

RIJKSUNIVERSITEIT GRONINGEN

BACHELOR RESEARCH PROJECT

# Electronic structure of element 123

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### Abstract

We compare the energies of different electronic configurations to determine the ground state of element 123 using a relativistic coupled cluster approach. We consider some predictions by others and make some predictions ourselves, and conclude that we can limit the possibilities to two configurations,  $[118]8s^26f^17d^18p^1$  and  $[118]8s^28p^3$ . We also explore the performance of different computational approaches and different basis sets by doing calculations on the ionization potentials of the group 2 elements. We find that the CCSD and CCSD(T) calculations have a much higher accuracy than the HF calculations, and that there is little difference between the pvdz, pvtz, and pvqz basis sets. We also find that there is little difference between relativistic X2C and 4c calculations, while both are much more accurate than non-relativistic calculations. Furthermore, we investigate the influence of relativity on the first and second ionization potentials of the group 1 elements. We find that relativistic calculations lead to a much higher accuracy for the first IP, but that they do not change much for the second IP.

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## Introduction

Recently, the International Union of Pure and Applied Chemistry (IUPAC) announced that it decided on the names for elements 113 (nihonium), 115 (moscovium), 117 (tennessine), and 118 (oganesson) [1]. This means that all 118 elements in the periodic table are now named. Of these elements, only the first 94 are known to exist in nature. The elements that do not appear in nature can still be created. This can happen in a particle accelerator or a nuclear reactor, where a beam of atoms is aimed at some other atoms. If two of these atoms collide, it is possible that they “stick” together and form a new atom. Then, the decay of this atom or its decay products can be detected, which verifies that the element was indeed produced. Elements heavier than uranium ( $Z = 92$ ) are commonly referred to as heavy elements or transuranium elements, and those heavier than lawrencium ( $Z = 103$ ) are known as superheavy elements.

Very little is known about the chemical properties of the heavy and superheavy elements. It takes a lot of money, time, and effort to create them, and their short lifetimes make them difficult to observe. Elements with  $Z > 118$  have never even been produced, which means that all we know about them, which is very little, comes from theory.

Because so little is known about the properties of these elements, it is important to have accurate theoretical predictions, so that scientists who do experiments know what they are looking for, and where they might find it. Theoretical predictions are also important to obtain fundamental knowledge about these elements, since not everything can be done with experiments.

The most fundamental electronic property of an element is its ground state. Knowing the ground state of an element allows us to place it in the periodic table. This is important, because we can then identify the (lighter) homologs of our new element. Some properties of our new element might be related to the properties of its homologs. It also allows us to predict how the element would interact with other elements, since this depends partly on the electron distribution in the outer shells of the atom. Furthermore, we can predict which compounds the element is likely to form. Lastly, when we have the ground state of an element, we are in a much better position than before to determine its first ionized state. If we have the ground state and the first ionized state, we can determine the ionization potential.

We are interested in determining the ground state of element 123, partly because of the reasons listed above, and partly because so far, no elements beyond element 122 have been studied with high accuracy.

There already exist predictions for the ground states of the elements with  $Z > 118$ . For element 119, Fricke et al. predict a ground state of  $[118]8s^1$  using Hartree-Fock calculations [2]. Pyykkö predicts the same from his Dirac-Fock calculations [3]. For element 120, Fricke et al. predict a ground state of  $[118]8s^2$  using Hartree-Fock calculations [2]. Pyykkö predicts the same from his Dirac-Fock calculations [3]. For element 121, Fricke’s Hartree-Fock study predicts a ground state of  $[118]8s^28p_{1/2}^1$  [2]. Eliav et al. predict the same [4] from their relativistic coupled cluster calculations, and so does the study by Umemoto and Saito using density functional theory [5]. For element 122, Fricke et al. predict a ground state of  $[118]7d_{3/2}^18s^28p_{1/2}^1$  using Hartree-Fock calculations [2]. Eliav et al. predict the same [6] from their relativistic coupled cluster study. Umemoto and Saito predict from their density functional theory calculations a different ground state,  $[118]8s^28p^2$  [5]. For element 123, the Hartree-Fock study by Fricke et al. predicts a ground state of  $[118]6f_{5/2}^17d_{3/2}^18s^28p_{1/2}^1$  [2]. Umemoto and Saito predicts the same, using density functional theory calculations [5].

## Method

The ground state of an element is the state in which it has its lowest energy. To determine this state, we need to find a number of possible electron configurations, and then determine the energy of each of these configurations. The configuration with the lowest energy is then probably the ground state. To determine a possible electron configuration, we can look at lighter elements that are in the same column in the periodic table as our element, and guess that their configurations will look alike. We can also look at elements with a lower atomic number than our element, and add electrons to different shells.

When determining the energy of a certain electron configuration of an atom theoretically, there are roughly three things to take into account: the treatment of relativity, the treatment of electron correlation, and the choice of basis sets. Relativistic effects are small in light elements, but start to become important for elements heavier than iron ( $Z = 26$ ). In multi-electron atoms, electrons interact both with the nucleus and with each other. The interaction between the electrons is known as electron correlation. Finally, we can describe the atomic orbitals in different ways, depending on our choice of basis sets.

## Relativity

It is possible to do either relativistic or non-relativistic calculations. For most systems, non-relativistic calculations are sufficient. However, for heavy and superheavy elements relativistic effects start to play an increasingly larger role, which means that we must use relativistic calculations. Nevertheless, doing non-relativistic calculations is still useful, because it shows how large the influence of relativistic effects on the energy and other properties of an atom is.

We will now loosely follow an explanation by Pershina [7]. Currently the best way to describe a many body system is the Dirac-Coulomb-Breit (DCB) Hamiltonian

$$h_{\text{DCB}} = \sum_i h_D(i) + \sum_{i < j} \left( \frac{1}{r_{ij}} + B_{ij} \right)$$

where  $h_D(i)$  is the one-electron Dirac operator

$$h_D(i) = c\vec{\alpha}_i\vec{p}_i + c^2(\beta_i - 1) + V^n(i)$$

where the  $\vec{\alpha}$  and  $\beta$  are the four-dimensional Dirac matrices,  $V^n$  is the nuclear attraction operator, which takes the finite nucleus size into account (as opposed to treating the nucleus as a pointlike particle), and  $B_{ij}$  is the Breit term

$$B_{ij} = -\frac{1}{2} \left[ \frac{(\vec{\alpha}_i\vec{\alpha}_j)}{r_{ij}^1} + \frac{(\vec{\alpha}_i\vec{r}_{ij})(\vec{\alpha}_j\vec{r}_{ij})}{r_{ij}^3} \right]$$

The operators in the DCB Hamiltonian, also referred to as the Dirac equations, are 4 x 4 matrix operators. The corresponding wave function is therefore a four-component (4c) vector. Methods that use this Hamiltonian are therefore referred to as 4c methods. In our calculations we use the DIRAC program [8], which does not implement the Breit term, so we have the  $h_{DC}$  Hamiltonian. By default, the DIRAC program does relativistic calculations. To do non-relativistic calculations, we set the speed of light in the program to a practically infinitely high value.

An approximation to the 4c methods are the two-component, or 2c, methods. In the 2c approximation, the positronic and electronic solutions of the Dirac-Hartree-Fock calculations are decoupled. This reduces the number of matrix elements in the Hamiltonian to interactions solely among electrons and nuclei. So, by using 2c methods, computational time and effort can be saved. In our research, we use the recently developed X2C approach [9]. This method accurately reproduces 4c results, and requires less computational effort.

## Electron correlation

In multi-electron atoms, the electrons are influenced not only by the nucleus, but also by each other. This interaction is called electron correlation. To make accurate predictions of the atomic energies we need to take this into account. In our research we use two different approaches: the (Dirac-)Hartree-Fock (DHF) approach and the coupled cluster approach. The Hartree-Fock approach does not treat electron correlation, but the coupled cluster approach does.

In the Hartree-Fock theory, the wave function of a system containing multiple orbitals is taken to be the product of the Slater determinants of the individual spin orbitals (the spatial orbitals multiplied with a spin function). It is assumed that an electron does not see all the other electrons individually, but rather feels the effect of the average positions of all the other electrons together. The Hartree-Fock equations are iterative, that means, to solve the Schrödinger equation for a multi-electron system using Hartree-Fock theory, one starts with an initial guess, and in each iteration the wavefunction is adjusted to minimize the energy. This continues until the calculation converges.

Because the Hartree-Fock approach does not treat electron correlation, its results do not have a high accuracy. However, DHF calculations can be used as the starting point for more sophisticated methods that do treat electron correlation, such as the coupled cluster approach.

The relativistic coupled cluster approach is considered one of the most powerful methods for the treatment of heavy systems. In the coupled-cluster (CC) method, the (non-relativistic) wave function is written as

$$\psi = e^{\hat{T}}\Psi_0$$

where  $\Psi_0$  is the normalized ground-state Hartree-Fock wave function and  $\hat{T}$  is the cluster operator

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

where  $n$  is the number of electrons and  $\hat{T}_i$  the  $i$ -particle excitation operator.

Using the approximation  $\hat{T} \approx \hat{T}_2$  gives an approximate CC approach, the coupled-cluster doubles or CCD method. Predictably, using the approximation  $\hat{T} \approx \hat{T}_1 + \hat{T}_2$  is called the coupled-cluster singles and doubles or CCSD method. In the case that only single and double excitations are taken into account, the coupled cluster equations look like

$$\langle \Psi_0 | (H - E_{\text{CCSD}}) e^{\hat{T}_1 + \hat{T}_2} | \Psi \rangle_0 = 0$$

To obtain the correlated energy of the system they are solved iteratively. The approximation  $\hat{T} \approx \hat{T}_1 + \hat{T}_2 + \hat{T}_3$  is called the coupled-cluster singles, doubles, and triples, or CCSDT, method. The CCSD(T) method is a less computationally demanding approximation of the latter method, as here the triple excitations are not calculated iteratively.

## Basis sets

A basis set is a set of functions (usually Gaussians) used to describe the orbitals of an atom. The larger the basis set, the more accurately it describes the atomic orbitals, but also the more time it takes to do calculations. We will explain a bit about basis sets following the book *Exploring Chemistry* by Foresman and Frisch [10].

There are different types of basis sets. Minimal basis sets use only the minimum number of basis functions that are needed for each atom. So, hydrogen and helium have only one function, while carbon has five (since the p shell can be divided in  $p_x$ ,  $p_y$ , and  $p_z$  shells). Split valence basis sets use multiple functions per orbital. The double zeta basis sets use two functions per atomic orbital, the triple zeta basis sets use three functions per atomic orbital, and the quadruple zeta basis sets use four functions per atomic orbital. Polarized basis sets add functions for orbitals with angular momentum that are not needed to describe the ground state of the atom. For example, polarized basis sets add a p function for hydrogen, and a d function for carbon.

We use, unless otherwise stated, the dyall.v2z, dyall.v3z, or dyall.v4z basis sets [11]. These basis sets are specifically made for relativistic calculations, and can be used for both light and heavy elements. For the elements with  $Z > 118$  we don't use the dyall basis sets, but the specially modified Fægri basis sets [12].

# Research project

## Alkaline earth metals

To determine which calculation methods and basis sets give the most accurate results, we first need to do some calculations for elements of which the ionization potentials are already known experimentally. To do this we use the alkaline earth metals, which are beryllium (Be,  $Z = 4$ ), magnesium (Mg,  $Z = 12$ ), calcium (Ca,  $Z = 20$ ), strontium (Sr,  $Z = 38$ ), barium (Ba,  $Z = 56$ ), radium (Ra,  $Z = 88$ ), and possibly element 120. We will not include beryllium in our calculations.

To find the effect of different treatments of electron correlation we compare the results of the Hartree-Fock (HF) calculations, the coupled cluster with single-double excitations (CCSD), and CCSD with perturbative triple excitations, CCSD(T), with the experimentally determined potentials, as shown in Table 1. These results were all obtained using the 4c method and the dyall.v3z basis set.

Table 1: IPs (eV) of the alkaline earth metals and their errors w.r.t. the experimental value, using HF, CCSD, and CCSD(T) calculations with the 4c method and the dyall.v3z basis set.

|                           | Mg    | Ca    | Sr    | Ba    | Ra    | E120  |
|---------------------------|-------|-------|-------|-------|-------|-------|
| experimental <sup>a</sup> | 7.646 | 6.113 | 5.695 | 5.212 | 5.278 | 5.838 |
| HF                        | 6.618 | 5.141 | 4.751 | 4.281 | 4.359 | 5.032 |
| r.e. HF (%)               | 13.45 | 15.91 | 16.85 | 19.87 | 17.41 | 13.80 |
| CCSD                      | 7.592 | 6.020 | 5.587 | 5.081 | 5.150 | 5.752 |
| r.e. CCSD (%)             | 0.71  | 1.53  | 1.90  | 2.51  | 2.44  | 1.48  |
| CCSD(T)                   | 7.632 | 6.089 | 5.664 | 5.170 | 5.241 | 5.841 |
| r.e. CCSD(T) (%)          | 0.19  | 0.40  | 0.54  | 0.81  | 0.71  | -0.05 |

<sup>a</sup>Mg [13], Ca [14], Sr [15], Ba [16], Ra [17]; There is no experimental value for element 120, this is the estimate made by Borschevsky et al. using DCB extended intermediate Hamiltonian Fock-space CC calculations [18]. The relative error (r.e.) is calculated using

$$\text{relative error} = 100\% * \left(1 - \frac{\text{calculated value}}{\text{experimental value}}\right)$$

We calculate the relative error in the calculations to see how much the results we obtained differ from the experimental results. This shows how accurate the calculation methods are. We see that for all methods the relative error increases as the atomic weight increases, but after barium this trend reverses, and the relative error goes down.

The relative error in the results obtained with the Hartree-Fock method is about five to twenty times as large as the relative error for the CCSD results, and 25 to 70 times as large as the relative error for the CCSD results. The relative error in the CCSD results is three to four times as large as the relative error in the CCSD(T) results.

So, the most accurate results are given by the CCSD(T) methods. The Hartree-Fock method is so inaccurate, even with light elements, that it should not be used even for exploratory calculations. The CCSD method is much more accurate than the Hartree-Fock method. While not as precise as the CCSD(T) method, it is still acceptable when performing exploratory calculations.

To determine the differences between the non-relativistic, X2C, and 4c calculations, we calculate the same ionization potentials again, again using the dyall.v3z basis set. However, now only the CCSD(T) values are shown.

Table 2: IPs (eV) of the alkaline earth metals and their errors w.r.t. the experimental value, using non-relativistic, X2C and 4c calculations with the CCSD(T) method and the dyall.v3z basis set.

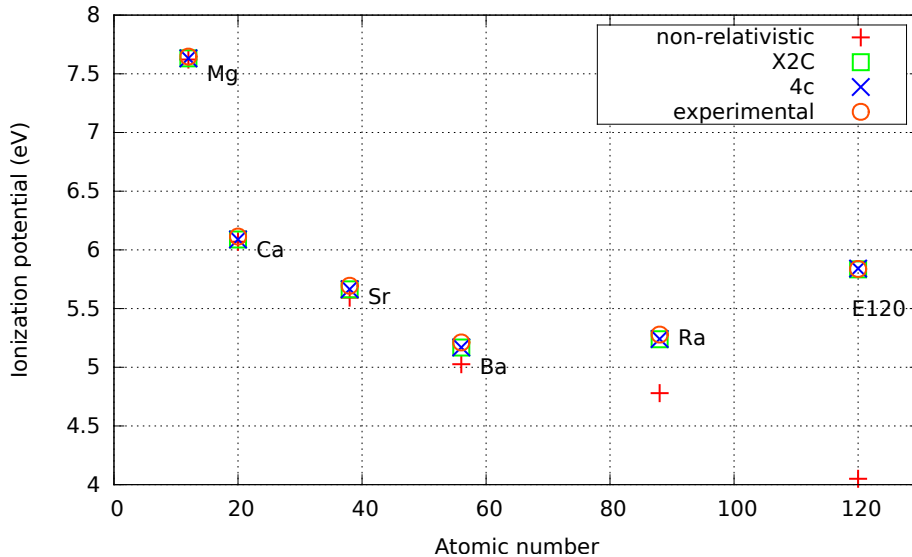
|                           | Mg    | Ca    | Sr    | Ba     | Ra    | E120  |
|---------------------------|-------|-------|-------|--------|-------|-------|
| experimental <sup>a</sup> | 7.646 | 6.113 | 5.695 | 5.212  | 5.278 | 5.838 |
| non-relativistic          | 7.622 | 6.069 | 5.593 | 5.0267 | 4.780 | 4.050 |
| r.e. non-relativistic (%) | 0.32  | 0.72  | 1.78  | 3.55   | 9.44  | 30.63 |
| X2C                       | 7.631 | 6.088 | 5.663 | 5.168  | 5.238 | 5.834 |
| r.e. X2C (%)              | 0.20  | 0.40  | 0.54  | 0.83   | 0.76  | 0.06  |
| 4c                        | 7.631 | 6.089 | 5.664 | 5.170  | 5.241 | 5.841 |
| r.e. 4c (%)               | 0.19  | 0.40  | 0.54  | 0.81   | 0.71  | -0.05 |

<sup>a</sup>Same sources as in Table 1.

For all the three methods, the relative error increases up to barium. For the X2C and 4c methods it then starts to decrease, but for the non-relativistic calculations it increases rapidly. The X2C and 4c methods both have a relative error smaller than 1% for all elements, but the relative error for the non-relativistic method increases rapidly for heavy elements.

Therefore, when doing exploratory calculations, the non-relativistic method should not be used, except for the lightest elements. The relative errors in the X2C and 4c calculations are basically the same. However, since X2C calculations are much faster than 4c calculations, the former are better suited for exploratory calculations, while the latter should be used when performing the final calculations.

Figure 1: Ionization potential (eV) versus atomic number for the non-relativistic, X2C, and 4c calculations and the experimental values.



In Figure 1, the ionization potential is plotted as a function of the atomic number for the non-relativistic, X2C, and 4c methods. We see that for the non-relativistic values, the ionization potential decreases as the atoms become heavier. For the X2C and 4c (and the experimental) values, this is only true up to barium ( $Z = 56$ ), since somewhere between barium and radium ( $Z = 88$ ) this downward trend reverses, and the ionization potentials increase. We also see that around strontium ( $Z = 38$ ), the gap between the non-relativistic results and the (relativistic) X2C and 4c results starts to become visible, and this gap becomes much larger after barium, when the relativistic values increase. Relativity causes the stabilization and contraction of the s orbitals. This increases the ionization potential, which explains the gap between non-relativistic and relativistic results.

To compare different basis sets, we calculate the same ionization potentials again. Here we use the X2C method, because it is much faster than the 4c method, and only show the CCSD(T) values. In Table 3 and Figure 2, ‘pvdz’ corresponds to the dyall.v2z basis set, ‘pvtz’ corresponds to



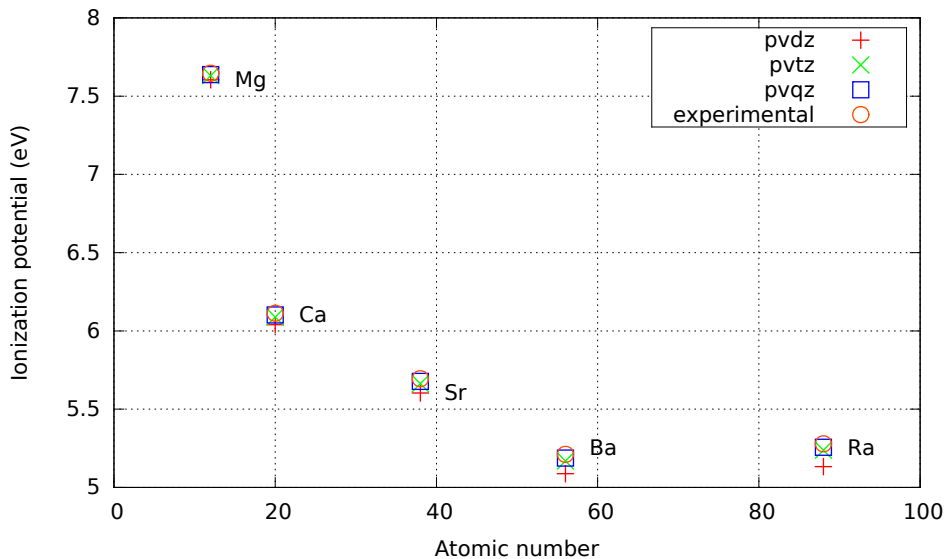
the dyall.v3z basis set, and ‘pvqz’ corresponds to the dyall.v4z basis set. The ionization potential of element 120 is not calculated this time because none of the aforementioned basis sets are available for this element.

Table 3: IPs (eV) of the alkaline earth metals and their errors w.r.t the experimental value (using the same sources as in Table 1), using pvdz, pvtz, and pvqz basis sets with the X2C approach and the CCSD(T) method.

|               | Mg         | Ca         | Sr         | Ba         | Ra         |
|---------------|------------|------------|------------|------------|------------|
| experimental  | 7.646 [13] | 6.113 [14] | 5.695 [15] | 5.212 [16] | 5.278 [17] |
| pvdz          | 7.605      | 6.040      | 5.604      | 5.088      | 5.133      |
| r.e. pvdz (%) | 0.54       | 1.19       | 1.60       | 2.38       | 2.75       |
| pvtz          | 7.631      | 6.089      | 5.663      | 5.169      | 5.238      |
| r.e. pvtz (%) | 0.20       | 0.39       | 0.56       | 0.83       | 0.76       |
| pvqz          | 7.639      | 6.102      | 5.678      | 5.188      | 5.257      |
| r.e. pvqz (%) | 0.09       | 0.18       | 0.30       | 0.46       | 0.40       |

We see that the relative error for the pvtz and pvqz calculations increases as the elements become heavier up to barium, and then decreases a little. For the pvdz calculations the relative error does not decrease after barium, but continues to increase. The relative error in the pvdz values is generally a factor three to four larger than the relative error in the pvtz and pvqz values. However, the pvdz calculations still mostly reproduce the trend, and their error is small, so they can still be used in exploratory calculations. The relative error in the pvtz calculations is about a factor two larger than the relative error in the pvqz calculations. Both errors are quite small, so both methods are suitable for exploratory calculations. When doing the final calculations, the pvqz method is preferable.

Figure 2: Ionization potential (eV) of the alkaline earth metals versus atomic number for the pvdz, pvtz, and pvqz calculations and the experimental values.



In Figure 2 the ionization potentials of the alkaline earth metals are plotted as a function of their atomic number, for different basis sets. We see that the pvtz and pvqz results are very close, both to each other and to the experimental values. We also see that the pvdz results are much more inaccurate than the pvtz and pvqz results.

We estimated the ionization energy of element 120 at 5.84084 eV, using 4c and CCSD(T) methods. Fricke [2] mentions a value of 5.3 eV, which was obtained using the Hartree-Fock method. Borschevsky et al. [18] mention a value of 5.838 eV, which was obtained using the relativistic coupled cluster method. Our results don’t agree with Fricke’s. This was to be expected, since the Hartree-Fock method is, as we have shown, much less accurate than the coupled-cluster method, which we used. Our results differ from Borschevsky’s by about 0.003 eV, which is small enough to say that they agree. This was to be expected, since we both use the coupled-cluster method.

## Alkali metals

To determine the magnitude of relativistic effects for different Z-numbers, we calculate the first and second ionization potentials of the alkali metals using relativistic and non-relativistic calculations.

The alkali metals are lithium (Li,  $Z = 3$ ), natrium, (Na,  $Z = 11$ ), kalium (K,  $Z = 19$ ), rubidium (Rb,  $Z = 37$ ), cesium (Cs,  $Z = 55$ ), francium (Fr,  $Z = 87$ ), and possibly element 119.

Table 4: Relativistic (X2C) and non-relativistic (NR) first ( $IP_1$ ) and second ( $IP_2$ ) ionization potentials (eV) of the alkali metals and their relative errors (r. e.) with respect to the experimental (exp.) value, using the CCSD(T) method and the dyall.v4z [11] basis set.

|                          | Li     | Na     | K      | Rb     | Cs     | Fr     | E119   |
|--------------------------|--------|--------|--------|--------|--------|--------|--------|
| exp. <sup>a</sup> $IP_1$ | 5.392  | 5.139  | 4.340  | 4.177  | 3.893  | 4.073  | 4.793  |
| X2C $IP_1$               | 5.389  | 5.136  | 4.334  | 4.164  | 3.872  | 4.052  | 4.783  |
| r. e. (%)                | 0.06   | 0.06   | 0.14   | 0.31   | 0.54   | 0.52   | -      |
| NR $IP_1$                | 5.389  | 5.129  | 4.316  | 4.095  | 3.726  | 3.582  | 3.383  |
| r. e. (%)                | 0.06   | 0.19   | 0.55   | 1.6    | 4.29   | 12.05  | -      |
| exp. <sup>b</sup> $IP_2$ | 75.640 | 47.286 | 31.63  | 27.290 | 23.157 | 20.02  | 23     |
| X2C $IP_2$               | 75.534 | 47.027 | 31.494 | 27.157 | 23.029 | 20.673 | 12.847 |
| r. e. (%)                | 0.14   | 0.55   | 0.43   | 0.49   | 0.55   | -      | -      |
| NR $IP_2$                | 75.530 | 47.119 | 31.597 | 27.429 | 23.481 | 21.765 | 19.958 |
| r. e. (%)                | 0.15   | 0.35   | 0.10   | 0.51   | -1.40  | -      | -      |

<sup>a</sup>Li [19], Na [20], K [14], Rb [14] Cs [21], Fr [22]; For E119 no experimental value is available, this is an estimate calculated by Eliav et al. using the DCB CCSD method [23].

<sup>b</sup>Li [14], Na [24], K [14], Rb [25], Cs [14]; No experimental value is available for either francium or element 119. For francium we use the calculation using artificial neural network theory by Sigman and Rives [26], for element 119 we use the value mentioned by Bonchev, who does not provide a good reference [27].

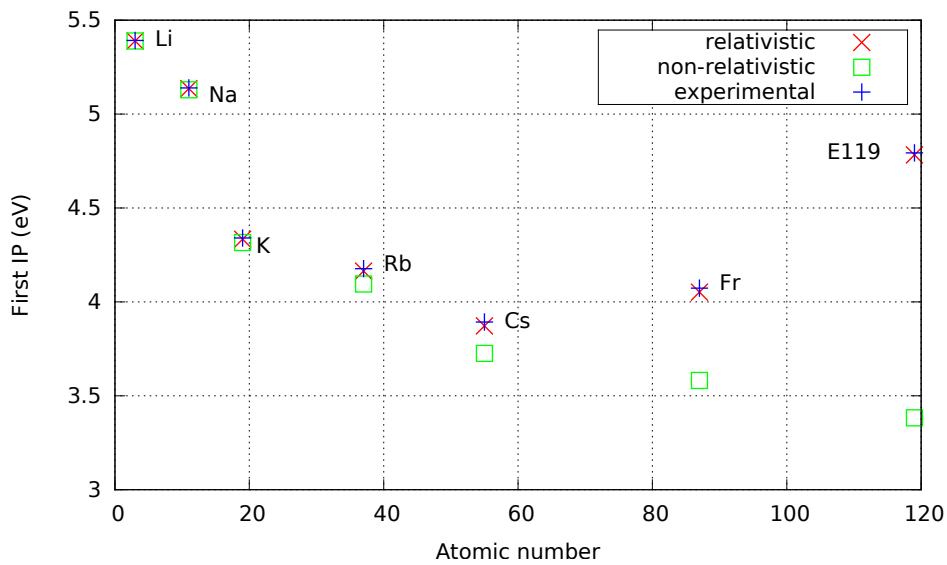
We see that for the first ionization potentials, the relative error in the relativistic results increases as the atoms become heavier, but decreases after cesium. The relative error in the non-relativistic results on the other hand continuously increases. The relative error in the relativistic results is always quite small, but the error in the non-relativistic results is much larger for cesium and francium. Therefore, when doing exploratory calculations on light atoms, one can use both methods, while for heavier atoms, the relativistic method is much better.

For the second ionization potentials, the relative error does not really show a trend, and is small for both the relativistic and the non-relativistic results. Contrary to for the first ionization potentials, the relativistic results for the second ionization potentials are not always better than the non-relativistic results. We do not have an explanation as for why this happens.

In Figure 3 the relativistic, non-relativistic, and experimental first ionization potentials of the alkali metals are shown as a function of the atomic number. We see that the relativistic values initially decrease as the atomic number increases, but starts to increase after cesium, following the experimental values. The non-relativistic potential does not follow the same trend, and decreases continuously.

Relativity causes the s orbital to be contracted and stabilized, which increases the ionization potential. This effect is negligible for light elements, but becomes noticeable for heavier elements. The relativistic X2C method takes this effect into account, but the non-relativistic method does not, hence the difference between the results of these two methods.

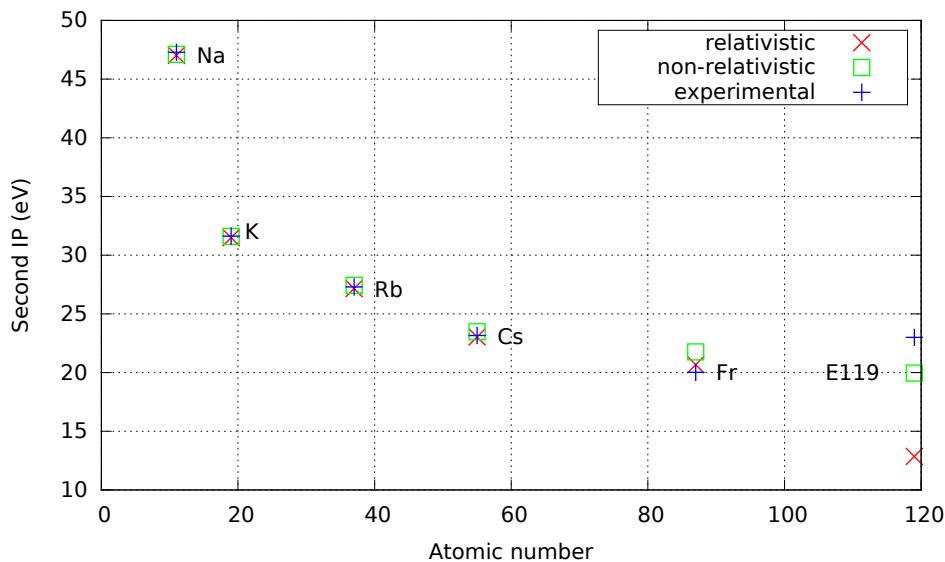
Figure 3: First ionization potential (eV) of the alkali metals versus atomic number for the relativistic (X2C), non-relativistic, and experimental values, using the dyall.v4z basis set and the CCSD(T) method.



In Figure 4, the relativistic, non-relativistic, and experimental second ionization potentials of the alkali metals are shown as a function of the atomic number. Lithium is omitted, because its potential is very high, which makes it difficult to see the differences between the three different values for each element. We see that the relativistic values decrease as the atomic number increases, and so do the non-relativistic and experimental values. Initially the relativistic and non-relativistic values follow the same trend, however around francium the decrease of the relativistic values continues, while the decrease of the non-relativistic values seems to flatten.

The difference between the relativistic and non-relativistic values can be explained partly by spin-orbit splitting. In their second ionized state, the alkali metals (except lithium) all have an outer p shell that is filled with 5 electrons. This p shell splits into a  $p_{3/2}$  shell that can fit 4 electrons, but in this case only contains 3, and a  $p_{1/2}$  shell with 2 electrons. Relativistically, the  $p_{3/2}$  shell has a higher energy than the  $p_{1/2}$  shell. The relativistic X2C method takes this into account, but the non-relativistic method does not. Instead, it just takes a single p shell filled with 5 electrons into consideration, with an energy below the relativistic  $p_{3/2}$  shell but above the relativistic  $p_{1/2}$  shell. This causes the non-relativistic method to report a higher energy than the relativistic method.

Figure 4: Second ionization potential (eV) of the alkali metals without lithium versus atomic number for the relativistic (X2C), non-relativistic, and experimental values, using the dyall.v4z basis set and the CCSD(T) method.



## Element 123

We made six different suggestions for a possible ground state of element 123. Praseodymium, a homolog of element 123, has the ground state  $[\text{Xe}]4f^36s^2$ , so this suggests that a possible ground state of element 123 is  $[118]6f^38s^2$ . Protactinium, another homolog of element 123, has the ground state  $[\text{Rn}]5f^26d^17s^2$ , which suggests that a possible ground state for element 123 is  $[118]6f^27d^18s^2$ . Fricke suggested the ground state  $[118]6f^17d^18s^28p^1$  [2]. Eliav suggested the ground state  $[118]8s^28p_{1/2}^1$  for element 121 [4]. If we continue to fill the 8p shell, we arrive at a possible ground state of  $[118]8s^28p_{1/2}^28p_{3/2}^1$ , or  $[118]8s^28p^3$  for element 123. Eliav also suggested the ground state  $[118]7d_{3/2}^18s^28p_{1/2}^1$  for element 122 [6]. If we continue to fill the 8p shell, we arrive at a possible ground state of  $[118]7d_{3/2}^18s^28p_{1/2}^2$  for element 123. If we continue to fill the 7d shell, we arrive at a possible ground state of  $[118]7d_{3/2}^28s^28p_{1/2}^1$  for element 123.

To determine the ground state of element 123, we need to calculate the energies of all the possible configurations. The configuration with the lowest energy will probably be the correct ground state.

The energies for the different electron configurations were calculated with both the X2C method and the 4c method, and are shown in Table 5, where the lowest energy is shown in boldface. Also shown is the difference in electronvolt between the energy of the configuration with the lowest energy and the other configurations.

Table 5: CCSD(T) energies (au) of the suggested possible electron configurations of element 123 for the X2C and 4c methods, with the configuration with the lowest energy shown in boldface. As  $[118]8s^2$  is present in all configurations, it is omitted. In the last two columns the difference between the energy of a certain configuration and the lowest configuration is shown in eV for both methods.

|                | X2C energy          | 4c energy           | X2C difference | 4c difference |
|----------------|---------------------|---------------------|----------------|---------------|
| $6f^17d^18p^1$ | <b>-61793.03372</b> | -61881.97210        | 0              | 0.143         |
| $6f^27d^1$     | -61792.97436        | -61881.92876        | 1.615          | 1.323         |
| $6f^3$         | -61792.97610        | -61881.90987        | 1.568          | 1.837         |
| $7d^28p^1$     | -61792.99003        | -61881.97720        | 1.189          | 0.005         |
| $7d^18p^2$     | -61792.97758        | -61881.93039        | 1.528          | 1.278         |
| $8p^3$         | -61793.03256        | <b>-61881.97737</b> | 0.032          | 0             |

Table 6: CCSD energies (au) of the suggested possible electron configurations of element 123, with the configuration with the lowest energy shown in boldface. As  $[118]8s^2$  is present in all configurations, it is omitted. In the last two columns the difference between the energy of a certain configuration and the lowest configuration is shown in eV for both methods.

|                | X2C energy          | 4c energy           | X2C difference | 4c difference |
|----------------|---------------------|---------------------|----------------|---------------|
| $6f^17d^18p^1$ | <b>-61792.99093</b> | -61881.91643        | 0              | 0.001         |
| $6f^27d^1$     | -61792.89664        | -61881.85461        | 2.564          | 1.683         |
| $6f^3$         | -61792.89949        | -61881.83092        | 2.487          | 2.327         |
| $7d^28p^1$     | -61792.90807        | -61881.90942        | 2.253          | 0.192         |
| $7d^18p^2$     | -61792.90011        | -61881.85682        | 2.470          | 1.623         |
| $8p^3$         | -61792.96879        | <b>-61881.91646</b> | 0.601          | 0             |

As we can see from tables 5 and 6, the relativistic X2C calculations show that the  $[118]6f^17d^18s^28p^1$  configuration has the lowest energy for both the CCSD and CCSD(T) methods. The relativistic 4c calculations, however, show that the  $[118]8s^28p^3$  configuration has the lowest energy for both the CCSD and CCSD(T) methods. For both the X2C and the 4c calculations, the difference between the  $[118]6f^17d^18s^28p^1$  configuration energy and the  $[118]8s^28p^3$  configuration energy is very small (except for the X2C+CCSD results). In the case of the 4c calculations, the difference between the  $[118]7d^28s^28p^1$  is also small, however, this does not show at all when looking at the X2C calculations. We thus consider the possibilities to be narrowed down to the  $[118]6f^17d^18s^28p^1$  and  $[118]8s^28p^3$  configurations.

Because the difference between the  $[118]6f^1 7d^1 8s^2 8p^1$  and  $[118]8s^2 8p^3$  configurations is so small, it would be good to do further research. There are several things that can be done to improve the calculations so that we can decide between these configurations, although this is beyond the scope of this thesis. Instead of just considering single, double and triple excitations, we can add higher excitations within the coupled cluster approach. We can also improve the treatment of relativity by switching from the Dirac-Coulomb Hamiltonian to the Dirac-Coulomb-Breit Hamiltonian. Finally we can also use a larger basis set.

The electronic configuration  $[118]6f^1 7d^1 8s^2 8p^1$  is quite remarkable. It does not look at all like the configurations of the lighter homologs of element 123, which are praseodymium ( $[\text{Xe}]4f^3 6s^2$ ) and protactinium ( $[\text{Rn}]5f^2 6d^1 7s^2$ ). Furthermore, it has three open shells. So far, no elements with a ground state that has three open shells are known. The configuration  $[118]6f^1 7d^1 8s^2 8p^1$  was earlier predicted to be the ground state of element 123 by Fricke et al. in 1971 [2] and by Umemoto and Saito in 1996 [5]. It is surprising that we found the same configuration as they did, because our methods differ a lot. Fricke et al. used the Hartree-Fock approach, which, as we discussed before, is very inaccurate compared to the CCSD and CCSD(T) approaches. Umemoto and Saito used relativistic density functional theory, which is a more approximate method than the coupled cluster approach, but is still better than the Hartree-Fock approach.

The configuration  $[118]8s^2 8p^3$  was a suggestion by ourselves, derived from the prediction by Eliav et al. that element 121 has the ground state  $[118]8s^2 8p_{1/2}^1$  [4]. Eliav et al. used the relativistic coupled cluster approach, like we did.

Something to note is that both configurations have one or more p electrons. This can be explained by considering the relativistic stabilization of the  $p_{1/2}$  orbital. Relativity causes this orbital to contract and stabilize. This lowers the energy, which means that the p orbital gets filled earlier than one would expect when not considering relativistic stabilization. When looking at praseodymium and protactinium, we see that neither of them have an open p orbital. This is because relativity does not play such a large role for these elements, since they are much lighter than element 123.

## Conclusion

We have investigated the performance of different computational approaches by doing calculations on the ionization potentials of the group 2 elements, also known as the alkaline earth metals. We looked into the Hartree-Fock method, the CCSD method, and the CCSD(T) method. We saw that the CCSD(T) method provided the most accurate results, closely followed by the CCSD method. The results given by the Hartree-Fock method were very inaccurate, regardless of atomic weight. We also compared non-relativistic results with relativistic X2C and 4c results. We saw that the non-relativistic results were relatively accurate for light elements, but inaccurate for heavier elements. We also saw that the relativistic X2C calculations provided basically the same accuracy as the 4c calculations, while taking much less computational time. Finally, we compared the differences between the pvdz, pvtz, and pvqz basis sets. While the pvqz basis set clearly gave the most accurate results, all three basis sets had low errors.

We performed relativistic X2C and non-relativistic calculations of the first and second ionization potentials of the group 1 elements, also known as the alkali metals. We compared the results of these calculations with each other and with experimentally determined values. For the first ionization potential, we found that the relativistic X2C results were very accurate, and followed the same trend as the experimental values. The non-relativistic results were accurate for light elements, but became much more inaccurate when the atomic weight increased. More importantly, the non-relativistic results did not follow the same trend as the experimental values. For the second ionization potential, the relativistic X2C results and the non-relativistic results were very close to each other, except for element 119. In general, the non-relativistic results were a bit higher, which is caused by the non-relativistic calculations ignoring the spin-orbit splitting. There was no clear trend in the relative errors in the calculations, and neither was there a real difference between the relativistic X2C accuracy and the non-relativistic accuracy. We could not explain this.

Finally, using the relativistic coupled cluster approach we calculated the energies of six different electronic configurations that we proposed as possible ground states of element 123. We limited the possible ground state configurations to  $2, [118]8s^26f^17d^18p^1$  and  $[118]8s^28p^3$ . The former was also predicted by Fricke et al. in 1971 [2] and by Umemoto and Saito in 1996 [5], the latter was not predicted by anyone, but was extrapolated by us from a prediction for the ground state of element 121 by Eliav et al. in 1998 [4]. We made some suggestions on how to improve our calculations, so that a decision can be made between these two configurations. We suggested that future research might increase the basis set, might use the DCB Hamiltonian, or might use a coupled cluster approach that considers excitations higher than triple excitations.

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