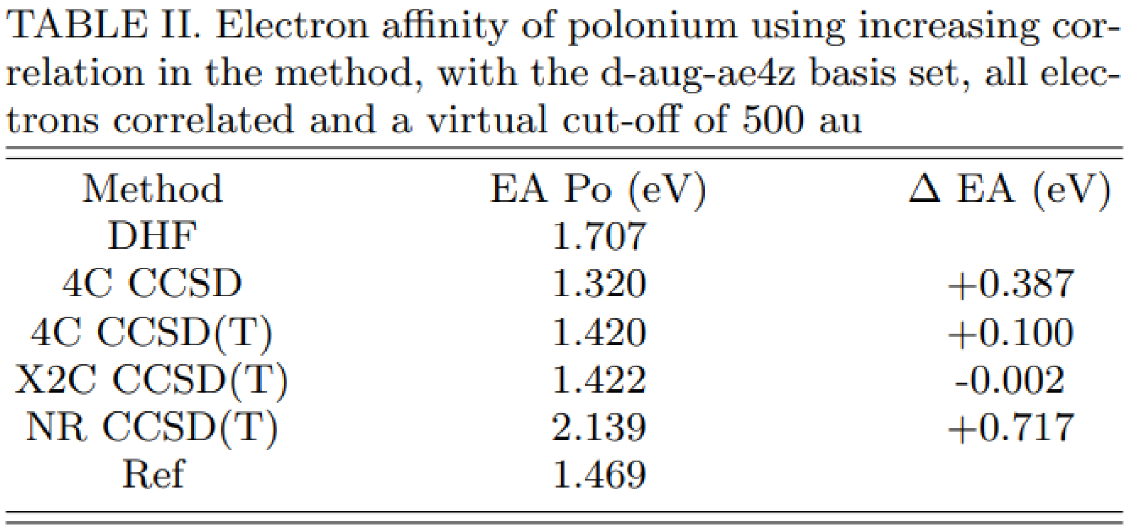


TABLE II. Electron affinity of polonium using increasing correlation in the method, with the d-aug-ae4z basis set, all electrons correlated and a virtual cut-off of 500 au

Method	EA Po (eV)	Δ EA (eV)
DHF	1.707	
4C CCSD	1.320	+0.387
4C CCSD(T)	1.420	+0.100
X2C CCSD(T)	1.422	-0.002
NR CCSD(T)	2.139	+0.717
Ref	1.469	

Extending our approach to Se (Z=36) and Lv (Z=116)

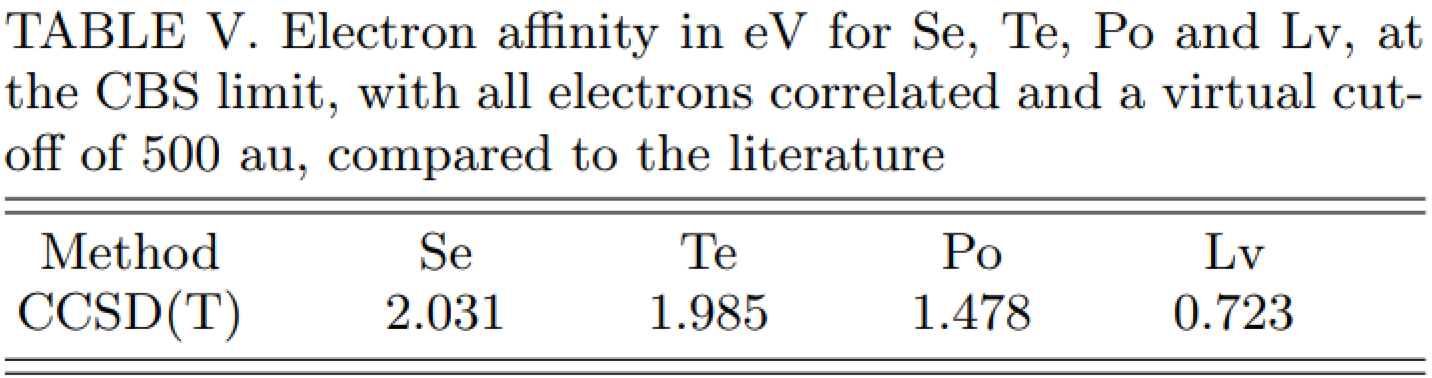
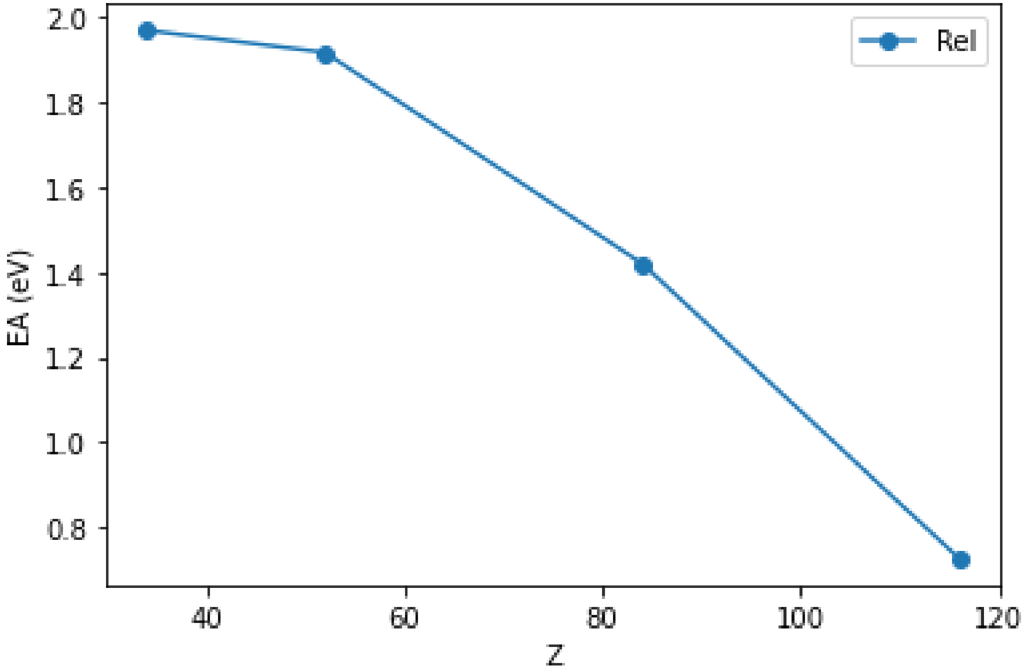


TABLE V. Electron affinity in eV for Se, Te, Po and Lv, at the CBS limit, with all electrons correlated and a virtual cut-off of 500 au, compared to the literature

Method	Se	Te	Po	Lv
CCSD(T)	2.031	1.985	1.478	0.723



Conclusion

- Basis set of our final calculation: d-aug-ae4z, after extrapolation to the CBS, we obtain:

$$\boldsymbol{EA(Po) = 1.478\ \mathrm{eV}}$$

- **Excellent agreement** with literature: within 10 meV
- Knowledge of the **influence** of the different **basis set parameters**
- For **tellurium** with the same approach, we obtain:

$$\boldsymbol{EA(\mathrm{Te}) = 1.985\ \mathrm{eV}}$$

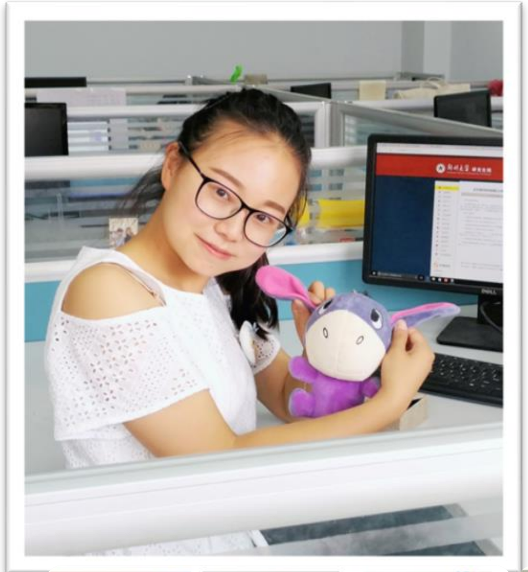
- **Excellent agreement** with the experimental value: 1.971 eV
- Calculation of the EA for Se, Te, Po, and Lv: predominance of relativistic effects while increasing Z, leading to a dramatic decrease of the EA

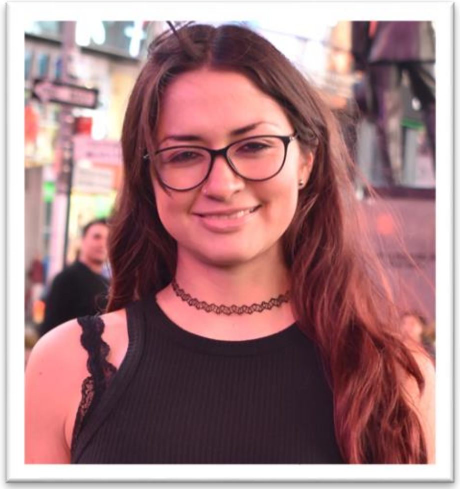
Outlook

- Estimation of the **uncertainty**
- **Non-relativistic** calculations
- **Higher order excitations,** beyond triples
- Calculation of the **Breit** contribution
- Calculation of **Quantum ElectroDynamic** (QED) effects

Great thanks to the people I work with…



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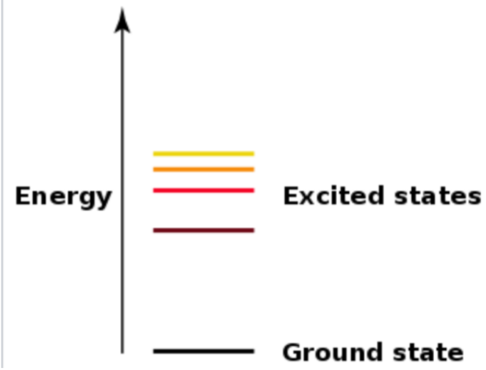
And thank you for your attention !

PhD project

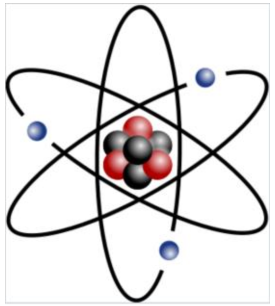
Input

- **Title**: « Relativistic coupled cluster (CC) and configuration interaction (CI) investigations of properties of heavy and superheavy elements »
- **Two secondments** of 3 months each:
  - University of New South Wales (UNSW) in Sydney (Australia)
  - Tel Aviv University (Israel)
- Use of the DIRAC and AMBiT programs and Tel Aviv package



Output

- **Calculations** of electronic structure, predicted spectra, ionization potential, electron affinity, hyperfine structure parameter, Isotope shift, with meV accuracy
- **Estimation** of relativistic and Quantum Electrodynamic Effects (QED), using CC and CI as complementary approaches
- Estimation of the **uncertainty**



Personal presentation

- Bachelor Degree in Physics and Chemistry, Clermont-Ferrand - 2015
- Master Degree in Theoretical Chemistry, Toulouse - 2017

- Teacher in Secondary School, La Rochelle - 2018
- Master degree in Education in Physics and Chemistry, Toulouse - 2019

- PhD candidate at the University of Groningen – 08/2020 – present day

Te: Effect of additional diffuse functions

Basis set	IP (eV)	ΔIP(eV)	EA (eV)	ΔEA(eV)
cv4z	9.014	**+0.005**	1.858	**-0.113**
s-aug-cv4z	9.024	**+0.015**	1.915	**-0.055**
d-aug-cv4z	9.024	**+0.015**	1.916	**-0.055**
t-aug-cv4z	9.024	**+0.015**	1.916	**-0.055**
Exp.	9.010		1.971	

→ Convergence reached

- The inclusion of **diffuse functions** reduces the error by half on the **EA**, and seems to cause a small increase of the error on the IP… But we have more effects to take into account.

Correlating space: -1200au to 1200au

Po: Effect of additional diffuse functions

Basis set	IP (eV)	ΔIP(eV)	EA (eV)
cv4z	8.395	**-0.031**	1.368
s-aug-cv4z	8.380	**-0.045**	1.424
d-aug-cv4z	8.380	**-0.045**	1.429
t-aug-cv4z	8.380	**-0.045**	1.429
4C+CCSD+ QED + Breit[*]			1.429
Exp.	8.426		

→ Convergence reached

- Larger effect than for tellurium: **double augmentation** improves the accuracy

Correlating space: -1200au to 1200au

Summ

Basis set	N_corr	Virtual cut-off (au)	EA (eV)	ΔEA(eV)
v2z	48	30	0.568	0
v3z	48	30	1.189	
v4z	48	30	1.372	
cv4z				
ae4z				
s-aug-ae4z				
d-aug-ae4z				
Ref.			1.469	