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BACHELORS SYMPOSIUM 2023

Calculation of electron affinity of polonium

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Outline :

1. Introduction
2. Theory and method
3. Results
4. Summary and outlook

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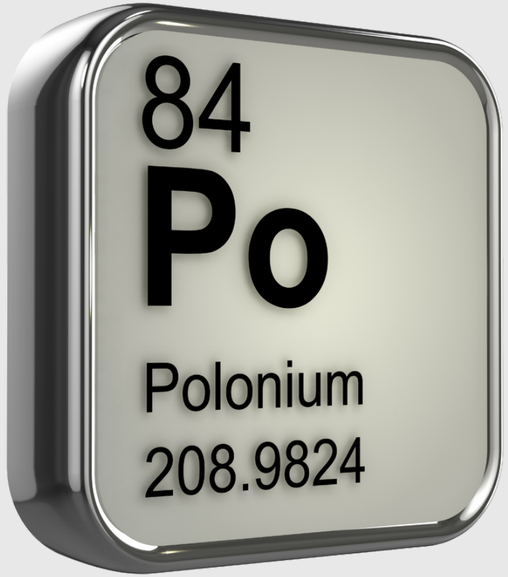
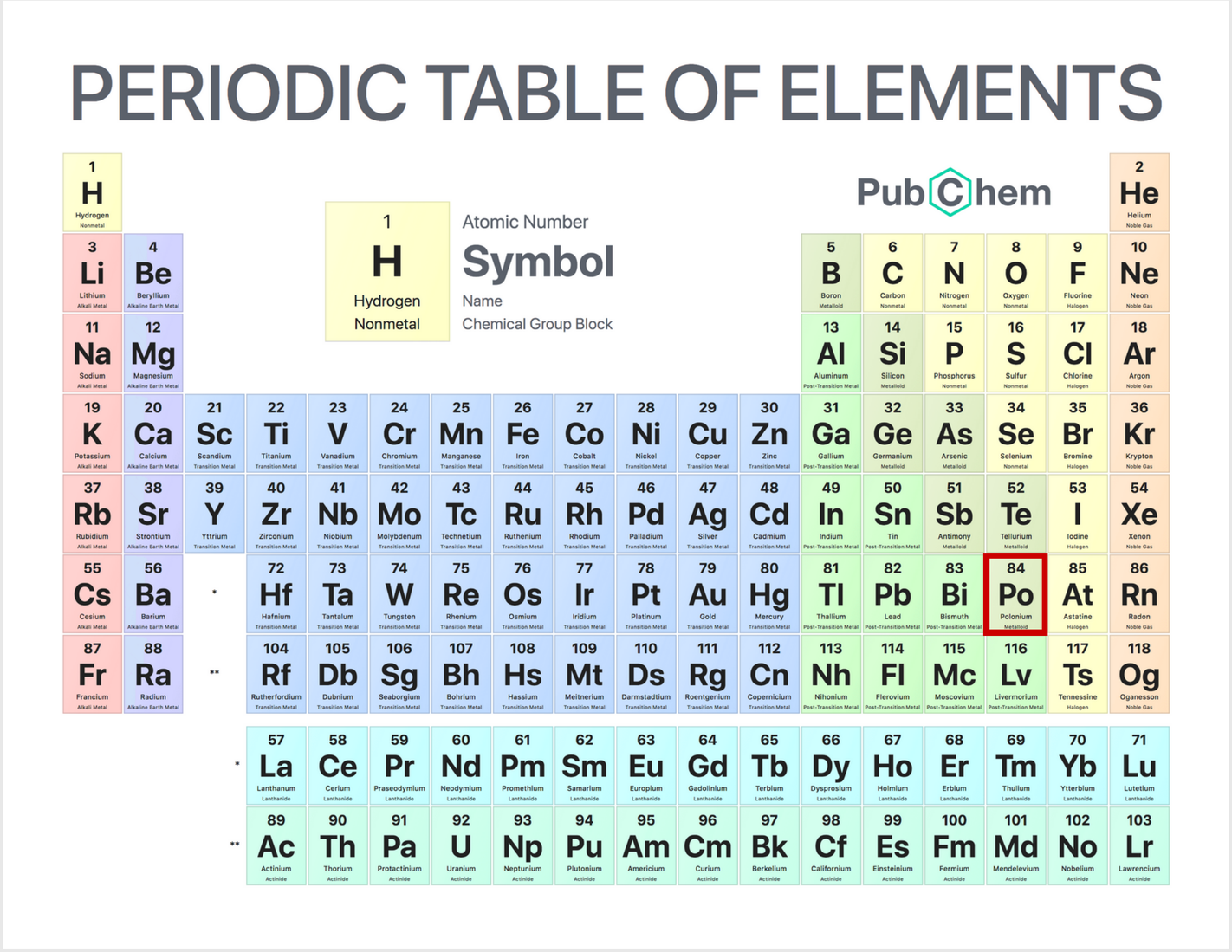
Basic properties



$$[Xe]\ 4f^{14}5d^{10}6s^{2}6p^{4}$$



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Basic properties

ELECTRON AFFINITY (EA)

The energy change that occurs when an electron is added to the neutral atom.

EA=E(neutral atom) - E(negative ion)

IONIZATION POTENTIAL (IP)

The energy change that occurs when an electron is removed from the neutral atom.

IP = E(positive atom)-E(neutral atom)

Theory and method

1

Dirac-Hartree-Fock

2

Coupled Cluster

3

Basis sets

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Dirac-Hartree-Fock

HARTREE-FOCK EQUATION

$$\hat{F}\chi_i = \epsilon_i \chi_i$$

DIRAC HAMILTONIAN

$$\hat{H}\Psi = [c\alpha \cdot \hat{p} + \beta mc^2 + V]\Psi$$

THE SLATER DETERMINANT

$$\Psi(x_1, x_2, ...x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & ... & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & ... & \chi_N(x_2) \\ . & . & . & . \\ . & . & . & . \\ . & . & . & . \\ \chi_1(x_N) & \chi_2(x_N) & ... & \chi_N(x_N) \end{vmatrix}$$

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Coupled cluster

ELECTRONIC CORRELATION

Correlation energy describes the influence of the presence of other electrons on the movement of one electron.

USE OF THE EXPONENTIAL ANSATZ

$$\Psi_{CC} = e^{\hat{T}}\chi$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + ... + \hat{T}_n$$

$$E_{CC} = \langle 0|\hat{H}|0\rangle \hat{H} = e^{-\hat{T}} H e^{\hat{T}}$$

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Basis sets

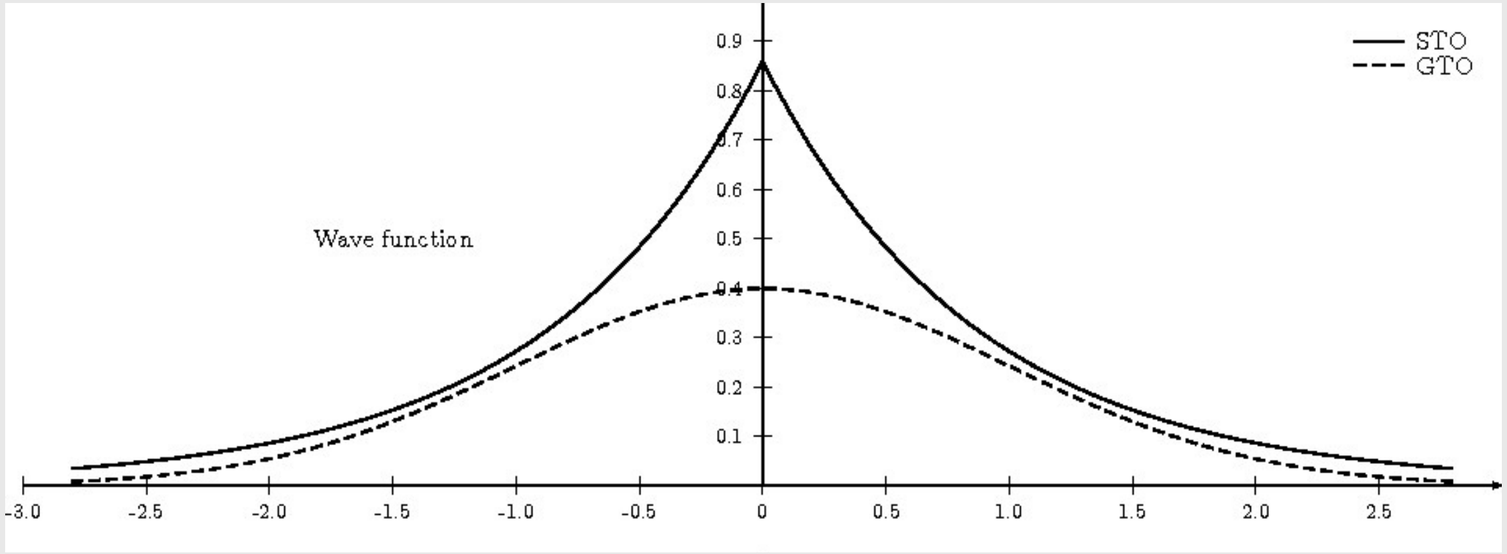

Figure 1: Comparison of the shape of a STO and GTO functions.

SLATER TYPE ORBITALS

$$\phi_{abc}^{STO}(x,y,z) = Nx^a y^b z^c e^{-\zeta r}$$

GAUSSIAN TYPE ORBITALS

$$\phi_{abc}^{GTO}(x,y,z) = Nx^a y^b z^c e^{-\zeta r^2}$$

CONTRACTED GAUSSIAN TYPE ORBITALS

$$\phi_{abc}^{CGTO}(x,y,z) = N \sum_{i=1}^{r} c_i x^a y^b z^c e^{-\zeta r^2}$$

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Basis sets

CARDINALITY

- Double zeta : 2 functions
- Triple zeta : 3 functions
- Quadruple zeta : 4 functions
- Quintuple zeta : 5 functions

NUMBER OF CORRELATION FUNCTIONS

- Valence (v)
- Core-valence (cv)
- All-electrons (ae)

DIFFUSE FUNCTIONS

- 1 added layer of diffuse functions : s-aug
- 2 added layers of diffuse functions : d-aug
- 3 added layers of diffuse functions : t-aug

COMPUTATIONAL DETAILS

Usage of the K.G. Dyall basis sets

Input into the program as Dyall.vXz ; Dyall.cvXz ; Dyall.aeXz

Or as : s-aug-dyall.YXz ; d-aug-dyall.YXz ; t-aug-dyall.YXz

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What parameters can we change ?

METHODS :

DHF ; CCSD ; CCSD(T)

VIRTUAL CUT-OFF

NUMBER OF CORRELATED ELECTRONS

BASIS SETS :

Cardinality

Correlation functions

Diffuse functions

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Results

1

DHF VS CC

2

Varying basis sets

3

Most accurate final result

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DHF VS CCSD and CCSD(T)

DHF VS CCSD(T)	DHF	Error	CCSD	Error	CCSD(T)	Error	Reference
IP in eV	7.810	0.608	8.357	0.061	8.407	0.011	8.418
EA in eV	0.628		1.355		1.456		1.461

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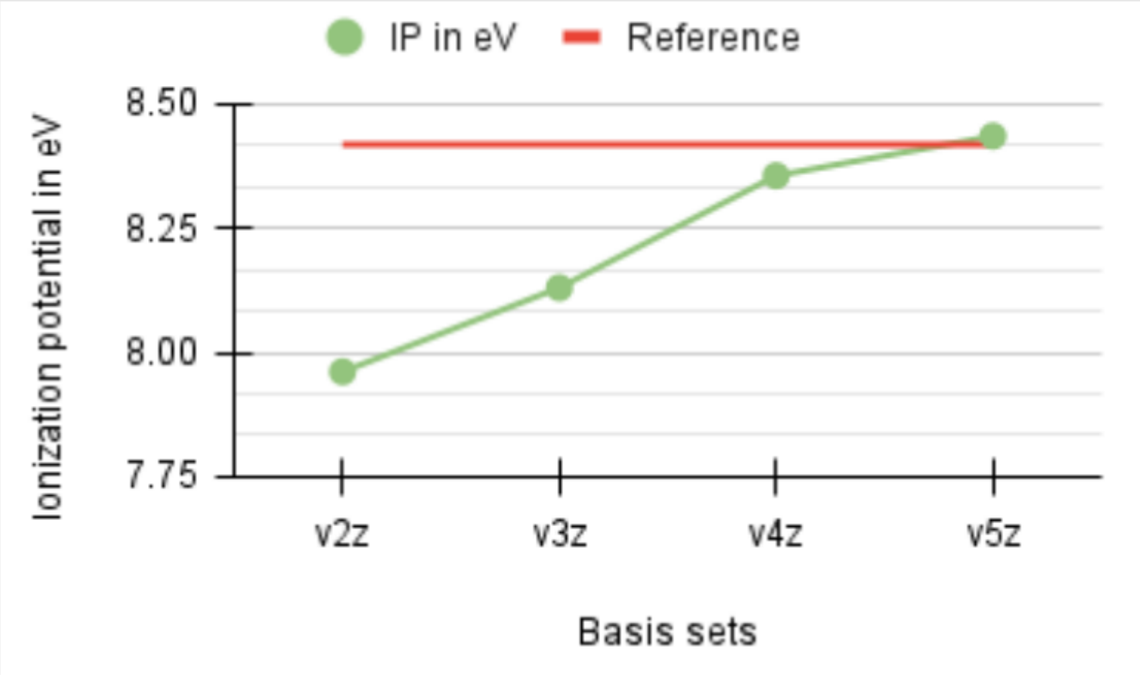
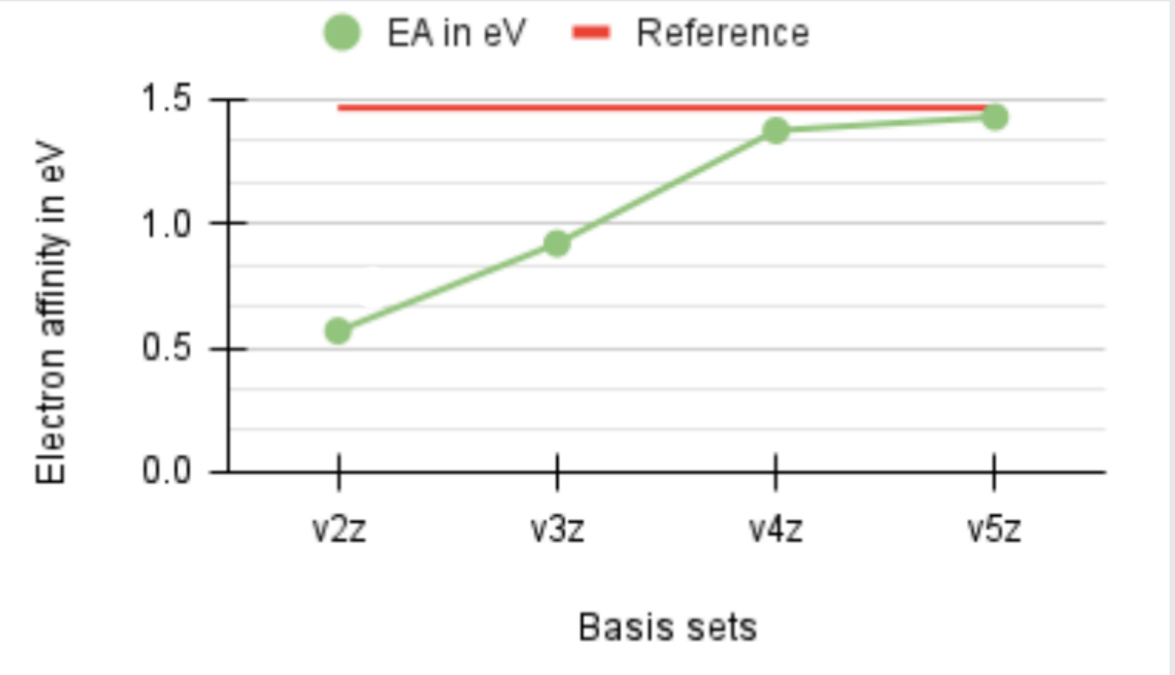
Influence of basis set cardinality





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Influence of correlation functions

Importance of correlated electrons	v5z	cv5z	ae5z	Reference
IP in eV	8.435	8.401	8.401	8.418
EA in eV	1.428	1.422	1.422	1.461

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Influence of diffuse functions

Importance of augmentation	ae5z	s-aug-ae5z	d-aug-ae5z	t-aug-ae5z	Reference
IP in eV	8.401	8.404	8.404	8.404	8.418
EA in eV	1.422	1.453	1.454	1.454	1.461

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Extrapolation to the complete basis set limit

$$E_{CBS1} = -\frac{E_{4z}^2 + E_{3z} * E_{5z}}{E_{3z} - 2 * E_{4z} + E_{5z}}$$

$$E_{CBS2} = \frac{4^3 * E_{4z} - 5^3 * E_{5z}}{4^3 - 5^3}$$

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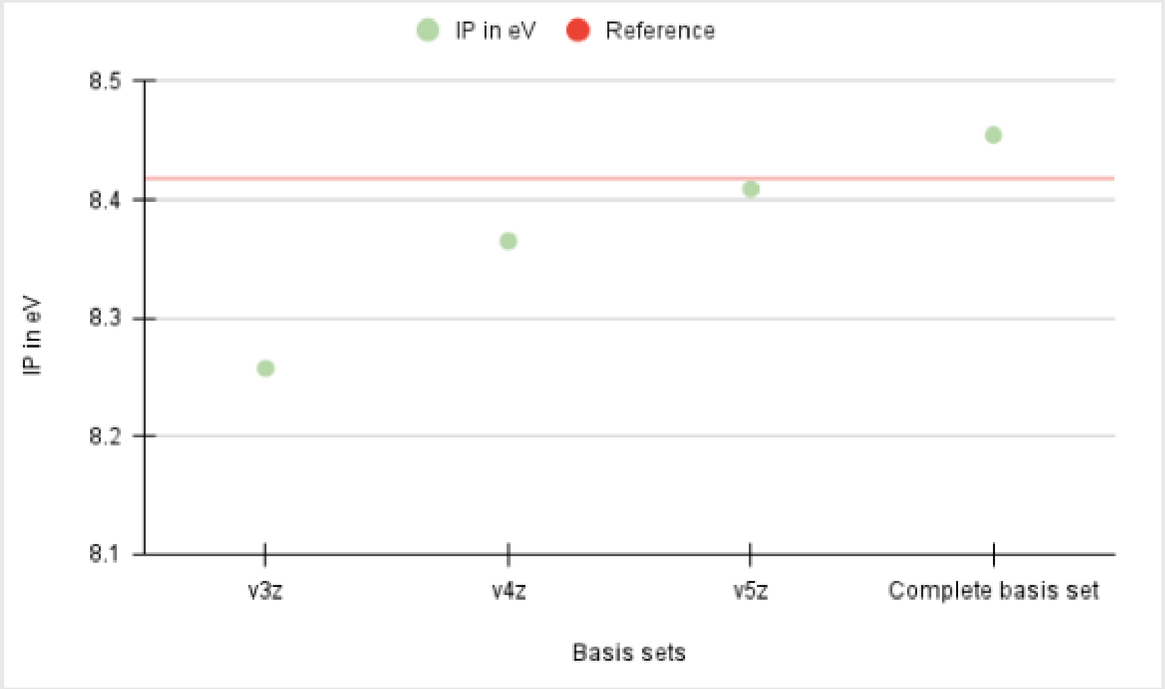
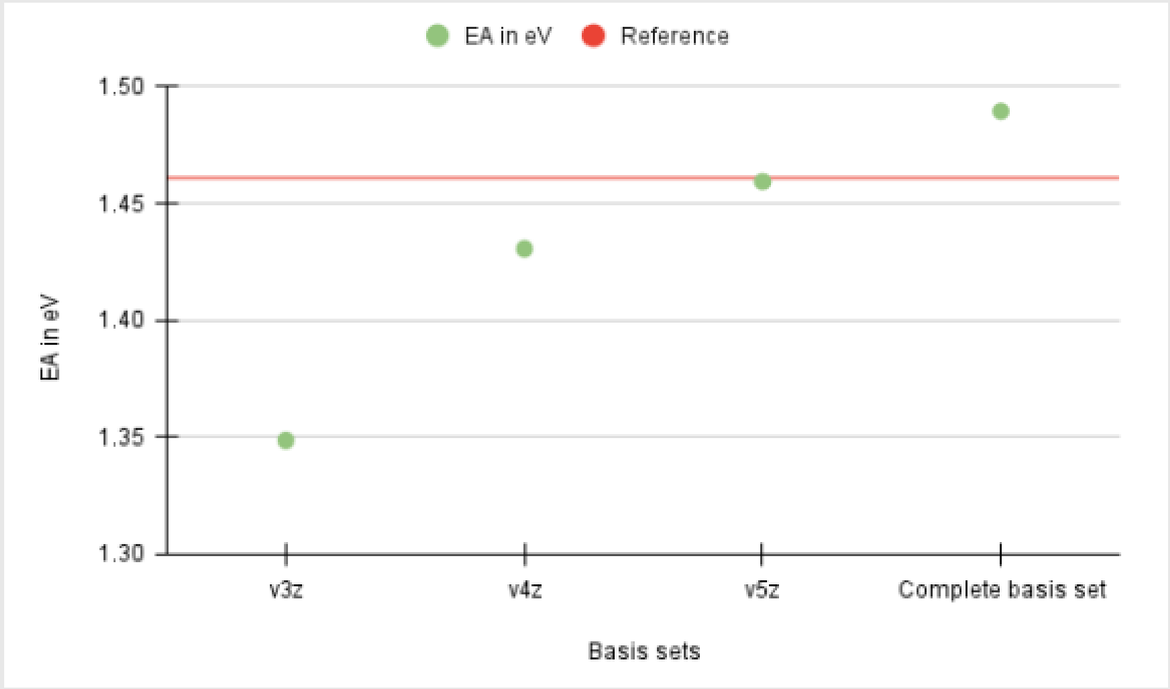
Extrapolation to the complete basis set limit





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Most accurate final result of EA and IP

Basis set	ae5z	s-aug-ae5z	CBS	Reference
IP in eV	8.401	8.404	8.455	8.418
EA in eV	1.422	1.453	1.489	1.461

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Katie Piner

Thank you for your attention

Any questions ?

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