

Predicting atomic properties of superheavy element 121

Stefan Kuipers

Under supervision of Anastasia Borschevsky and Remco Havenith

July 2018

Abstract

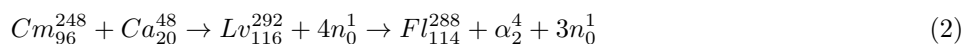
In the last 80 years, the heaviest element in the periodic table has changed from Uranium, element 92, to Oganesson, element 118. However, there may exist even more elements beyond that. This thesis attempts to predict the ionization potential and ground state of element 121, which has not been discovered yet. To predict the energy of element 121 and its lighter homologues with their ionized and double ionized version, the Coupled Cluster method was used in combination with the relativistic Dirac-Coulomb Hamiltonian. Due to relativistic effects, the ground state of element 121 is expected to be $[E118]8s^28p_{1/2}^2P_{1/2}$ [1] unlike its lighter homologues, which have a ground state of the form $ns^2(n-1)d_{3/2}^2D_{3/2}$. The predicted ionization potential for element 121 is 4.51977 electronvolt, while its second ionization potential is predicted to be 12.5102 electronvolt. Since the model used for the prediction is not perfect, this prediction could be 0.1 or 0.2 electronvolt off from the real value.

Contents

1	Introduction	3
2	Methodology	4
2.1	Relativistic effects	4
2.2	Hamiltonian	5
2.3	Hartree-Fock	5
2.4	coupled-cluster	6
2.5	QED and Breit effects	7
2.6	basis sets	7
3	Results	8
3.1	Lighter homologues	8
3.2	Element 121	10
4	Discussion	11
4.1	findings and explanations	11
4.2	limitations and suggestions for further research	11
5	Conclusion	12
	List of Tables	13

1 Introduction

Today, the periodic table contains 118 elements, which is a lot more than before 1940. At that time, no atom larger than uranium, which is element number 92, had been observed [2]. All atoms with more protons in the nucleus than uranium are unstable and are hence almost never observed in nature. Those elements are called "transuranium elements". Of all those elements, only the first two, neptunium and plutonium, can be observed in extremely small quantities in nature as decay products of uranium. Both of these atoms can be created by neutron capture of the uranium-238 isotope [3]. Since most of the transuranium elements cannot be found in nature, they had to be made artificially. The heaviest of those transuranium elements, those with more than 103 protons, are called "Superheavy elements". Using various methods, all elements between Neptunium, element number 93, and element 118 have been created, completing the first 7 rows of the periodic table. Elements beyond element 118 have not yet been discovered. This includes element 121, of which certain properties will be predicted in this thesis. The first transuranium elements until fermium, element 100, were all created by successively irradiating heavy nuclei with α -particles and neutrons [2]. However, for elements even heavier, other methods needed to be used. The method used to create the even heavier atoms was ion fusion, where a heavy nucleus was fused with a smaller atom. A few examples of fusion reactions used to discover those elements can be seen below: [4, 5, 6, 7]



Note that the heaviest elements discovered have all been produced by using Ca_{20}^{48} atoms, this is because the reaction cross-section for reactions with the Ca_{20}^{48} ions is very high for extremely heavy nuclei when compared to other reaction cross-sections, which normally decrease rapidly with the proton number [2]. In these kind of reactions, a beam of lighter elements, in this case the Ca_{20}^{48} ions, is fired upon a heavy target atom.

No element with a higher number than 118 has been discovered at this point. There has been an attempt by a German team from the GSI Helmholtz centre to synthesize element 120 in 2011, but they could not prove that they had found the element [8].

The ion fusion reactions need to be done one atom at a time, while the lighter elements could be produced in weigh-able quantities [2]. This means that the superheavy elements that are being discovered will probably never be of practical use, since it is impossible to get a substantial amount of them. However, finding and observing properties of those elements and even theorizing about elements that have yet to be discovered have their uses. The observed properties of superheavy elements can namely be used to check or improve current atomic models, which helps the understanding of atoms that have practical uses. Theoretical predictions of properties of undiscovered superheavy elements can in turn make it easier to find such elements and carrying out experiments with those elements, often limiting the range of possible energies for the atom the experimenters want to create.

This paper predicts the ground state of element 121 and its ionization potential. The ionization potential is the amount of energy needed to remove the least bound electron from the atom, and the ground state is the state of the electron configuration with the lowest energy. The ionization potential will be analyzed since it is a fundamental property of the atom and it can easily be calculated from the predicted energy of the ground state of the atom and its ionized version.

To calculate the ionization potential, the energy of the ground state and the energy of the ionized ground state of the atom, the ground state of the atom with one electron removed, is needed. The difference between those energies is the ionization potential. Note that the ground state of element 121 is not known, hence the energy of a few likely candidate ground states will be calculated. Then our predicted ground state will be the state with the lowest energy.

Since the ground state of elements in the same column of the periodic table is comparable, the lighter elements in the same group will also be analyzed. Namely element 21 scandium, element 39 yttrium, element 57 lanthanum and element 89 actinium. Those elements are called the lighter homologues of element 121. For those elements, the ground states and ionization potentials will be calculated using the same method as for predicting the properties of element 121. When comparing the results to the experimental values, we can check how accurate our calculations are and hence how accurate our predictions are for element 121.

There have been other papers predicting the ionization potential and ground state of element 121. In the paper of E. Eliav [1], the excitation energies of different states and the ionization potentials of element 121 and the lighter homologues actinium and lanthanum were predicted. In table 1, the predictions for the ground state and ionization potentials are given.

Table 1: Ground states and ionization potential predicted in the paper of E. Eliav et al. [1] using the Dirac–Coulomb–Breit coupled-cluster method with single and double excitations compared with the experimentally obtained IP’s

Atom	ground state	1st IP (eV)	exp. 1st IP(eV)	ionized ground state
Scandium	$[Ar]4s^23d_{3/2}^2D_{3/2}$		6.56149 [9]	$[Ar]4s3d_{3/2}^3D_1$
Yttrium	$[Kr]5s^24d_{3/2}^2D_{3/2}$		6.2173 [10]	$[Kr]5s^2^1S_0$
Lanthanum	$[Xe]6s^25d_{3/2}^2D_{3/2}$	5.582	5.5769 [11]	$[Xe]5d^2^3F_2$
Actinium	$[Rn]7s^26d_{3/2}^2D_{3/2}$	5.32	5.380226 [12]	$[Rn]7s^2^1S_0$
Element 121	$[E118]8s^28p_{1/2}^2P_{1/2}$	4.447		$[E118]8s^2^1S_0$

Table 2: ionized Ground states and second ionization potentials predicted in the paper of E. Eliav et al. [1] using the Dirac–Coulomb–Breit coupled-cluster method with single and double excitations compared with the experimentally obtained IP’s. Note that experimental IP’s with a * are predicted semi-empirically and not confirmed experimentally

Atom	ionized ground state	2nd IP (eV)	exp. 2nd IP (eV)	double ionized ground state
Scandium	$[Ar]4s3d_{3/2}^3D_1$		12.79977 [9]	$[Ar]3d_{3/2}^2D_{3/2}$
Yttrium	$[Kr]5s^2^1S_0$		12.224 [13]	$[Kr]5s^2S_{1/2}$
Lanthanum	$[Xe]5d^2^3F_2$	11.330	11.059* [14]	$[Xe]5d_{3/2}^2D_{3/2}$
Actinium	$[Rn]7s^2^1S_0$	11.90	11.75* [15]	$[Rn]7s^2S_{1/2}$
Element 121	$[E118]8s^2^1S_0$	12.67		$[E118]7s^2S_{1/2}$

The ionization potentials found by E. Eliav et al. for the lighter elements are rather close to the values obtained experimentally, being within 0.1 eV for all elements. The second ionization potentials are somewhat off from the results obtained semi-empirically, but since the semi-empirical results themselves could also be somewhat off from the real second IP’s, it is not possible to say how accurate those results are. The predicted ionization potential of element 121 is 4.447 eV, which is lower than the ionization potential of its lighter homologues. The most significant difference however is the change in the ground state. Instead of being $[E118]8s^27d_{3/2}^2D_{3/2}$, like its lighter homologues, it changes to $[E118]8s^28p_{1/2}^2P_{1/2}$. This results from relativistic effects that will be explained in the methodology section.

The results from this thesis are expected to be more accurate than those of the paper of E. Eliav et al. This is because they used a simpler, and hence less accurate, coupled cluster approach. They used the CCSD approach, while this thesis will use the CCSD(T) approach. These terms and the coupled cluster method in general will be explained in the methodology section.

2 Methodology

2.1 Relativistic effects

Relativity has a enormous effect on the properties of heavy atoms. Since a heavier nucleus has a stronger attraction on electrons moving around the nucleus than a light nucleus, the electrons will move faster. If the electrons move at a sizable fraction of the speed of light, what is the case for heavier atoms, they will experience an increase in mass according to the following formula[2]:

$$m = \frac{m_0}{\sqrt{1 - (\frac{v}{c})^2}} \quad (5)$$

The orbital radius of the electron is then, according to the Bohr model:

$$r = \frac{Ze^2}{mv^2} \quad (6)$$

$$v = \frac{2\pi e^2 Z}{nh} \Rightarrow r = \frac{n^2 h^2}{(2\pi)^2 e^2 Z m} \quad (7)$$

According to this formula, when m increases, r will decrease. Since the innermost electrons, the ones in the 1s

shell, will move at a sizable fraction of the speed of light for heavy elements, their mass will increase and hence the orbital radius will decrease. Because of orthogonality between the s shells, the other s shells will also experience a decrease in their radius. As a result from this contraction of orbitals, the nucleus becomes better screened, and because of that the outer d and f orbitals will expand and become less stable [16]. A third relativistic effect is the spin-orbit splitting, which splits the energy of orbitals into two levels. For example, the d-shell is split into a $d_{3/2}$ and $d_{5/2}$ subshell. This does not happen for the s-shell however. Note that the splitting decreases with the orbital quantum number, so the $p_{1/2}$ - $p_{3/2}$ splitting is larger than the $f_{5/2}$ - $f_{7/2}$ splitting [16]. All these effects scale approximately with Z^2 , where Z is the atom number.

2.2 Hamiltonian

Since we are dealing with superheavy elements, relativity is extremely important in the calculations, therefore a relativistic Hamiltonian is needed. The Hamiltonian used in the final calculations is the four-component Dirac-Coulomb Hamiltonian:

$$H = \sum_i h_i + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \quad (8)$$

note that h_i denotes the Hamiltonian of a single electron i , and r_i denotes the position of electron i . This has a relativistic one-electron part and a non-relativistic two electron interaction part. The one electron part is given by the Dirac Hamiltonian, which is given by [17]:

$$h = c\alpha \cdot p + \beta c^2 + V_{nuc} \quad (9)$$

Here, V_{nuc} is the nuclear attraction operator, α is a vector of 3 Dirac four dimensional Dirac matrices and β a single four dimensional Dirac matrix as given below:[18]

$$\alpha_i = \begin{bmatrix} 0_2 & \sigma_i \\ \sigma_i & 0_2 \end{bmatrix} \quad i = 1, 2, 3 \quad (10)$$

$$\beta = \begin{bmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{bmatrix}$$

Where σ_i is one of the three Pauli spin matrices as given below:

$$\sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (11)$$

Note that the nucleus cannot be assumed to be a point charge anymore when including relativity. The inner electrons of heavy atoms are close enough to the nucleus to observe that the nucleus is finite. This in turn also affects the electrons in outer orbitals, and hence the change becomes significant. The charge in the nucleus will then be modeled by a distribution. This distribution could be Gaussian, uniform or a Fermi distribution, but the results are not sensitive to the specific distribution used to model the finite nucleus [17]. In this case, the Gaussian distribution will be used.

2.3 Hartree-Fock

Now that we have obtained a Hamiltonian, the method will be explained. Firstly, this method will solve the Hartree-Fock equations, and then the coupled cluster equations.

The Hartree-Fock method is often used to model atoms and will be explained like it is in the book of P. Adkins and R. Friedman [19]. The main assumption of the method is that each electron moves in a potential which is the average of the potential induced by all the other electrons and the nuclei, hence in this method it does not experience the charges of the other electrons from their exact locations.

The total wave function of the atom is written as a Slater determinant. The wavefunction of an atom with N electrons is written as follows:[19]

$$\psi = \frac{1}{N!} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) & \dots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) & \dots & \phi_z(2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_a(N) & \phi_b(N) & \phi_c(N) & \dots & \phi_z(3) \end{vmatrix} \quad (12)$$

Here ϕ_a, ϕ_b etc. are the different spin-orbital wavefunctions of the electrons, of which there should be N , equal to the amount of electrons.

In this method, the Hartree-Fock equations, which are derived from the Schrödinger equation, are integrated for that electron and its potential. This procedure is also done for all other electrons. Each time, a wavefunction is assumed for the other electrons and those are used to calculate the wavefunction of the electron. After the new wavefunctions are calculated for all electrons, those are used to calculate the wavefunctions again. This process is repeated until the wavefunctions converge. Note that a approximate wavefunction is needed at the start of this procedure for all electrons.

The Hartree-Fock equation for a electron 1 is then:

$$(h_1 + \sum_r (2J_r - K_r))\psi_s(1) = \epsilon_s \psi_s(1) \quad (13)$$

Here the ψ_s are the one-electron states in the Slater determinant, and the h_1 term is the one electron part of the Dirac Hamiltonian for electron 1. Note that here J_r and K_r are operators, respectively the coulomb and exchange operator, which do the following:

$$J_r \psi_s(1) = \left(\int \psi_r^*(2) \frac{1}{|r_1 - r_2|} \psi_r(2) d\tau_2 \right) \psi_s(1) \quad (14)$$

$$K_r \psi_s(1) = \left(\int \psi_r^*(2) \frac{1}{|r_1 - r_2|} \psi_s(2) d\tau_2 \right) \psi_r(1) \quad (15)$$

The one-electron energy ϵ_s can then be derived from the equation as:

$$\epsilon_s = \int \psi_s^*(1) h_1 \psi_s(1) d\tau_1 + \sum_r (2J_{sr} - K_{sr}) \quad (16)$$

here we have:

$$J_{sr} = \int \psi_s^*(1) J_r \psi_s d\tau_1 \quad (17)$$

$$K_{sr} = \int \psi_s^*(1) K_r \psi_s d\tau_1 \quad (18)$$

The total energy of the closed shells of the atom can then be calculated by:

$$E = 2 \sum_s \epsilon_s - \sum_{r,s} (2J_{rs} - K_{rs}) \quad (19)$$

Note that this is not simply the sum of all the orbital energies, since in that case, all the interactions would be counted twice. Hence half of the interaction energy is subtracted. Also note that since there are 2 electrons in each filled orbital, we have to multiply the right side of the equation by 2, since we sum over all the orbitals.

2.4 coupled-cluster

The difference between the energy obtained by the Hartree-Fock method and the real atomic energy is called the correlation energy. This difference exists because the electrons do not experience only an averaged potential around the nucleus, what is implied in the Hamiltonian. Those electrons experience also the charges of the other electrons from the exact positions of those electrons. This lowers the atomic energy significantly and hence some method needs to be used incorporate this effect if accurate results are needed. In this paper, the coupled-cluster method will be used to incorporate the correlation energy.

The coupled cluster method uses the obtained wavefunction from the Hartree-Fock method as a starting point. The method relates the exact wavefunction to the Hartree-Fock wavefunction by:

$$\psi = e^C \psi_{HF} \quad (20)$$

With ψ_{HF} as the optimized Hartree-Fock wavefunction and ψ as the newly predicted wavefunction. Also, e^C can be expanded as follows: [19]

$$e^C = 1 + C + \frac{1}{2!} C^2 + \frac{1}{3!} C^3 + \dots \quad (21)$$

C is also defined as the sum of the one-electron excitation operator C_1 , two electron excitation operator C_2 , etc. until C_N . Here N is the amount of electrons and hence there are no extra terms needed after C_N , since it is not possible to excite more than N electrons.

$$C = C_1 + C_2 + \dots + C_N \quad (22)$$

Where:

$$C_1\psi_{HF} = \sum_{a,p} t_a^p \psi_a^p \quad (23)$$

$$C_2\psi_{HF} = \sum_{a,b,p,q} t_{ab}^{pq} \psi_{ab}^{pq}$$

etc.

Here t_a^p are called the single-excitation amplitudes, t_{ab}^{pq} the double excitation amplitudes, etc. So t_a^p is a coefficient for the excitation of an electron in orbital a to orbital p . Here the orbitals also include orbitals that are normally unoccupied by electrons.

The coupled cluster equations, which will be solved iteratively are then obtained by filling in the Schrödinger equation:

$$He^C\Psi_0 = Ee^C\Psi_0 \quad (24)$$

Most of the time, not all of C_1 , C_2 , etc. are included since that is computationally intensive. In the CCSD approach, C is taken as $C_1 + C_2$. In that case, the rest of the terms is neglected to make the computation easier. In the CCSDT approach, the C_3 term is added, so then $C = C_1 + C_2 + C_3$. Because of this inclusion, the CCSDT approach should be more accurate than the CCSD approach. The approach used in this paper will be somewhere between CCSD and CCSD(T). The triple excitations will be treated non-iteratively within many-body perturbation theory, unlike the single and double excitations which are treated iteratively. The CCSD(T) approach is also the main reason why the results of this paper should be more accurate than those of the paper of E. Eliav et al, since they used the CCSD approach and hence did not include triple excitations at all.

2.5 QED and Breit effects

Quantum electrodynamics can also cause a change in energy of the atom. This effect is smaller than the other relativistic effects, but it can still change the ionization potential of the superheavy elements with a few hundreds of an electronvolt. Examples of QED effects are vacuum polarization and electron self-energy [2]. Likewise, Breit effects can also change the ionization potential by a few hundreds of an electronvolt and are usually bigger than the QED effects ([2]). Breit effects are first order corrections to the two-electron part of the Dirac-Coulomb Hamiltonian, which are necessary since the two-electron part is taken non-relativistic. Breit effects can be incorporated by changing the Dirac-Coulomb Hamiltonian. The new Hamiltonian, called the Dirac-Coulomb-Breit Hamiltonian will then be as follows [17]:

$$H = \sum_i h_i + \frac{1}{2} \sum_{i \neq j} \left(\frac{1}{|r_i - r_j|} + B_{ij} \right) \quad (25)$$

Where the Breit operator B_{ij} is defined as follows:

$$B_{ij} = \frac{1}{2r_{ij}} \left(\frac{\alpha_i \cdot \alpha_j + (\alpha_i \cdot r_{ij}) \cdot (\alpha_j \cdot r_{ij})}{r_{ij}^2} \right) \quad (26)$$

Both of these effects will not be accounted for during the calculation because they are not very large and hard to take into account.

2.6 basis sets

Basis sets are sets of one-particle functions which are used to model molecular orbitals. These functions are exponential functions and are either Slater type orbitals or Gaussian type orbitals. In this project, the Gaussian

type orbitals will be used, of which the functions are in this form:[20]

$$\phi_{abc}^{GTO} = Nx^a y^b z^c e^{-\zeta r^2} \quad (27)$$

Here, ζ is a constant that controls the width of the orbital, N is a normalization constant, and a , b and c are non-negative integers that control the angular momentum.

The simplest of basis sets use just one basis function for each atomic orbital. However, multiple basis functions per atomic orbital can be used, which increases the accuracy of the model. In this paper, a quadruple-zeta all-electron basis will generally be used, which uses four basis functions per atomic orbital. The Dirac program also gives an option to choose between a valance, core-valance or all-electron basis set [21]. The valance and core-valance basis set do not include all possible functions for electron correlation between the different shells, while the all-electron basis set includes all possible electron correlation functions. In this case, the all-electron basis set will obviously give more accurate results. However, the computation time will be extended when compared to the core-valance and valance basis sets. Diffuse functions can also be added to the basis set to increase the space where the basis functions have effect. They are extra one-particle functions that can be included in the basis set. Those diffuse functions have a low value for ζ , and therefore have only a significant effect at long distances from the nucleus. Here there is again the option to include multiple diffuse functions which results in better results but longer computational time. Because of this large increase in computational time, we will add only one diffuse function per shell for all lighter homologues for our final calculation. Due to time constraints, there was also no diffuse function added for the final calculation of element 121.

To check the influence of the basis sets, we will check the ionization potential of the lighter homologues of element 121 for different basis sets.

The program that will be used to calculate the properties of element 121 and its lighter homologues is called the Dirac program. This is a program that can be used for atomic and molecular calculations [21].

3 Results

3.1 Lighter homologues

A comparison between the relativistic ionization potential and the non-relativistic ionization potential for the lighter homologues of element 121 was made using a small basis set, namely the Dyall triple-zeta basis set and the CCSD(T) approach. This was done to check how much relativity affects the ionization potential, and hence to see if it is necessary to include it in the calculations, even though we strongly expect it is.

We would expect that including relativity would decrease the ionization potential of the lighter homologues of element 121 if they have an ionized ground state of ns^2 , since the d-shell becomes weaker bound when relativity is included. However, the ionization potential of Scandium and Lanthanum is expected to increase (assuming that the ionized ground state does not change). This happens because for those atoms, at least one of the s-electrons is weaker bound than the d-electron, and the s-electrons get stronger bound when relativity is included. For Lanthanum this effect is even stronger since the other s-electron is swapped out for a d-electron in the ionized ground state. Hence the ionization potential for Scandium and especially Lanthanum is expected to decrease unlike Yttrium and Actinium, assuming the ground states do not change.

Table 3: ionization potential for lighter homologues of element 121 including and excluding relativistic effects using a Dyall triple-zeta basis set and the X2C Hamiltonian. It is assumed that the ground state and ionized ground state do not change due to relativity

Atom	IP (eV) incl. relativity	IP (eV) excl. relativity	experimental IP (eV)
Scandium	6.694	6.651	6.561
Yttrium	5.939	6.266	6.217
Lanthanum	5.838	4.660	5.577
Actinium	5.159	5.987	5.380

Note that due to the small basis set, the ionization potential is often somewhat off from the experimentally obtained ionization potential. The difference between the relativistic and non-relativistic IP is rather small for Scandium, around 0.04 eV, but is significant from Yttrium onwards. For Lanthanum, the relativistic IP even differs more than 1 eV from the non-relativistic IP.

Note that the results in table 3 largely reflect the predictions. The IP of Scandium and Lanthanum decreases while

the IP of Yttrium and Actinium increases. The predicted IP for Lanthanum excluding relativity is a lot lower than that when including relativity, this probably results in a different ground state when relativity is not included. Because of this, the true ionization potential without relativity will likely be higher. Since relativistic effects in general increase with the size of the atom, it is expected that relativity will definitely have a significant effect on the IP for element 121.

Different basis sets have been used for the lighter homologues of element 121. In table 4 below, the results are shown for different basis sets, showing the effects of the increase in the basis set.

Table 4: ionization potential the lighter homologues of element 121 using different basis sets, a X2C Hamiltonian and the CCSD(T) coupled cluster method. A * indicates a missing result

Atom	vtz	vqz	aeqz	s-aug-aeqz	experimental
1-st IP Scandium	6.68645	6.69566	6.69533	6.69415	6.56149
2-nd IP Scandium	12.61029	12.61387	12.61292	12.61363	12.79977
1-st IP Yttrium	5.93783	6.09778	6.08413	6.08514	6.2173
2-nd IP Yttrium	12.42441	12.28714	12.31590	12.31461	12.224
1-st IP Lanthanum	5.83830	5.8447	5.76897	*	5.5769
2-nd IP Lanthanum	10.74800	10.79819	*	*	11.059
1-st IP Actinium	5.15863	*	4.70013	4.69083	5.380226
2-nd IP Actinium	*	*	11.94877	11.74425	11.75

First, note that some results (the ones with a *) are missing. This happened because the cluster on which I was running the Dirac program went down for some time, unfortunately making me unable to run those atoms. Also, note that the ionization potential for the aeqz and s-aug-aeqz basis set for Actinium are too low compared to the experimentally obtained IP. Also, the difference between the second IP of Actinium for the aeqz and augmented aeqz basis is too large when compared to the other differences in IP between the aeqz and augmented aeqz basis. I will explain why this could have happened in the discussion.

In this table, it sees that increasing the basis set affects the bigger atoms significantly, but not Scandium. Also note that using a bigger basis set doesn't always get the result closer to the experimentally obtained IP. The ionization potential of for example Yttrium gets worse when going from the vqz to the aeqz basis.

In table 5, a comparison will be made between the predicted IP's using different Hamiltonian, namely the X2C Hamiltonian and the 4-component Hamiltonian.

Table 5: ionization potential the lighter homologues of element 121 using the single augmented Dyall aeqz basis set (except for Ac, for which the unaugmented Dyall aeqz basis is used for the 4C Hamiltonian), different Hamiltonian and the CCSD(T) coupled cluster method. A * indicates a missing result

Atom	X2C	4C	experimental
1-st IP Scandium	6.69415	6.69529	6.56149
2-nd IP Scandium	12.61363	12.61454	12.79977
1-st IP Yttrium	6.08514	6.08074	6.2173
2-nd IP Yttrium	12.31461	12.32319	12.224
1-st IP Lanthanum	*	5.61728	5.5769
2-nd IP Lanthanum	*	*	11.059
1-st IP Actinium	4.69083	4.68469	5.380226
2-nd IP Actinium	11.74425	11.75028	11.75

The results do not seem to change significantly for the two Hamiltonians. The difference between the two Hamiltonians is always less than 0.01 electronvolt for the lighter homologues of element 121.

In table 6, the ionization potentials obtained by using different coupled cluster methods are given and are compared with the experimental ionization potential and the ionization potential for the case where the coupled cluster method is not used.

Table 6: ionization potential the lighter homologues of element 121 using the single augmented Dyall aeqz basis set, a 4-component hamiltonian and different couple cluster methods. A * indicates a missing result. Note that for Actinium, the results from the X2C hamiltonian are given.

Atom	SCF	CCSD	CCSD(T)	experimental
1-st IP Scandium	4.62493	6.62408	6.69529	6.56149
2-nd IP Scandium	11.56265	12.57535	12.61454	12.79977
1-st IP Yttrium	5.22470	6.03522	6.08074	6.2173
2-nd IP Yttrium	10.83907	12.19806	12.32319	12.224
1-st IP Lanthanum	4.26083	5.52404	5.61728	5.5769
2-nd IP Lanthanum	*	*	*	11.059
1-st IP Actinium	4.28259	4.62109	4.69083	5.380226
2-nd IP Actinium	10.57311	11.59465	11.74425	11.75

Note that for all atoms, the ionization potential using no coupled cluster method (SCF) is far off from both the coupled cluster ionization potentials and the experimental ionization potentials. Hence electron correlation has a significant effect on the ionization potential and thus it is necessary to include it when making predictions about element 121.

Another thing to note is that that the difference between the CCSD approach and the CCSD(T) approach is always around 0.1 electronvolt, where it seems to be slightly bigger for the heavier atoms. Hence the difference between those two coupled cluster approaches is not negligible.

3.2 Element 121

In table 7, the predicted ionization potential for element 121 is given using the different coupled cluster approaches and is compared to the IP's predicted by the paper of E. Eliav [1]. Here I assumed that the ground state and the ionized ground states of element 121 were the same as in that paper, which can be seen in table 1 and 2.

Table 7: ionization potentials for element 121 using the ground states for the neutral atom and its ionized versions from the paper of E.Eliav, a 4-component Dirac-Coulomb hamiltonian, different coupled cluster approaches and the Faegri basis set

Atom	SCF	CCSD	CCSD(T)	result paper
1-st IP E121	3.99154	4.46467	4.51977	4.447
2-nd IP E121	11.54398	12.40867	12.5102	12.67

As expected, the predicted IP of the atom without coupled cluster is far off from that predicted with the coupled cluster method and the prediction of E. Eliav [1]. The prediction for the IP's with the CCSD(T) approach is a bit different from that of the paper, but still within 0.2 electronvolt. These results were obtained without the augmentation of the basis set, so that could also change the predicted results a bit.

I was originally planning on comparing the energy of the ground state of element 121 predicted by E. Eliav [1] to the energy of another plausible ground state, namely the $[E118]8s^27d_{3/2}^2D_{3/2}$ state. This state is also a plausible ground state because the ground state of all lighter homologues are of the same form, namely $ns^2(n-1)d_{3/2}$. However, due to the combination of destabilization of the d-shell and the stabilization of the $p_{1/2}$ shell by spin-orbit splitting, of which the strength increases with the size of the atom, it makes sense that the $[E118]8s^28p_{1/2}^2P_{1/2}$ -state is the true ground state as predicted by the paper. Unfortunately, due to the earlier explained breaking down of the cluster used to run the program, I was unable to do this comparison and see whether I ended up at the same ground state as the paper.

I was also planning on calculating the ionization potential and comparing the two plausible ground states without including relativity. Since relativity destabilizes the $7d_{3/2}$ -electron and stabilizes the $8p_{1/2}$ electron, it is likely that $[E118]8s^27d_{3/2}^2D_{3/2}$ would be the true ground state.

Finally, I would have liked to compare the predicted ionization potentials using the 4-component Hamiltonian with those using the X2C Hamiltonian and check whether the Hamiltonian used has a significant effect on the ionization potential. Since the choice of Hamiltonian did not have much impact on the IP's of the lighter homologues, I would

not expect it to affect the IP of element 121 by more than a few hundreds of an electronvolt.

4 Discussion

4.1 findings and explanations

The ionization potential for element 121 has been predicted at 4.51977 eV. This is lower than the ionization potentials of its lighter homologues, and is close to the prediction from E. Eliav et al. [1]. The second ionization potential has been predicted at 12.5102 eV and is somewhat lower than the prediction of E. Eliav et al, but higher than the second ionization potentials of all lighter homologues except Scandium. Both of these result, when compared to lighter homologues were to be expected. The ionization potential should be lower than that of actinium, since the the d-shell containing the least bound electron of actinium destabilizes when the mass of the atom increases. However, it should still be higher than the difference between the energy of the $[Rn]7s^27p_{1/2}^2P_{1/2}$ -state of Actinium and its ionized ground state $[Rn]7s^2\ ^1S_0$. This energy difference is namely the energy needed to remove the $7p_{1/2}$ electron from actinium, and the energy to remove a $p_{1/2}$ -electron should increase with the mass of the atom due to the spin-orbit splitting [16]. Since the ground state of element 121 is predicted to be the $[E118]8s^28p_{1/2}^2P_{1/2}$ -state, it's ionization potential should also be the energy to remove the p-electron. According to the paper of E. Eliav et al [1], the energy to remove the $p_{1/2}$ electron from the $[Rn]7s^27p_{1/2}^2P_{1/2}$ -state is 4.336 eV, which is less then our predicted ionization potential. Hence the predicted ionization potential of element 121 is plausible.

Since element 121 and Actinium both have 2 s-electrons as the least bound electrons in their (predicted) ground state, and have both 1 s-electron in their (predicted) ionized ground state, the second ionization potential is for both atoms the energy needed to remove one of the two s-electrons. Due to relativistic effects, the s-electrons become stronger bound [16] when the mass of the atom increases. Hence the second ionization potential of element should be higher than the second ionization potential of actinium, which I predicted to be around 11.75 eV. The predicted ionization potential of element 121 is higher than that value, so it seems to be a plausible prediction.

Unfortunately, I have not been able to predict the energy of the $[E118]8s^27d_{3/2}^2D_{3/2}$ -state, which is also a plausible ground state, even though the d-electron is weaker bound in element 121 than in its lighter homologues. The paper of E. Eliav et al [1] predicted that the energy of this state would be 0.389 eV lower than that of the $[E118]8s^28p_{1/2}^2P_{1/2}$ -state. Hence it is rather unlikely that the $[E118]8s^27d_{3/2}^2D_{3/2}$ -state is the true ground state, but it would have been nice to confirm this.

For the lighter homologues, there are some weird results. The most striking one is the extremely low ionization potential of actinium. Using the augmented dyall aeqz basis set, the X2C Hamiltonian and the CCSD(T) coupled cluster approach, I ended up at an ionization potential of 4.69083 eV, which is more than a half eV lower than the experimentally confirmed ionization potential of 5.380226 eV. Since a big basis set, an accurate coupled cluster approach and a rather accurate Hamiltonian were used, one would expect that the predicted ionization potential would be at least as close to the experimental ionization potential as the prediction of E. Eliav et al. [1], which was within 0.1 eV of the experimental value. Hence there went something wrong with the prediction. Note that the second ionization potential is very close to the experimental value. Hence I expect that the prediction of the energy of the ionized atom and the double ionized atom went well and in that case, there must have gone something wrong with the neutral atom. The Hartree-Fock part of the prediction seemed to have gone well, according to the output, so the fault is probably with the coupled cluster part. I think that the coupled cluster method has converged to the wrong wavefunction and because of that, the predicted energy of the neutral atom and the ionization potential are too low.

The results for the smaller atoms are also less accurate than I expected. The predicted ionization potential of the lighter homologues of element 121 is often more than 0.1 eV off from the real value, which is rather large when compared to the predictions of E. Eliav et al, which are always within 0.1 eV for the lighter homologues. For some these atoms, it may again be caused by convergence of the coupled cluster method to the wrong wavefunction. But since the results are not very far off from the experimental values it could also be caused by a combination of imperfections of the model, which will be discussed below.

4.2 limitations and suggestions for further research

The method used to predict the ionization potentials is not perfect, there are a multitude of effects not taken into account that could result in a difference of at least a few hundreds of an electronvolt between the predictions and the real values. In the methodology section, Breit effects and QED effects are briefly discussed. Both of these effects are not taken into account in this paper and could change the ionization potential by a few hundreds of an electronvolt. Note that Breit effects are only the first order correction to the non-relativistic two-electron part of

the Dirac-Coulomb Hamiltonian, so even when including those effects, the Hamiltonian is still not perfect. The Faegri basis set used in the final calculations for element 121 was not augmented. Augmenting this Faegri basis set, like I originally intended, could also improve the prediction. Multiple augmentations to that basis set should lead to even more accurate results with longer computation times, although the effectiveness of the augmentations will likely drop with each additional augmentation.

The CCSD(T) coupled cluster approach is more accurate than the CCSD approach used by E. Eliav et al [1]. However, the triple excitations are not taken into account completely, like in the CCSDT approach. Hence using the CCSDT approach should lead to more accurate results. Of course, quadruple or even more excitations could also be taken into account, leading to far longer computational times but more accurate results.

Hence, my suggestion for further research is to predict the ionization potential of this element again using a larger basis set, better coupled cluster approach, including Breit effects and including QED effects. Note that this will likely increase the computational time by a lot.

Finally, the best way to predict the ionization potential of element 121 is to create a relatively stable isotope of that element and obtain the properties experimentally. However, such an isotope or even the element itself has not been created yet, so this is a suggestion for future research after the element has been discovered.

5 Conclusion

Due to relativistic effects, the ground state of element 121 is expected to be $[E118]8s^28p_{1/2}^2P_{1/2}$ [1] unlike its lighter homologues, which have a ground state of the form $ns^2(n-1)d_{3/2}^2D_{3/2}$. The predicted ionization potential for element 121 is 4.51977 electronvolt, while its second ionization potential is predicted to be 12.5102 electronvolt. These results are rather close to the predictions made by E. Eliav et al [1], and are probably more accurate since the paper of E. Eliav et al did not use the CCSD(T) coupled cluster approach, but instead the less accurate CCSD approach. However, there is room for improvement. The basis set can be augmented, Breit and QED effects could be included and a better coupled cluster approach like CCSDT could be used. The predicted ionization potentials for the lighter homologues were also off by up to 0.2 eV and the ionization potential of Ac was not predicted correctly. Because of this, the real ionization potential could be 0.1 or possibly 0.2 electronvolt off from my predictions.

References

- [1] E. Eliav et al. "Transition energies of lanthanum, actinium, and eka-actinium (element 121)". In: *Journal of Chemical Physics* (1998), pp. 3954–3958.
- [2] A. Türler and V. Pershina. "Advances in the production and chemistry of the heaviest elements". In: *Chemical Reviews* (2013), pp. 1237–1312.
- [3] Wikipedia. *Unbinilium*. 2018. URL: <https://en.wikipedia.org/wiki/Neptunium>.
- [4] A. Ghiorso et al. "Positive Identification of Two Alpha-Particle-Emitting Isotopes of Element 104". In: *Physical review letters* (1969), pp. 1317–1320.
- [5] Y. Oganessian et al. "Observation of the decay of 116^{292} ". In: *Physical review C* (2000).
- [6] Y. Oganessian et al. "Synthesis of a New Element with Atomic Number $Z=117$ ". In: *Physical review letters* (2010).
- [7] Y. Oganessian et al. "Synthesis of the isotopes of elements 118 and 116 in the Cf^{249} and $Cm^{245}+Ca^{48}$ fusion reactions". In: *Physical review C* (2006).
- [8] S. Hofmann et al. "Remarks on the fission barriers of SHN and search for element 120". In: *Exotic Nuclei: EXON-2016 Proceedings of the International Symposium on Exotic Nuclei* (2016), pp. 155–164.
- [9] J. Sugar and C. Corliss. "Atomic energy levels of the iron-period elements: potassium through nickel". In: *Journal of physical and chemical reference data* (1985).
- [10] Z. J. Jakubeh and B. Simard. "Rydberg series and the first ionization potential of platinum and yttrium atoms". In: *Journal of physics B* (2000).
- [11] R. Zalubas W. C. Martin and L. Hagan. *Atomic Energy Levels - The Rare Earth Elements*. U.S. Department of Commerce, 1978.
- [12] J. Roßnagel et al. "Determination of the first ionization potential of actinium". In: *Physical Review A* (2012).
- [13] A. E. Nilsson et al. "The spectrum of singly ionized yttrium, Y II". In: *Physica scripta* (1991).
- [14] J. Sugar and J. Reader. "Ionization Energies of the Singly Ionized Rare Earths". In: *Journal of the Optical Society of America* (1965).

[15] W. C. Martin et al. In: *Journal of physical and chemical reference data* (1974).

[16] P. Pyykko and J-P. Desclaux. “Relativity and the periodic system of elements”. In: *Accounts of chemical research* (1979), pp. 276–281.

[17] U. Kaldor. *Quantum Chemistry (Heavy atoms and molecules)*. 2008.

[18] T. Saue. “Relativistic hamiltonians for physics: a primer”. In: *ChemPhysChem* (2011).

[19] P. Adkins and R. Friedman. *Molecular Quantum Mechanics Fifth edition*. Great Clarendon Street, Oxford: Oxford University press, 2011.

[20] C. David Sherrill. *basis sets in quantum chemistry*.

[21] T. Saue et al. *DIRAC*. 2018. URL: <http://www.diracprogram.org/doku.php>.

List of Tables

1	Ground states and ionization potential predicted in the paper of E. Eliav et al. [1] using the Dirac–Coulomb–Breit coupled-cluster method with single and double excitations compared with the experimentally obtained IP’s	4
2	ionized Ground states and second ionization potentials predicted in the paper of E. Eliav et al. [1] using the Dirac–Coulomb–Breit coupled-cluster method with single and double excitations compared with the experimentally obtained IP’s. Note that experimental IP’s with a * are predicted semi-empirically and not confirmed experimentally	4
3	ionization potential for lighter homologues of element 121 including and excluding relativistic effects using a Dyall triple-zeta basis set and the X2C Hamiltonian. It is assumed that the ground state and ionized ground state do not change due to relativity	8
4	ionization potential the lighter homologues of element 121 using different basis sets, a X2C Hamiltonian and the CCSD(T) coupled cluster method. A * indicates a missing result	9
5	ionization potential the lighter homologues of element 121 using the single augmented Dyall aeqz basis set (except for Ac, for which the unaugmented Dyall aeqz basis is used for the 4C Hamiltonian), different Hamiltonian and the CCSD(T) coupled cluster method. A * indicates a missing result	9
6	ionization potential the lighter homologues of element 121 using the single augmented Dyall aeqz basis set, a 4-component hamiltonian and different couple cluster methods. A * indicates a missing result. Note that for Actinium, the results from the X2C hamiltonian are given.	10
7	ionization potentials for element 121 using the ground states for the neutral atom and its ionized versions from the paper of E.Eliav, a 4-component Dirac-Coulomb hamiltonian, different coupled cluster approaches and the Faegri basis set	10