

BACHELORS SYMPOSIUM 2023

# Calculation of electron affinity of polonium

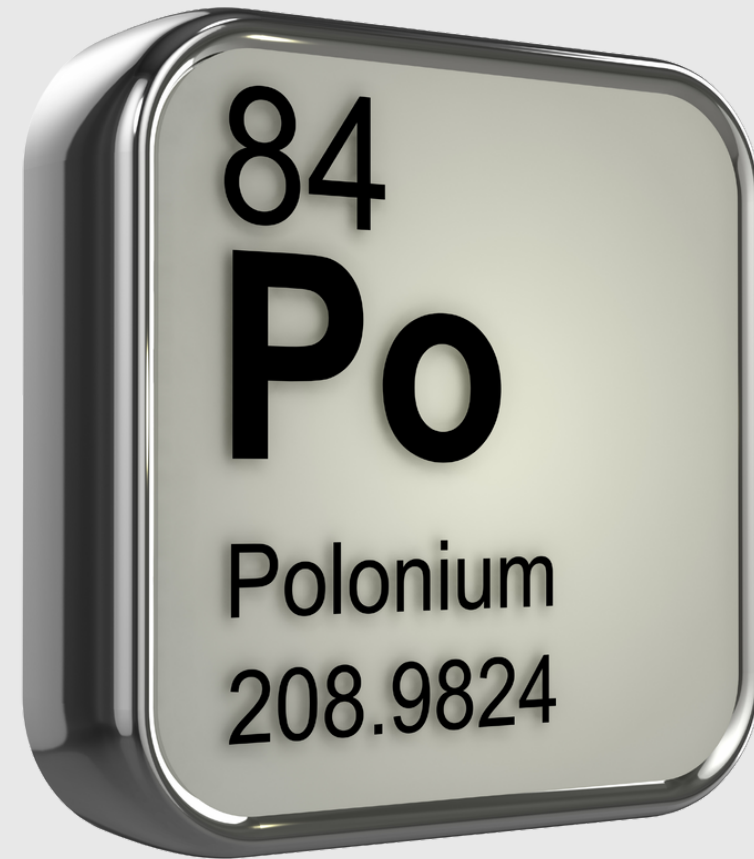
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# Outline :

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

# Basic properties



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## PERIODIC TABLE OF ELEMENTS

PubChem

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

# Basic properties

## ELECTRON AFFINITY (EA)

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

$$EA = E(\text{neutral atom}) - E(\text{negative ion})$$

## IONIZATION POTENTIAL (IP)

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

$$IP = E(\text{positive atom}) - E(\text{neutral atom})$$



# Theory and method

1

Dirac-Hartree-Fock

2

Coupled Cluster

3

Basis sets



# 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

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



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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

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

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

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





# Basis sets

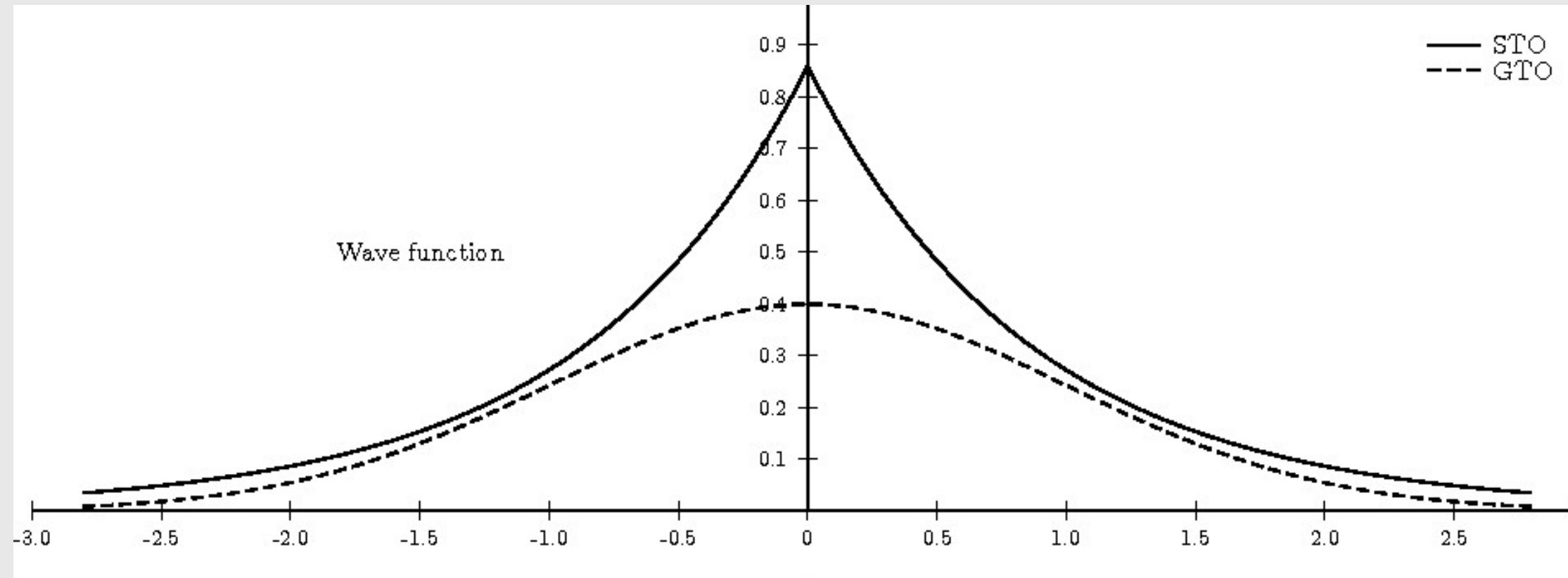


Figure 1: Comparison of the shape of a STO and GTO functions.

## SLATER TYPE ORBITALS

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

## GAUSSIAN TYPE ORBITALS

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

## CONTRACTED GAUSSIAN TYPE ORBITALS

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





# Basis sets

## CARDINALITY

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

## 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

## NUMBER OF CORRELATION FUNCTIONS

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

## 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

# What parameters can we change ?

METHODS :

DHF ; CCSD ; CCSD(T)

VIRTUAL CUT-OFF

NUMBER OF CORRELATED ELECTRONS

BASIS SETS :

Cardinality

Correlation functions

Diffuse functions

# Results

1

DHF VS CC

2

Varying basis sets

3

Most accurate final  
result



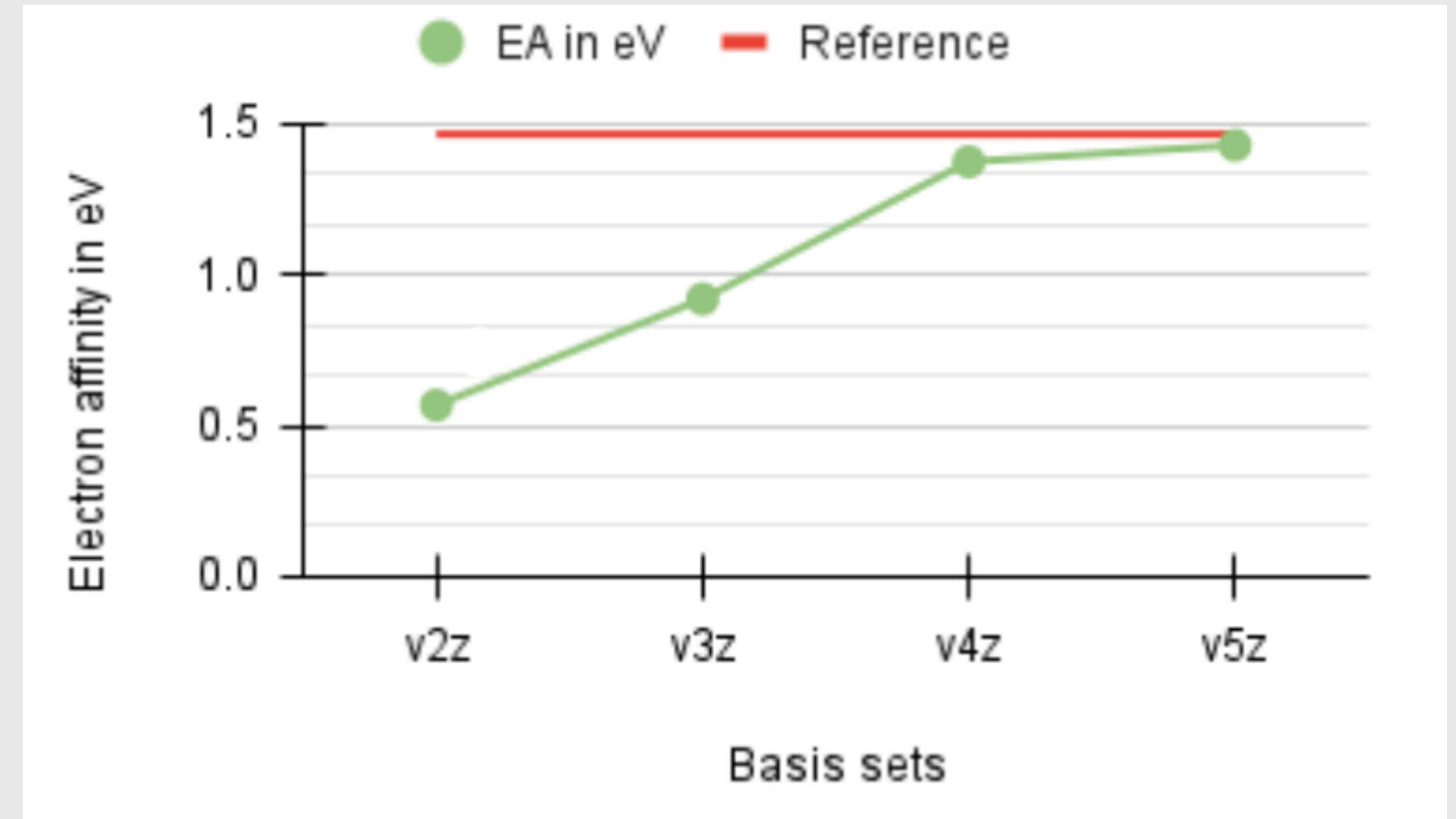
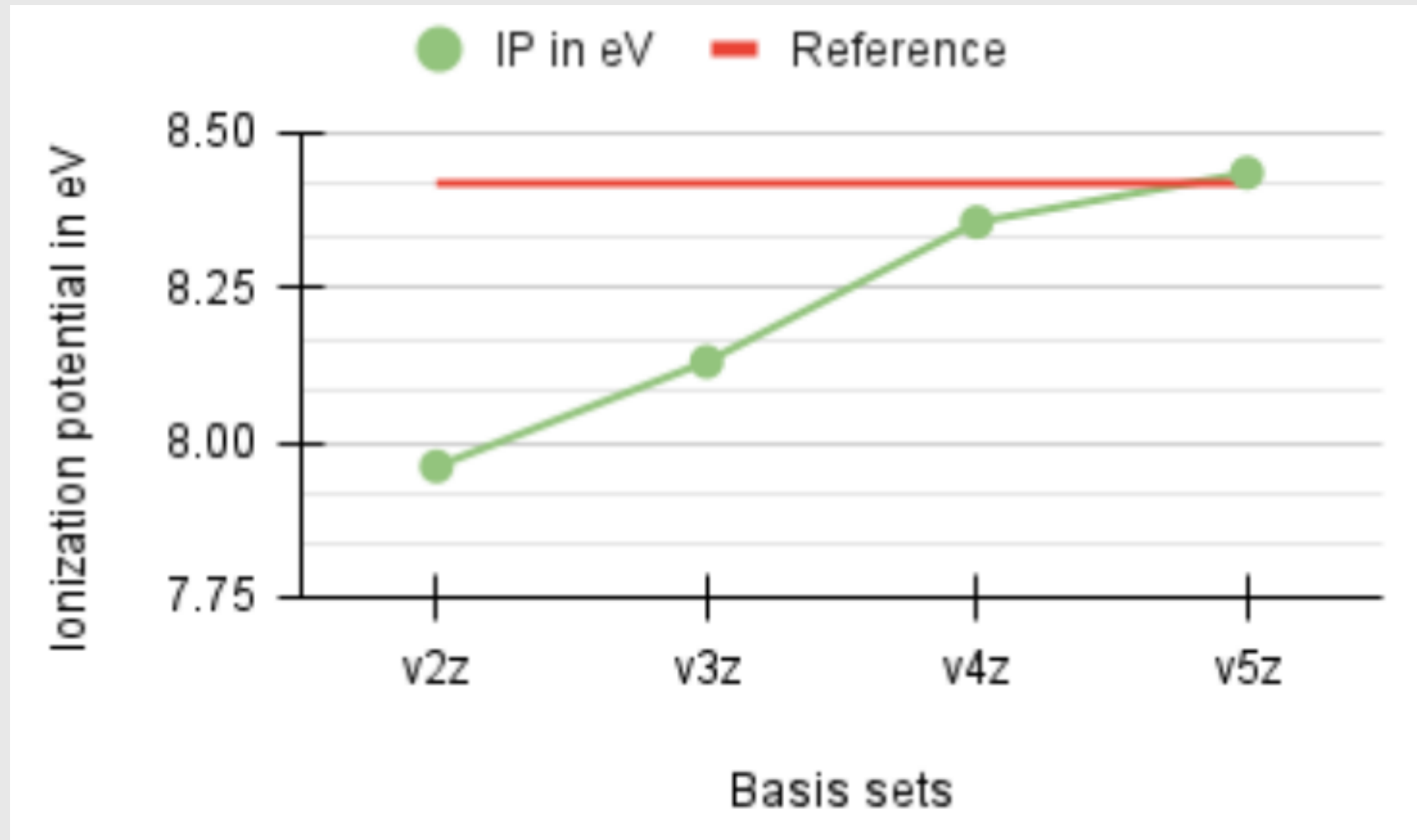
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# DHF VS CCSD and CCSD(T)

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



# Influence of basis set cardinality



# 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



# 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





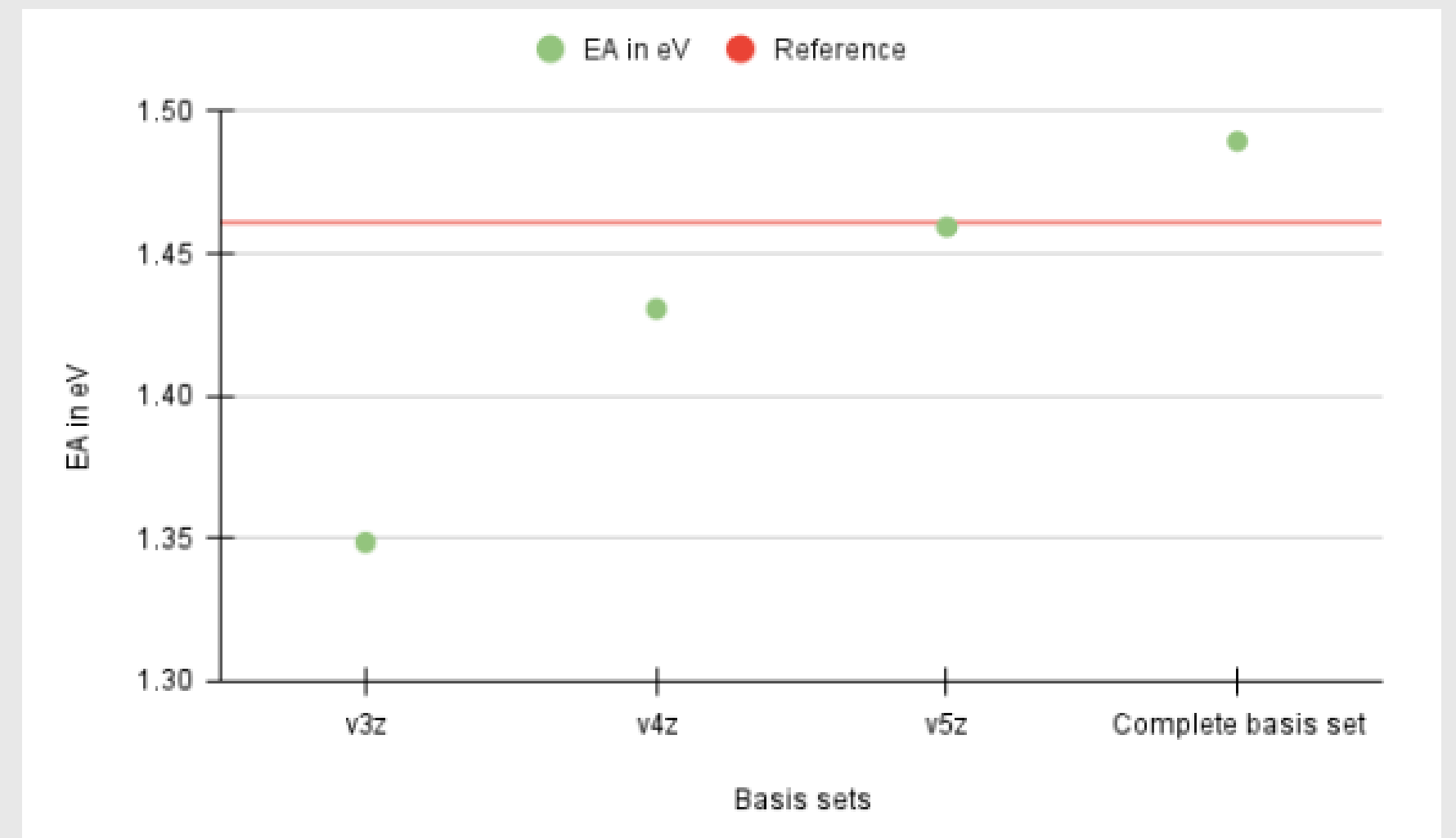
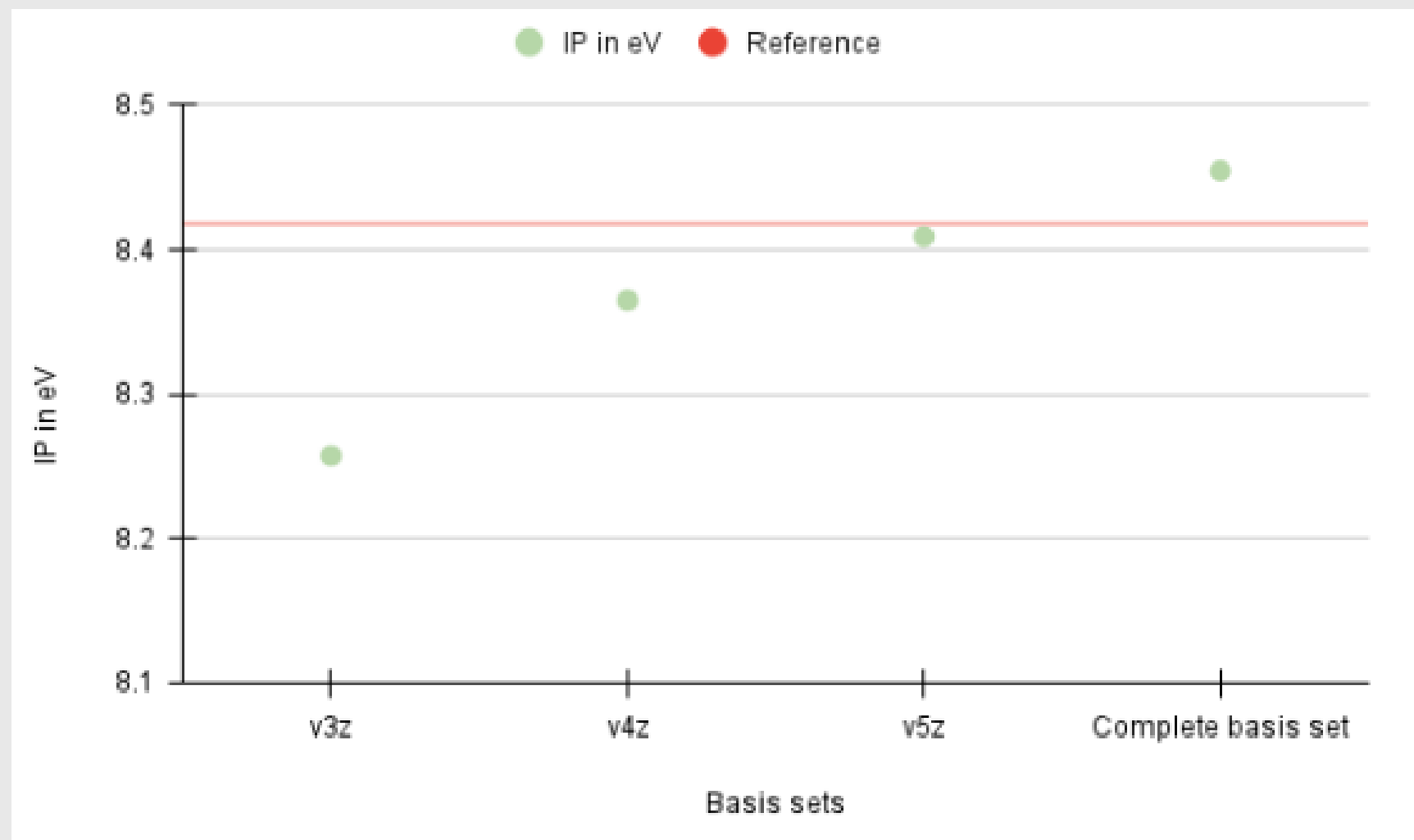
# Extrapolation to the complete basis set limit

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

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



# Extrapolation to the complete basis set limit



# 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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**Thank you for your  
attention**

Any questions ?



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