

The ionization potentials and electron affinities of polonium and its homologues Tellurium and Livermorium

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Abstract. The ionization potentials and electron affinities of tellurium, polonium and livermorium have been calculated using the Dirac-Hartree-Fock (DHF) method and the coupled cluster approach with single, double and perturbative triple excitations (CCSD(T)). The most accurate calculations for Te were performed with the d-aug-ae4z Dyall basis set, the most accurate calculations for Lv used the d-aug-v4z basis set and the calculations for Po were performed with the s-aug-ae4z basis set. All calculations were performed with extra Gaunt corrections, a four-component relativistic Hamiltonian and all electronic orbitals considered. To investigate the influence of relativity and the choice in basis set for each element, calculations with a non-relativistic and a two-component (X2C) Hamiltonian have been performed, next to basis set calculations ranging from double-zeta to quadruple-zeta basis sets, including extra diffuse functions, and valence, core-valence and all-electron basis sets. Lastly, the significance of adding extra Gaunt corrections and taking into account all electronic orbitals has been investigated, eventually leading to the most accurate approach for calculating the ionization potentials and electron affinities of Te, Po and Lv, with results deviating from their reference values in the order of 10 meV.

Introduction

Polonium, the radioactive element found as a product of the decay of the well-known uranium-238, was discovered by Marie and Pierre Curie in 1898 in their research of uranium ore and was appropriately named after Marie's homeland Poland [1]. Two of polonium's homologues, which are the elements that share the same valence electrons, are the lighter element tellurium ($Z=52$) and the superheavy element livermorium ($Z=116$), which occur in the same group in the periodic table, as can be seen in figure 1.

Periodic Table of the Elements

1 IA 1A	2 IIA 2A												13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen (1.00794(1.00811))	3 Li Lithium (6.941(0.003))	4 Be Beryllium (9.0121831(5))											5 B Boron (10.806(10.821))	6 C Carbon (12.0096(12.0116))	7 N Nitrogen (14.00643(14.00703))	8 O Oxygen (15.999(15.9997))	9 F Fluorine (18.9984031(3))	10 Ne Neon (20.1797(2))
11 Na Sodium (22.9897692(2))	12 Mg Magnesium (24.304(2.4.207))	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8		9 VIII 9	10 VIII 10	11 IB 1B	12 IIB 2B	13 Al Aluminum (26.9815386(6))	14 Si Silicon (28.085(28.086))	15 P Phosphorus (30.973761998(5))	16 S Sulfur (32.059(32.07))	17 Cl Chlorine (35.446(35.453))	18 Ar Argon (39.948(1))
19 K Potassium (39.0983(1))	20 Ca Calcium (40.078(4))	21 Sc Scandium (44.955912(6))	22 Ti Titanium (47.88(1))	23 V Vanadium (50.9415(1))	24 Cr Chromium (51.9961(6))	25 Mn Manganese (54.938045(5))	26 Fe Iron (55.845(2))	27 Co Cobalt (58.933194(4))	28 Ni Nickel (58.6934(4))	29 Cu Copper (63.546(3))	30 Zn Zinc (65.38(2))	31 Ga Gallium (69.723(1))	32 Ge Germanium (72.630(8))	33 As Arsenic (74.921595(6))	34 Se Selenium (78.9718(8))	35 Br Bromine (79.901(79.907))	36 Kr Krypton (83.798(4))	
37 Rb Rubidium (85.4678(3))	38 Sr Strontium (87.62(1))	39 Y Yttrium (88.90584(2))	40 Zr Zirconium (91.224(2))	41 Nb Niobium (92.90638(2))	42 Mo Molybdenum (95.94(1))	43 Tc Technetium (98)	44 Ru Ruthenium (101.07(2))	45 Rh Rhodium (102.90550(2))	46 Pd Palladium (106.42(1))	47 Ag Silver (107.8682(2))	48 Cd Cadmium (112.411(4))	49 In Indium (114.818(1))	50 Sn Tin (118.710(7))	51 Sb Antimony (121.757(3))	52 Te Tellurium (127.603(2))	53 I Iodine (126.90447(3))	54 Xe Xenon (131.29(1))	
55 Cs Cesium (132.90545196(3))	56 Ba Barium (137.327(2))	57-71 Lanthanide Series	72 Hf Hafnium (178.49(2))	73 Ta Tantalum (180.94788(2))	74 W Tungsten (183.84(1))	75 Re Rhenium (186.207(1))	76 Os Osmium (190.23(2))	77 Ir Iridium (192.222(1))	78 Pt Platinum (195.084(4))	79 Au Gold (196.966569(4))	80 Hg Mercury (200.59(2))	81 Tl Thallium (204.38(2.04.383))	82 Pb Lead (207.2(1))	83 Bi Bismuth (208.9804(1))	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222.018(4))	
87 Fr Francium (223)	88 Ra Radium (226)	89-103 Actinide Series	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 Ds Darmstadtium (267)	111 Rg Roentgenium (268)	112 Cn Copernicium (269)	113 Nh Nihonium (270)	114 Fl Flerovium (271)	115 Uup Ununpentium (272)	116 Lv Livermorium (273)	117 Uus Ununseptium (274)	118 Uuo Ununoctium (276)	
Lanthanide Series		57 La Lanthanum (138.90547(7))	58 Ce Cerium (140.12(1))	59 Pr Praseodymium (140.90768(2))	60 Nd Neodymium (144.242(3))	61 Pm Promethium (145)	62 Sm Samarium (150.36(2))	63 Eu Europium (151.964(1))	64 Gd Gadolinium (157.25(3))	65 Tb Terbium (158.9251(5))	66 Dy Dysprosium (162.500(1))	67 Ho Holmium (164.93032(2))	68 Er Erbium (167.256(1))	69 Tm Thulium (168.934(2))	70 Yb Ytterbium (173.054(1))	71 Lu Lutetium (174.967(1))		
Actinide Series		89 Ac Actinium (227)	90 Th Thorium (232.0377(4))	91 Pa Protactinium (231.03688(2))	92 U Uranium (238.02891(3))	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)		

Figure 1: The periodic table of elements with polonium and its homologues tellurium and livermorium highlighted in red.

Due to the almost identical electronic structure of the three atoms, the chemical and physical properties are found to be very similar. These similarities can be useful tools to study heavier elements' properties by comparing its characteristics to the lighter homologue, which calculations are generally easier to compute.

Two of the more basic and fundamental properties for any element are the ionization potential (IP) and the electron affinity (EA), which describe the energy needed to remove or add an extra electron to the valence shell, respectively. These energies give important insight in the electronic structure and reactivity of a given element, and are therefore needed to fully comprehend an element and its behavior. Due to their relevance to the characteristics of an element, the ionization potential and electron affinity energies can be used as benchmark values, where any deviation from these values can show influences in the calculations which are not taken into account appropriately. Predictions of these basic properties, based on theory and computational methods, are very important to consider before trying to obtain these values experimentally. These predictions can serve as a guideline for experiments, giving a sense of accuracy to the experimental values on which the experimental methods can be based. When no experiment is available yet, as for the EA of polonium and the IP and EA of livermorium, these predictions can also function as accurate reference values for other experiments and research in need of these values, and could help to predict other properties for elements that are not found in nature and are difficult to produce, as for livermorium.

When experiment has been done, as for the EA and IP of tellurium and the IP of polonium, it becomes interesting to look back at the predictions and see how accurate these were in order to investigate how well the used theories describe, and can predict properties of elements. This

organic back-and-forth between predictions and experiment is vital to eventually obtain the most accurate values, and is the main motivation for doing theoretical calculations.

In this paper different approaches to calculate the IPs and EAs of the three homologues are presented, starting with the computationally cheap Dirac-Hartree-Fock method and building up to coupled cluster calculations with single, double and perturbative triple excitations (CCSD(T)) with extensive basis sets and the first correction to the Coulomb repulsion. The significance of each of the different approaches are examined, as well as the influence of relativity on the three homologues with various atomic numbers.

Theoretical Background

The tools needed for calculating ionization potentials and electron affinities for any atom are the energy levels of the neutral, positively and negatively charged ions. The electronic energy is found as the eigenvalue of the electronic Hamiltonian, and by subtracting the electronic energies of the neutral and either the negative or positive ion, the electron affinity and the ionization potential, respectively, can be calculated. Determining the electronic energies of the different ions can be done in various ways, each with their own accuracies and computational costs. These accuracies depend on a lot of different factors such as the choice in basis set, which interactions between the electrons in the system are considered, which orbitals of the atoms are taken into account, and to what extent relativity is considered important in the calculations. All these methods together will contribute to the total accuracy of the calculations, but with the expansion to more accurate method also comes the increase in computational cost. The atom will be described as a many-electron system where the nucleus is placed and kept in the middle, the useful Born-Oppenheimer approximation, and will be subject to the methods described below.

Dirac-Hartree-Fock method

The Dirac-Hartree-Fock method (DHF), which is the relativistic variant of the Hartree-Fock method (HF), approximates the motion of electrons to that of a single-particle orbital that does not instantaneously depend on the motion of other electrons in the system [2]. The DHF method solves the electronic Schrödinger equation, which is constructed from the time-dependent Schrödinger equation while taking the Born-Oppenheimer approximation [3].

By taking the approximation that the n electrons in the system don't interact with each other, the electronic Hamiltonian will become separable and the total wavefunction transforms to the product of the n one-particle wave functions. The motivation behind this approximation is that the product of the one-particle wave function is a far easier tool to work with than the wave function of interacting electron functions [2]. The downside to this approximation is that now the total wave function doesn't satisfy the anti-symmetry principle anymore, meaning that a new form of the wave function is needed. The so-called Slater determinants are a good representation for the total wave function and describes all the wave functions from the n particles in one determinant

$$\Psi(x_1, x_2, \dots, x_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \cdots & \chi_n(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \cdots & \chi_n(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(x_n) & \chi_2(x_n) & \cdots & \chi_n(x_n) \end{vmatrix} \quad (1)$$

where $\chi(x) = \omega\psi(r)$, for which r are the electronic degrees of motion and ω is the generic intrinsic spin coordinate which can be either α or β [2].

Together with the fact that now the wave function satisfies the anti-symmetry principle, and therefore also the Pauli principle, each electron is also indistinguishable, meaning each electron is associated with each orbital, due to the functional form of the determinant [2].

The fact that the expression for the expectation value of the electronic energy is symmetric,

meaning the Hamiltonian is Hermitian, makes it possible to use the variational theorem, which states that the calculated energy is always an upper bound to the true energy [4]. We can therefore vary the parameters of the wave functions to minimize the electronic energy and therefore find (an approximation to) the true molecular orbitals.

The Hartree-Fock equation that defines the orbitals is given as

$$[h(x_1) + \sum_j J_j(x_1) - K_i(x_1)]\chi_i(x_1) = \epsilon_i \chi_i(x_1) \quad (2)$$

with ϵ_i as the energy eigenvalue of the orbital χ_i , $h(x_1)$ the one-electron integral, and where

$$J_i(x_1) = \int d\mathbf{x}_2 |\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1} \quad (3)$$

$$K_i(x_1) = \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_i(\mathbf{x}_2) \quad (4)$$

which are the Coulomb and exchange term respectively [2]. The Coulomb term gives the effect due to the average charge distribution of all the electrons in the system, and the exchange term arises from the anti-symmetrization of the Slater determinants and exchanges the orbitals χ_i and χ_j [3].

Combining the Coulomb and exchange term gives the the HF potential v_{HF} , which is given as

$$v_{HF}(x) = \sum_j J_j(x_1) - K_i(x_1) \quad (5)$$

and which is a one-electron mean-field potential that approximates the two-electron interaction [2]. The DHF method does not take into account any other electron-electron interactions outside of the HF potential, which reduces the accuracy of the calculations for the spin orbitals. Any electron-electron effect that is not within the DHF approximation is called the electron correlation and will reduce the DHF approximated energy. This is due to the fact that the approximation which says that the electrons only experience the mean field potential of the system treats the electrons as if they come closer to each other than in reality. This leads to more repulsion between the electrons, leading to higher energies, and thus leads to the fact that taking into account more electron-electron interactions than the DHF method, i.e. correlation, lowers the energy [5].

Even though the HF method is not accurate enough to approximate the energy levels of any atom, it is a useful tool to examine the electron configuration due to it relatively low computational cost.

Post-DHF

Correlation

Any electron-electron interaction that is not accounted for by the DHF method is called correlation. The DHF method treats the electron states of a system as a so-called 'filled Fermi sea' where all the electron shells are filled according to the Pauli exclusion principle [6]. According to this description, the many-particle system is approximated by an effective potential, describing the electrons as moving independently, only influenced by the mean electron movement of the system without any explicit electron-electron interaction [7].

A next step for a better approximation of the many-body system is the excitation picture, where the excitations placing electrons outside of the filled Fermi sea are taken into account. Two electrons could interact and lift (i.e. excite) each other above the initially occupied states, leaving holes in the deserted orbitals. Multiple excitations, double, triple or even higher numbers, could occur simultaneously and will influence the many-body system significantly [6].

Configuration-interaction method (CI)

One of the more straight-forward methods that describes electron-electron interactions beyond the DHF method is the Configuration-interaction method, which expands the HF determinants by including the single- and higher-excited determinants. Similar to the DHF method, the ground-state energy is found by minimizing the CI energy [8].

For relatively small systems of n particles, up to n -fold excitations can be taken into account, also called 'full configuration-interaction' (FCI), which gives rise to exact wave functions for the system within a given basis set. A downside to the CI method is that for larger systems, the FCI method is no longer computationally possible, leading to the necessity of not using all the excitation levels. By not including all the possible n -fold excitations, the systems is no longer 'size-consistent', meaning that the total energy of the system with n particles is no longer necessarily the sum of the total energy of all individual n particles [9].

Perturbation method

A size-consistent method for treating the excited states of the many-body system is the perturbation method, which determines the n -th order corrections to the ground state energy and the corresponding wavefunction starting with a zero-th order Hamiltonian which is perturbed by a perturbation operator \hat{V} multiplied by a coupling constant λ [8].

When the zero-th order Hamiltonian is chosen to be the HF Hamiltonian, the perturbation method is called the Møller-Plesset perturbation method, and the perturbation operator \hat{V} becomes the difference between the electron-electron Coulomb interaction and the HF potential v_{HF} [9]. The second order correction, MP2, describes the correlation energy for the system by taking into account only the double excitations of the electrons. The computational costs for this method are relatively low and thus serves this method as a cheap size-consistent post-DHF method.

Coupled cluster method (CCM)

One of the most accurate extensions of the HF method used in quantum chemistry is the coupled cluster method. This size-consistent method builds further on the HF wavefunction with the so-called exponential ansatz

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Psi_0\rangle \quad (6)$$

where $|\Psi_0\rangle$ is the HF wavefunction and \hat{T} is the cluster operator, which is the sum of all cluster operators of different excitation levels $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$ [8].

A single excitation can be described with \hat{T}_1 , indicating that one electron will get excited to get lifted outside of the initially occupied orbitals. Expanding the exponential representation of the cluster operators

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots \quad (7)$$

we can, after some rearranging, write the series as a sum of all the different excitation levels \hat{C} :

$$e^{\hat{T}} = 1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \dots \quad (8)$$

where

$$\hat{C}_1 = \hat{T}_1 \quad (9)$$

$$\hat{C}_2 = \hat{T}_2 + \frac{1}{2}\hat{T}_1^2 \quad (10)$$

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{1}{6}\hat{T}_1^3 \quad (11)$$

meaning that for example the second excitation level can be reached by either simultaneous excitations of two electrons, \hat{T}_2 , or two single excitations \hat{T}_1^2 .

Taking all excitations into account would actually just yield a nonlinear reparametrization of the FCI equation [8]. The gain in accuracy of the coupled cluster method comes from the fact that even if only the first two excitation cluster operators, \hat{T}_1 and \hat{T}_2 , are taken into account, the wavefunction will contain much more excited states than the CI wavefunction, still remaining size-consistent [7].

A downside to the CC method is the fact that in contrary to the DHF method, the coupled cluster energies are not necessarily upper bounds to the true energy, i.e. the energies do not follow the variational theorem [10]. This follows from the fact that the Hamiltonian operator \hat{H} in the formula for the CC energy

$$E_{CC} = \langle 0 | \hat{H} | 0 \rangle, \quad \hat{H} = e^{-\hat{T}} H e^{\hat{T}} \quad (12)$$

is not Hermitian, meaning that the expectation value above is asymmetric and does not follow the Hellmann–Feynman theorem necessary for the variational theorem [9, 10]. Even though the variational method is an approximation that does not hold for the coupled cluster method, using the CC method with double or triple excitation levels by minimizing the coupled cluster energy can give accurate results for relatively non-complex systems such as atoms [9]. Increasing the amount of excitations that are taken into account leads to more accurate calculations due to the fact that it is a more realistic description of the system, but also comes with the price of more computational costs. For the calculations done in this paper, up to perturbative triple excitations have been used, which is called the CCSD(T) energy, which means that the single and double excitations are fully treated, where on the other hand the triple excitations are approximated by perturbative theory.

Basis functions

A basis set in this context is defined as the set of non-orthogonal single-particle functions that can be used to describe a many-particle system. Using an appropriate basis set reduces the computational time and increases the accuracy of the calculations significantly [6]. For an accurate calculation of a many-electron system, basis sets of appropriate size and quality need to be considered. Basis sets can consist of different types of basis functions, usually being either Slater- or Gaussian-Type-Orbitals, STO and GTO respectively, which operate in different ways because of their distinct exponential dependence on the distance to the nucleus r

$$\begin{aligned} \phi_{STO} &= N x^a y^b z^c e^{-\zeta r} \\ \phi_{GTO} &= N x^a y^b z^c e^{-\zeta r^2} \end{aligned}$$

where $a + b + c = L$, L being the angular momentum, N the normalization factor and ζ determines the width of the orbital [3].

The STO's are more accurate with respect to the actual atomic orbitals due to the fact that they share the same r -dependence, but are far more difficult to compute compared to the Gaussian functions [11]. A solution to describe the atomic orbitals as accurately as possible with reasonable computational time is to approximate the computational heavy STO's by a linear combination of GTO's, which is the most common way to use basis sets and an example of approximating an STO with increasing amounts of GTO's can be seen in figure 2.

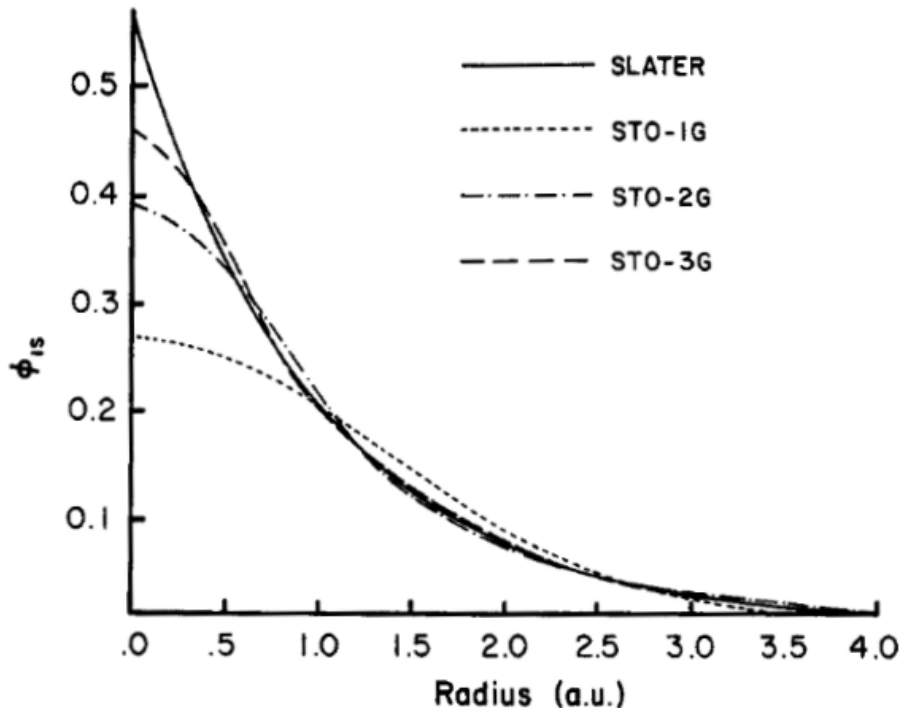


Figure 2: A combination of GTO's, called STO- n G, where n is the amount of GTO's, approximating an STO for different values of n [12].

The fact that the Gaussian functions follow the Gaussian-functions product rule, which describes a product of Gaussian functions as another Gaussian function centered on a different point, decreases the computational time significantly, which makes another argument for using the linear combination of GTO's [3].

Increasing the amount of GTO's per atomic orbital increases the accuracy of the calculations, but will also increase the amount of computational time by $\approx N^4$ where N is the amount of basis functions used [11]. Using only one GTO per orbital is called the minimal basis set, which can be expanded by increasing the amount of GTO's per orbital to two, three or more, which are called double-zeta, triple-zeta or higher orders of zeta respectively. Because the core orbitals, i.e. the orbitals closest to the nucleus, are not contributing that much to the electronic states, especially for heavier elements, it is also possible to use the so-called split-valence basis. The 'split' indicates that there is a difference in basis functions used for the core orbitals and the outer orbitals which will make up the valence electrons. To reduce computational costs, a minimal basis is used for the core orbitals, but a higher order basis can be applied to the valence orbitals [3].

To account for electrons that are in orbitals relatively far from the nucleus, diffuse functions are an important element to include in the basis sets. A diffuse function has a small ζ -value, making the orbital very wide, and including these in the basis set means taking one of these functions into account for every different angular momentum state that is used in the basis set. For a basis set consisting of s , p and d orbitals this would mean three added diffuse functions, denoted by the "aug-" prefix in the name of the basis function.

Relativity

Increasing with the atomic number Z , the influence of relativity changes the mass of the electrons to a higher value due to the higher velocities the electrons orbit the nucleus with [5]. A consequence of this is the fact that the orbitals of the electrons split up, also called spin-orbit splitting, based on their angular momenta [13]. The p -shell will split up in a $p_{\frac{1}{2}}$ - and a $p_{\frac{3}{2}}$ -shell, which hold two

and four electrons respectively whereas the d -shell, for example, will split into three shells, with angular momentum values ranging from $\frac{1}{2}$ to $\frac{5}{2}$.

The effect of relativity is different for the different electron shells, depending on how close the electrons come to the nucleus. The close s - and $p_{\frac{1}{2}}$ -shells will contract, meaning they will be closer to the core and will have a more efficient screening from the positive charge in the center of the atom. The $p_{\frac{3}{2}}$ -, d - and f -shells, and all other shells with higher angular momentum, are affected in an opposite way, where these shells will expand away from the nucleus and will, contrary to the low angular momentum shells, destabilize. This is not a direct effect of the higher velocities of the electrons, but is mostly due to the indirect consequence that because of the better screening by the close-lying electrons, the outer shells are shielded more effectively from the charge of nucleus, and will therefore become less bound to the core [5].

Hamiltonians

An important decision that has to be made before doing any calculations on a many-body system is the choice of the Hamiltonian. The most generic Hamiltonian used to describe the electrons in a given system is the electronic Hamiltonian, satisfying the Born-Oppenheimer approximation

$$H = \sum_i \hat{h}(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_{NN} \quad (13)$$

where V_{NN} is the classical repulsion part and \hat{h} and \hat{g} are the one- and two-electron parts of the Hamiltonian respectively [13].

As mentioned above, for heavier atoms it is necessary to account for the relativistic effects to get the most accurate results, and it is therefore needed to transform the non-relativistic electronic Hamiltonian into a relativistic one. This is done by using the relativistic energy $E^2 = m^2c^4 + p^2c^2$ instead of the classical one, and quantizing it, obtaining the time-independent Dirac equation which accounts for the relativistic effects

$$[\beta mc^2 + c(\boldsymbol{\alpha} \cdot \mathbf{p})] \Psi = 0 \quad (14)$$

$$\Psi = \begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix}, \quad \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix} \quad (15)$$

where α and β are the Dirac matrices, consisting of Pauli and identity matrices, see equation 16, and Ψ^L and Ψ^S are the large and small components of the wavefunction respectively [13].

$$I_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (16)$$

Because the Hamiltonian is quantized to get turned into the Dirac equation, the negative energy-values are not possible to disregard anymore. This is due to the fact that in classical mechanics the negative-energy values could be disregarded as non-physical because the energy could only change in a continuous way. With the influence of quantum mechanics also comes the possibility of quantum leaps, a discontinuous change in energy, and hence the negative values of the energy become a physical possibility [13]. The difference between the non-relativistic and the four-component Hamiltonian is that first of all that the one-particle component of the electronic Hamiltonian transforms from a scalar operator to a 4x4 matrix operator, and secondly that the first correction to the Coulomb term, i.e. the Breit term, splits into a Gaunt and a gauge term. [13].

Breit corrections

Describing the electron-electron repulsion only using Coulomb's law will, especially for heavier atoms, not be sufficient to make precise calculations on the electronic structure of many-electron systems [14]. The first order correction on the Coulomb repulsion is called the Breit correction and accounts for magnetic interactions, also called the Gaunt term, and retardation effects. Because even for heavy elements the magnetic term dominates the retardation effect, usually only the magnetic part of the correction is used which also simplifies the correction [15]. The Breit corrections are mostly focused on the exchange interaction between core and valence electrons because the interactions between valence-valence and core-core electrons are of a significantly low order that they will not affect the calculations for heavy atoms [13].

Dirac-Coulomb Hamiltonian

The most standard four-component Hamiltonian used is the Dirac-Coulomb Hamiltonian (DCH), which is a combination of the Dirac Hamiltonian h_D and the electron-electron Coulomb operator g^C , where

$$h_D = \beta' mc^2 + c(\boldsymbol{\alpha} \cdot \mathbf{p}) + V, \quad \beta' = \beta - I_4 \quad (17)$$

$$g^C(1, 2) = \frac{e^2}{r_{12}}. \quad (18)$$

with $V = -e\psi_{nuc}$, where ψ_{nuc} is the electrostatic potential of clamped nuclei and e is the elementary charge [13].

To use the DCH in an appropriate way, it is necessary to first of all use a finite nucleus model, where in contrast to non-relativistic calculations the nucleus is not seen anymore a point charge, but rather has a finite size. This gives a better description of the nucleus and gets rid of some of the singularities in the electronic wave function caused by using a point-charge nucleus in the relativistic domain [13]. Another important aspect to take into account for the DC Hamiltonian is the coupling of the large- and small-components of the Dirac equation

$$\Psi^S = R\Psi^L, \quad R(E) = \frac{1}{2mc} B(E)(\boldsymbol{\sigma} \cdot \mathbf{p}) \quad (19)$$

$$B_+(E) = \left[1 + \frac{E^+ - V}{2mc^2} \right]^{-1}, \quad B_-(E) = \frac{2mc^2}{E^- - V} \quad (20)$$

where E^+ and E^- account for the positive- and negative-energy solutions respectively. Equation 19 shows the coupling relation between Ψ^S and Ψ^L , which are related by the coupling parameter R , and also illustrates that for the positive-energy solutions the small- and large-components differ in a factor c , which also explains their names [13].

The so-called *continuum dissolution* associated with the DC Hamiltonian states that there are no bound solutions for the DCH due to the fact that the electron-electron repulsion V_{NN} has nonzero matrix elements between positive- and negative-energy eigenfunctions of h_D [16]. The problem arises from the fact that the negative-energy solutions are taken into account which causes both the positive- and negative-energy determinants to appear in the Slater determinant basis sum [13]. The fact that there are no bound states for this Hamiltonian, also called the Brown–Ravenhall disease, can be prevented with the use of projecting operators which get rid of determinants containing the negative-energy orbitals [13].

Using the DC Hamiltonian gives rise to the splitting of m_j -levels, also called the spin-orbit interaction, which is a consequence due to the relativistic effects that are accounted for by using a relativistic Hamiltonian. The splitting of the energy levels is reduced when introducing the Gaunt term due to the fact that this results in the appearance of the spin-other-orbit interaction [13]. Together with the spin-same-orbit interaction, the spin-other-orbit interaction arises from the two-electron part of the DC Hamiltonian and is solely derived from the Gaunt term of the Breit correction [13].

Exact two-component Hamiltonians

Instead of using a four-component relativistic Hamiltonian, a two-component Hamiltonian can also be used for relativistic calculations, where contrary to the four-component one, the two-component Hamiltonian only produces the positive-energy spectrum of the four-component Hamiltonian [13]. The exact two-component (X2C) Hamiltonian is based on the method of using the initial four-component Hamiltonian and obtaining its solutions for the one-electron part in a matrix form. To get the exact coupling of the large- and small-components from the one-electron solutions, only matrix algebra is needed which will not require any solving of integrals, making it computational cheap. After gaining the exact coupling, the X2C-Hamiltonian can be constructed by decoupling the large- and small- components [13]. The X2C is a good alternative to the four-component Hamiltonian due to the fact that it is significantly more accurate than a non-relativistic approach, but still requires considerably less computational power.

Computational details

To obtain the ionization potential and the electron affinity of the desired atoms, the energy levels of the neutral, positive and negative ions of the different atoms have to be calculated. These calculations have been performed with the Dirac program which makes it possible to use various approaches to get the desired energies [17].

First, the DHF energies of all the ions have been calculated, giving an insight in the different occupied orbitals of the ions, which are needed to select appropriate orbitals for the coupled cluster calculations. After the occupied orbitals have been obtained, a few different coupled cluster calculations have been done, with varying basis sets, Hamiltonians and orbitals that have been taken into account. Non-relativistic and X2C Hamiltonians have been used to compare the effect of relativity for the three different atoms, with very different atomic numbers. To use a non-relativistic Hamiltonian for the coupled cluster calculations, the value for the speed of light c has been manually set to a much higher value, namely 10000 atomic units, instead of the ≈ 137 atomic units that it is normally, replicating a non-relativistic environment where relativistic effects are small. Lastly, the Gaunt-corrections have been taken into account to observe its influence for the different atoms.

The basis sets used for the calculations are the sets that have been developed by K.G. Dyall, which are denoted as "dyall..." basis sets in the Dirac program. The dyall basis sets already include polarization functions and can be used to do relativistic calculations, and can be expanded from a double-zeta to a quadruple-zeta basis with the options of using extra diffuse functions, denoted as *n-aug-...*, where the n can either be s for singly, or d for doubly, which means either one or two diffuse functions are used per outer orbital [17, 18]. The last option for the choice in basis set is either using the valence, core-valence or all-electron basis set, which shows how the basis functions are distributed over the orbitals. The valence basis set assigns extra functions to the valence shells, the core-valence basis set does the same but also assigns more functions to the core orbitals, and the all-electron basis set includes extra functions for all shells of the system [18]. The order in which these types of basis sets are described here also shows the order of extensiveness, where the valence basis set assigns the least amount of functions, and the all-electron basis set would generate the most accurate results, with of course also the highest computational time. In order to obtain a sense of accuracy of the calculations, the uncertainties for the all-electron

basis set calculations of Te and Po have been determined using three sources of uncertainty: the incompleteness of the basis sets, and both the QED influences and the high excitations of the coupled cluster method that have not been taken into account. To construct the uncertainty of the used basis set, the DHF and correlation energies from the CCSD(T) calculations have been extrapolated separately to investigate their convergence-behavior towards the complete basis set (CBS) limit. The complete basis set energy is the energy obtained in the limit of using an infinitely large basis set, which shows an indication of how large the basis needs to be in order to get its fully converged value. After extrapolating the two different energies, the difference between these values and the fully converged ones can be found. This difference between the CBS energy and the calculated energy will be used as the uncertainty of not using a large enough basis set and will be of the order of 10 to 100 meV, and will decrease when using more extensive basis sets.

The lack of taking into account the high-order QED influences can be compensated by an uncertainty of 0.003 eV, whereas the lack of high order excitations that are not considered in the CCSD(T) calculations can be accounted for by an uncertainty of 0.004 eV, which was found in a similar study on CCSD(T) energies [19]. All the different uncertainties will be added up to obtain the total uncertainty, which will differ for each calculation due to the fact that it is dependent on the size of the used basis set.

Results

A variety of calculations have been performed for the ionization potentials and the electron affinities of the three different homologues Te, Po and Lv. These calculations differ in the use of basis sets, extra Gaunt corrections, the electronic orbitals that have been taken into account and the three different types of Hamiltonians concerning relativity: the four-component, the two-component and the non-relativistic Hamiltonians. In order to demonstrate the influence of each of these parameters, the results section will show each variation in comparison to the most accurate calculations for each individual atom, which are the quadruple-zeta all-electron basis set calculations with doubly augmented diffuse functions (d-aug-ae4z) for Te, the quadruple-zeta all-electron basis set with singly augmented diffuse functions (s-aug-ae4z) for Po, and the quadruple-zeta valence basis set with doubly augmented diffuse functions for Lv, all with extra Gaunt corrections, all orbitals taken into account and using the four-component relativistic Hamiltonian. These calculations are the most accurate in the sense that they were the most extensive and realistic calculations that were possible to run, with the largest basis sets possible for each element.

Table 1: The most accurate CCSD(T) IP calculations in eV.

	ae4z	Uncertainty	s-aug-ae4z	Uncertainty	d-aug-ae4z	Uncertainty	Reference
Te	9.018	0.1	9.045	0.08	9.057	0.05	9.010 [20]
Po	8.358	0.1	8.395	0.07	-	-	8.418 [21]
	v4z	Uncertainty	s-aug-v4z	Uncertainty	d-aug-v4z	Uncertainty	Reference
Lv	6.760	-	6.780	-	6.781	-	6.848 [22]

Table 2: The most accurate CCSD(T) EA calculations in eV.

	ae4z	Uncertainty	s-aug-ae4z	Uncertainty	d-aug-ae4z	Uncertainty	Experiment
Te	1.857	0.1	1.920	0.03	1.936	0.03	1.971 [23]
Po	1.363	0.1	1.435	0.04	-	-	1.464 [22]
	v4z	Uncertainty	s-aug-v4z	Uncertainty	d-aug-v4z	Uncertainty	Experiment
Lv	0.604	-	0.730	-	0.734	-	0.773 [22]

The all-electron basis set could not be used for the calculations for Lv due to the fact that the superheavy element was too big of a system, making the computational costs too high to run within reasonable time. This made it necessary to use the less accurate valence basis set for Lv, and also caused the fact that the calculations needed for the uncertainties of Lv were not possible to run within the available time. This was unfortunately also the case for the d-aug-ae4z calculations for polonium, where the system was found to be too massive for the calculations when including the extra diffuse functions.

The most accurate results including uncertainties are listed in tables 1 and 2, where the reference values are the experimental values for tellurium and the ionization potential of polonium, whereas the electron affinity of polonium and both the ionization potential and electron affinity for livermorium have reference values obtained by similar calculations done by Borschevsky et al. [22].

The reference values are included within the measured values and their uncertainties for the IP and EA calculations of Po and the IP calculations for Te. The IP calculations for Te and Po therefore show good agreement with the experimentally obtained values, while the EA values for Po were found to be similar to its reference value. The results for the IP and EA of Po can also be seen in figures 3 and 4.

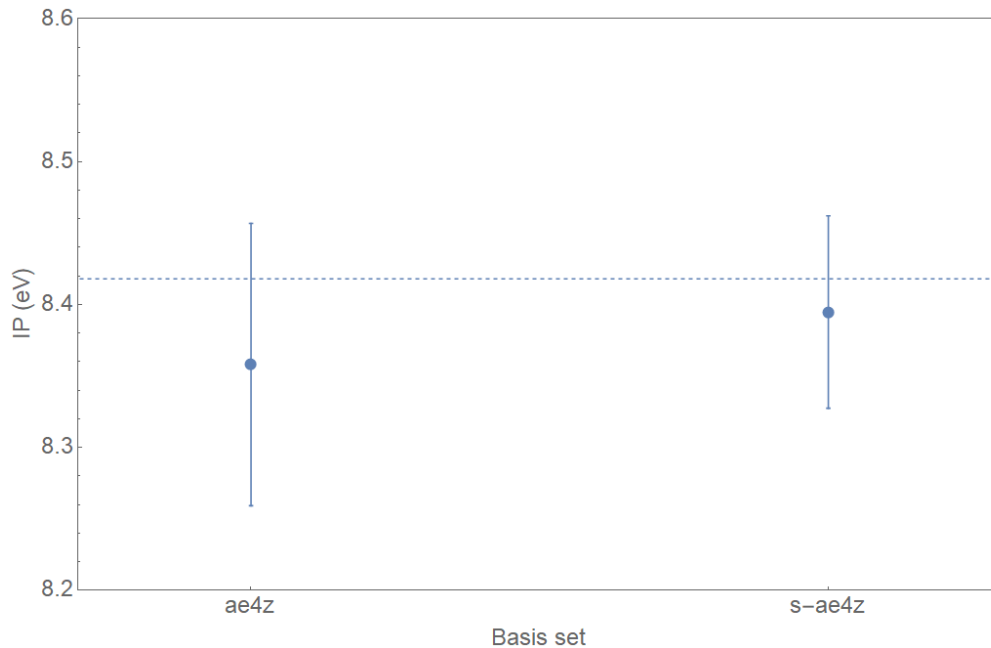


Figure 3: The most accurate ionization potential calculations for polonium, with and without diffuse functions. The dotted line is the value of the experimentally obtained value.

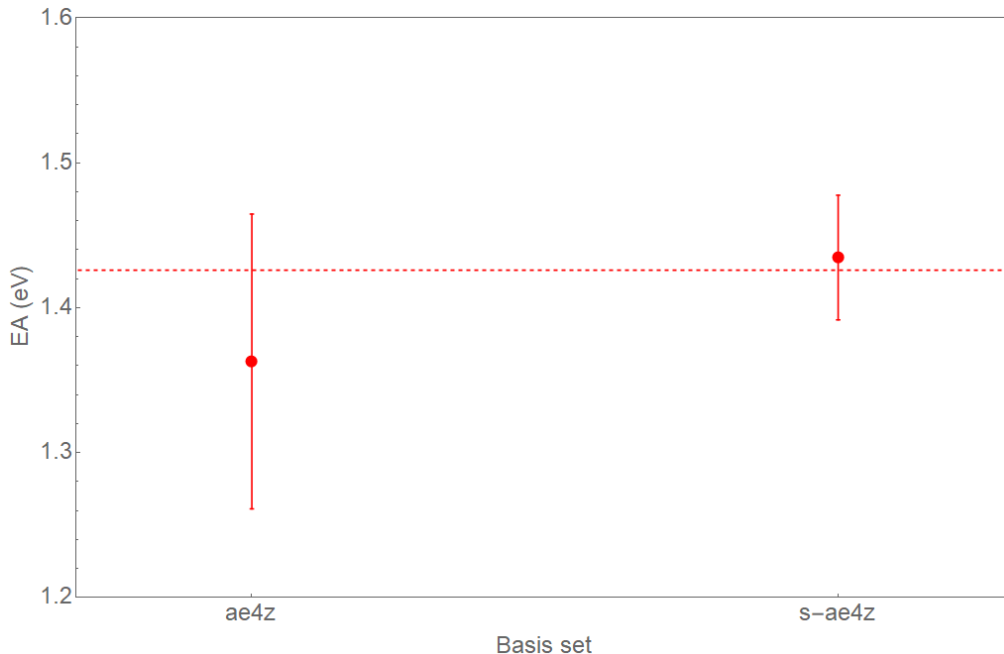


Figure 4: The most accurate electron affinity calculations for polonium, with and without diffuse functions. The dotted line is the value of the EA obtained by similar calculations done by Borschevsky et al. [22].

The calculations for the EA and IP of Lv and the EA of Po were performed with more extensive basis sets than the ones used for the reference values of Borschevsky et al., and are therefore found to be more accurate than these previous calculations. Another difference between the reference calculations and the calculations presented in this paper is the fact that the calculations for the reference values only took orbitals into account above an energy of -50 atomic units, while the values in tables 1 and 2 were obtained by taking into account all orbitals. The possible effect of this will be discussed in the section *Orbitals + Gaunt*.

The augmented EA calculations for Te resulted in deviating values from the experimental ones when including its uncertainties. This indicates that either the used calculations were not accurate enough, or that more uncertainties need to be taken into account to compensate for the lack of accuracy. No particular anomalies were found in these calculations that would indicate a systematic error, which makes the deviation from the experimental EA values interesting considering the fact that the same kind of calculations were run for all three homologues. Only when the EA of polonium will be calculated experimentally, it becomes possible to check whether or not the EA calculations for Po would actually also deviate from the experimental values, giving more insight in how accurate the computational methods and theories describe the electron affinity.

DHF vs. CCSD(T)

The first considered variable that significantly influenced the results for all three atoms was the choice in either using the DHF method or the coupled cluster approach with in this case taking into account up to triple excitations. It was found that the CCSD(T) results were a lot closer to the experimentally obtained values than the DHF results, as is seen in table 3, where for example the DHF values for Lv deviated 66 times more from the reference values than the CCSD(T) ones. This is of course not surprising considering that the CCSD(T) calculations could take up more than a thousand times the computational time of a DHF calculation due to the correlation that is taken into account, which makes the CCSD(T) calculations much more accurate. Table 3 also shows that the deviation of the DHF calculations from the CCSD(T) ones increases with increasing

atomic number: the IP deviations for the DHF energy compared to the CCSD(T) values increase with approximately an order of magnitude per homologue.

	IP (eV)					EA (eV)				
	DHF	Error	CCSD(T)	Error	Ref	DHF	Error	CCSD(T)	Error	Ref
Te	8.926	0.07%	9.057	0.05%	9.010	1.694	14%	1.936	1.8%	1.971
Po	8.584	1.8%	8.395	0.4%	8.426	1.707	16.6%	1.435	2%	1.464
Lv	8.801	22.8%	6.781	4.7%	6.848	2.554	330%	0.734	5.1%	0.773

Table 3: A comparison between the DHF, CCSD(T) and reference values, where the errors listed in the table are the deviations from these reference values. The CCSD(T) results are the the most accurate calculations for the three homologues, as seen in tables 1 and 2.

Different basis sets

The results from the calculations with different basis sets also varied significantly with respect to the most accurate and reference values. The results for polonium can be seen in table 4, where double-, triple- and quadruple-zeta basis sets were used to compare the results for the valence, core-valence and all-electron basis sets for the CCSD(T) calculations, including singly- and doubly-augmented diffuse functions for the quadruple-zeta variations.

Po	2z	3z	4z	s-aug-4z	d-aug-4z	Reference
Valence	-	8.224	8.352	8.362	8.363	8.418
	-	1.187	1.370	1.428	1.428	1.464
Core-valence	8.031	8.229	8.360	8.387	8.402	8.418
	0.604	1.185	1.366	1.438	1.447	1.464
All-electron	8.032	8.227	8.358	8.295	-	8.418
	0.604	1.181	1.363	1.435	-	1.464

Table 4: A comparison between the results from different basis sets for Po, where all values are the CCSD(T) values.

The table shows that the CCSD(T) values for the different basis sets always increase for more extensive basis sets, meaning that in this case the higher the value, the more accurate it seems to be. This is not an unusual result due to the fact that calculations with more expanded basis sets always tend to converge toward the CBS value, and therefore the calculations with increasing n-tuple-zeta values will never be higher than the CBS limit but will more and more slowly come closer to this theoretical value [24].

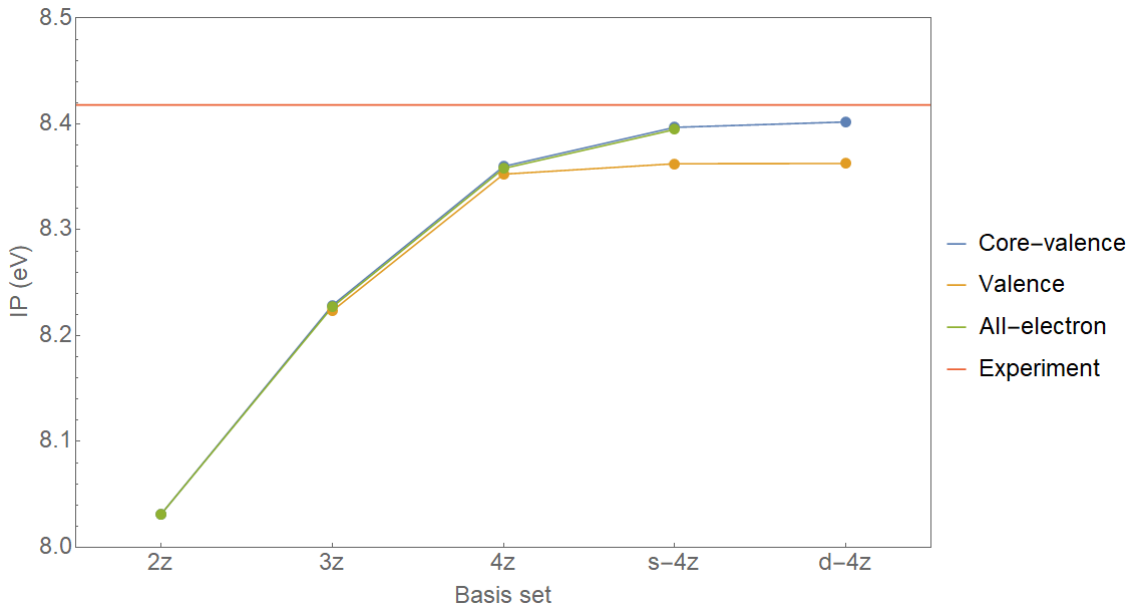


Figure 5: The most accurate ionization potential calculations for polonium, with and without diffuse functions. The dotted line is the value of the experimentally obtained value.

Figure 5 shows the results from table 4 in a graph, where the differences between the three types of basis sets are displayed more clearly, and is also compared to the experimental value. It can be seen from this figure that the values for the core-valence and all-electron basis sets are almost similar, whereas the valence basis set deviates significantly from these values. This indicates that taking into account extra functions for the core orbitals, which are included in the core-valence and all-electron basis sets, are important when trying to obtain the most accurate results, and lead to significantly different values closer to the experimental one. The same holds for the use of diffuse functions, where especially for the core-valence and all-electron sets the results move significantly closer to the experimental reference value when including more diffuse functions.

Relativistic effects

The biggest divergence from the most accurate and reference values comes from the non-relativistic calculations, as can be seen in table 5, which gave significantly higher values than the four-component calculations. The two-component results on the other hand were very similar to the four-component calculations, with only slight deviations.

	IP (eV)				EA (eV)			
	NR	X2C	4c	Ref	NR	X2C	4c	Ref
Te	10.256	8.945	8.946	9.010	2.116	1.924	1.922	1.971
Po	9.796	8.368	8.363	8.426	2.131	1.434	1.429	1.464
Lv	9.163	6.784	6.781	6.848	2.127	0.738	0.734	0.773

Table 5: A comparison between the non-relativistic (NR), two-component (X2C), four-component (4c) and experimental CCSD(T), where the four-component values are the most accurate d-aug-v4z values for all the different atoms.

The influence of relativity can be seen in table 5 and can be explained by using the theory discussed before: the $p_{\frac{3}{2}}$ shell, which is the valence shell for all three homologues, destabilizes due to stabilization of the s - and $p_{\frac{1}{2}}$ -shells which shield the $p_{\frac{3}{2}}$ -shell from the nucleus, decreasing the amount of attractive force experienced by the $p_{\frac{3}{2}}$ -shell. This causes the fact that both the EA and IP decrease when taking into account relativity, which can be seen in table 5, because first of all less energy is needed to remove one electron from the destabilized valence shell, meaning a lower IP, and secondly it becomes harder to place an extra electron in the valence shell due to the fact that the attractive force from the nucleus decreases, making the electrons less bound than without any relativistic effects, meaning the EA decreases as well.

The results in table 5 also show the increase in relativistic effects for elements with higher atomic numbers: where the non-relativistic values for the IP of Te are still within a 15% range from the four-component values, the non-relativistic results for Lv deviate more than 25% from the four-component calculations. The two-component approach results in values that are a lot closer to the four-component values, and is therefore a well-suited computationally cheap replacement to the four-component calculations, without a great loss in accuracy.

Orbitals + Gaunt

Variables that did not make a significant impact on the results were first of all the orbitals that were chosen to take into account, and secondly the use of extra Gaunt corrections. In the Dirac program it was possible to choose a cut-off energy where no orbitals would be considered if their energy would be below this value. To investigate whether or not this cut-off value would influence the results, calculations were performed with no orbitals considered below -30 atomic units, the first and fifth column in table 6, and with a cut-off low enough that all orbitals were considered for each element, as can be seen in the second and sixth column from table 6. The cut-off energies needed for all orbitals to be taken into account varied for the three homologues due to the fact that the heavier elements had more low-energy orbitals.

	IP (eV)				EA (eV)			
	-30 au	-1200 au	Gaunt	Ref	-30 au	-1200 au	Gaunt	Ref
Te	8.949	8.947	8.947	9.010	1.923	1.922	1.922	1.971
	-30 au	-3600 au	Gaunt	Ref	-30 au	-3600 au	Gaunt	Ref
Po	8.360	8.363	8.363	8.426	1.426	1.428	1.428	1.464
	-30 au	-8000 au	Gaunt	Ref	-30 au	-8000 au	Gaunt	Ref
Lv	6.778	6.780	6.781	6.848	0.733	0.734	0.741	0.773

Table 6: A comparison between energy levels taken into account and for the use of extra Gaunt functions, where all calculations were performed with the d-aug-v4z basis set.

It was found that changing the cut-off energy had a relatively small impact on the results, where the **-30 au** values only deviated in the order of 0.01% from the calculations with all orbitals considered, even though the increase in computational time was significant. This shows that the orbitals with energies below -30 atomic units don't significantly influence the electronic energy calculations for both the IP and EA, and are less important to take into account when also considering the added computational time.

Another variation was done by doing the same IP and EA calculations as for the most accurate ones, changing only the fact that this time no extra Gaunt corrections were used, while still taking all orbitals into account, i.e. **Gaunt** columns in table 6. These extra corrections to the Coulomb repulsion should in theory increase the accuracy of the calculations due to the fact that it gives more accurate descriptions of the spin-orbit splitting [18], but it was found that adding these corrections did not make a significant change to the results. It can be seen in table 6 that the only

results which are influenced by the Gaunt corrections with an order of magnitude above 0.1 meV are the values for Lv, which deviate slightly from the calculations that didn't take into account the Gaunt corrections. The fact that a considerably amount of extra time is needed for the calculations with the Gaunt corrections with only a relatively small increase of accuracy makes taking into account these corrections, like the orbitals below -30 atomic units, less essential to consider for the calculations compared to the choice in basis set and the relativistic effects taken into account.

Conclusion

The ionization potentials and electron affinities for polonium, tellurium and livermorium, including their uncertainties, have been calculated using the DHF method and the CCSD(T) approach, and have been compared with reference values ranging from the experimental values for Te and the IP of Po, to the values from similar calculations performed by Borschevsky et al. for Lv and the EA of Po. Different aspects of the calculations, such as relativity, choice of basis set and corrections to the Coulomb repulsion have been varied to obtain the influence of each of these variables on the results. It was concluded that the choice in basis set and the degree of relativity considered had a significant impact, where on the other hand the inclusion of extra Gaunt corrections and taking into account orbitals below -30 atomic units seemed to not substantially change the results.

Non-relativistic calculations demonstrated the importance of relativity on the results, especially with increasing atomic number, showing that for all homologues the values for the IPs and EAs deviated significantly from the four-component values when relativity was not considered. This deviation was found to be less significant for the two-component calculations, which could be performed in significantly less time with only a slight loss in accuracy. It was found that the EAs and IPs for all homologues decreased when taking into account relativistic effects due to the fact that the $p_{\frac{3}{2}}$ -shell, which is the valence shell for all the homologues, destabilized and got further away from the core due to relativity, causing the electrons to be less bound by the attractive force from the nucleus.

Double-zeta basis set calculations turned out to be not accurate enough for computing the IPs and EAs properly, where the difference between the valence basis set and the all-electron basis set calculations was also found to be significant. The results showed that including extra basis functions in the orbitals closer to the nucleus as well as for the valence shells, i.e. the core-valence and all-electron basis sets, increased the accuracy of the results compared to the calculations where only extra functions for the valence shells were used, which was the case for the valence basis set. The same was found for including diffuse functions, where the results from the calculations which included two diffuse functions per outer orbitals, i.e. the doubly-augmented (d-aug) basis set, were significantly more accurate compared to the values obtained without using any diffuse functions.

The most accurate results were therefore obtained by using the d-aug-ae4z basis set for the calculations of Te, and, unfortunately due to a lack of time, the d-aug-v4z basis set for Lv and the s-aug-ae4z basis set for Po, using a four-component Hamiltonian for all three homologues. The calculations could still be improved by taking into account more extensive basis sets, not only for Po and Lv, for which the most accurate basis sets from the Dirac program were not used yet, but also for Te, where the comparison between the the most accurate value and the CBS energy showed that increasing the basis set even more would still benefit the accuracy of the calculations. Including higher excitations than the triple excitations used for the CCSD(T) method, as well as taking into account more QED corrections could also improve the results considerably, giving more insight in their significance and how accurate the approximated uncertainties used in this paper were compared to their real values.

Besides the EA of Te, all the values for Te and Po included their reference values with their uncertainties, which showed that the results were of a high quality compared to these reference values. The values for the EA of Po and the EA and IP of Lv were even found to be more accurate in comparison to the results from Borschevsky et al. due to the fact that more extensive basis sets were used. The fact that the results for the EA of Te deviated from the experimental values does

indicate that this could also be the case for the EAs of Po and Lv, for which even less accurate calculations were performed. The fact that the ionization potential calculations showed accurate agreement with the experimental values of Te and Po would on the other hand indicate that the similar calculations performed for Lv would be a good representation of reality. This could be investigated by doing more accurate calculations, or by experimentally obtaining the values for these heavier homologues. These predictions therefore serve as important tools for first of all understanding the properties of elements where no experiments are available in the near future, as is the case for Lv. Secondly, they can give values which can work as guidelines for upcoming experiments like the determination of the electron affinity of polonium, and lastly, after experiments have been performed, these theoretical predictions can give insight in the computational methods and theories used to obtain these values, possibly improving their accuracy when deviation from experiment is found.

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