Ionization Potential and Electron Affinity of Darmstadtium

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Abstract

In this paper calculations are performed for Darmstadtium and its lighter homologue Platinum. Experiments are hard to do on superheavy elements, due to their short lifespans, picobarn cross-sections, and low production rates. Theoretical calculations can predict chemical properties, serving as a benchmark of what to look for when performing experiments. Calculations are performed in the DIRAC19 program, with the relativistic 4-component Dirac-Coulomb coupled cluster (CCSD(T)) method and large augmented basis sets. For Platinum, results were produced within a percent of the experimental values. Consequently, for Darmstadtium, an IP of 9,701 eV and EA of 1,749 eV were produced. The CBS limit is applied, yielding final results for the IP and EA of Darmstadtium of 9,765 eV and 1,776 eV, respectively.

Acknowledgements

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Contents

1   Introduction

Superheavy elements are the elements in the periodic table with atomic number greater than or equal to 104, $Z \geq 104$. These elements are also commonly referred to as the transactinides. Studying these elements requires the constant improvement and development of new techniques to achieve the goal of chemically isolating a single atom to perform further experiments on. Experiments have shown that the properties of the heaviest elements cannot be predicted based on trends that emerge in the groups and rows of the periodic table. Since production of the transactinides is so scarce, chemical information on them is hard to obtain. Experiments can at most reveal whether or not an element conforms to the chemical trends of its lighter homologues. This makes theory a very important part in the prediction of chemical properties, and it is often the only source of information. It is also incredibly useful to compare expensive experiments with theoretical results, as a benchmark of what to look for and how to interpret outcomes. Furthermore, only theory allows for a review of relativistic effects for heavier elements. Due to advances in computational algorithms and relativistic quantum theory, very accurate calculations can be performed on the transactinides [1]. The transactinide element in question in this report is Darmstadtium, with $Z = 110$. It is a group 10 element in the 7th period.

Figure 1: Darmstadtium in the periodic table of elements in orange, with the transactinides in blue.

Darmstadtium cannot be found naturally in nature, meaning it has to be produced artificially. The discovery of Darmstadtium is accredited to Sigurd Hofmann's research group at the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany, where it was first produced in 1994 [2]. The production of the new element followed the reaction

$$^{62}\text{Ni} + {}^{208}\text{Pb} \rightarrow {}^{269}110 + 1\text{n}.$$
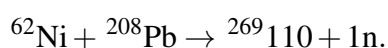
While the International Union of Pure and Applied Chemistry (IUPAC) recognizes [2] as the collaboration which discovered Darmstadtium in a 2003 technical report [3], they also recognize the possible production of Darmstadtium in a number of other collaborative experiments happening around the same time. These are the production of element 110 with a ^{59}Co beam striking a ^{209}Bi target [4] [5], the bombardment of ^{244}Pu with ^{34}S [6], and striking a ^{208}Pb target with ^{64}Ni [7].

Darmstadtium is very unstable and radioactive. The most stable known isotope is ^{281}Ds with a half-life of 12.7s [8]. Other isotopes are much more unstable and have shorter half-lives [9] [10]. The short lifespan of the isotopes, along with picobarn cross-sections, makes it difficult to experimentally determine chemical properties of the element. These properties can be determined computationally, which is what this report strives to do using the Program for Atomic and Molecular Direct Iterative Relativistic All-electron Calculations (named after P.A.M. Dirac, the father of relativistic electronic structure theory) [11].

Two properties will be calculated, namely the ionization potential (IP) and the electron affinity (EA) for Darmstadtium. The ionization potential is the amount of energy required to remove an electron from an atom, creating a positively charged ion. The electron affinity is the energy released when an electron is added to an atom, creating a negatively charged ion. These two properties will be calculated with the Dirac program, with the CCSD(T) method. First, the IP and EA of Platinum, are calculated with the DHF, CCSD, and CCSD(T) method for a number of different basis sets, in order to find out which combination of method with basis set produces the most accurate results compared to experiment. Platinum is expected to be the most similar to Darmstadtium, since Pt is below Ds in the periodic table as can be seen in Figure 1, where Pt with $Z = 78$ is in the same group as Ds. If Darmstadtium has a lighter homologue, it would most likely be Platinum. Darmstadtium is expected to have similar chemical properties to Platinum, so performing electronic structure calculations on a similar chemical element to Darmstadtium should provide similarly accurate results for Darmstadtium as well. The significance of relativistic effects is also presented by performing calculations on both relativistic and non-relativistic approximations for the atoms.

2   Theory

Darmstadtium, with $Z = 110$, represents a many body atomic system. This system is described by a Hamiltonian $\mathbf{H}$, and the aim is to solve the time-independent Schrödinger equation for the ground state wave function $|\Psi\rangle$ and energy E,

$$\mathbf{H}|\Psi\rangle = E|\Psi\rangle. \tag{1}$$

The framework in which we will try to solve this equation, is the coupled cluster method. The coupled cluster method builds upon the Hartree-Fock method in order to account for electron correlation.

2.1   Hartree-Fock method

The Hamiltonian for a many body system is composed of the kinetic energy of electrons, the kinetic energy of the nuclei, the Coulomb attraction between electrons and nuclei, the repulsion between electrons, and the repulsion between nuclei, such that

$$\mathbf{H}_{atomic} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}. \tag{2}$$

Invoking the Born-Oppenheimer approximation, which states that the nuclei moves a lot slower relative to the kinetic energy of the electrons, and it can be assumed that the electrons move in the field of fixed nuclei, such that the second term in the Hamiltonian is zero and the last term can be taken as constant. What is left is the electronic Hamiltonian for N electrons [12] [13],

$$\mathbf{H}_{elec} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\frac{Z}{r_i} + \sum_{i=1}^{N}\sum_{j>1}^{N}\frac{1}{r_{ij}}, \tag{3}$$

with which the aim is to solve the electronic Schrödinger equation,

$$\mathbf{H}_{elec}|\Psi_{elec}\rangle = E_{elec}|\Psi_{elec}\rangle. \tag{4}$$

To solve this equation, the N-electron Hamiltonian $\mathbf{H}_{elec}$ is broken down into one-electron terms. The first term in Eq. 3 is the sum of kinetic energies of individual electrons, the second term is the sum of attractions between individual electrons and the nuclei. Both of these terms can be broken down into one-electron equations, since they are both based on forces of individual electrons. The third term is the sum of repulsion between all electrons, and cannot be written in one-electron terms. Hartree proposed that each electron moves in the average electric field of all other electrons. Now, the probability of two independent events occurring at the same time is equal to the product of the probability of two individual one-electron wave functions. So Ψ_{elec} of N electrons independent from each other should be equal to the product of their individual one-electron wave functions, known as the Hartree product,

$$\Psi_{HP}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N). \tag{5}$$

Eq. 5 does not satisfy the Pauli exclusion principle, however, and the wave function needs to be antisymmetric. For two electrons, the antisymmetry principle can be satisfied by

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}[\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)]. \tag{6}$$

Here, the coordinates are written as space-spin coordinates $\mathbf{x} = \{\mathbf{r}, \omega\}$, with ω a generic spin coordinate and spatial orbitals $\phi(\mathbf{r})$ are written as $\chi(\mathbf{x})$, spin orbitals. The two electron wave function can be written in matrix form,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_2) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_1) \end{vmatrix}, \tag{7}$$

and consequently, the generalization for N electrons becomes

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}. \tag{8}$$

This is called the Slater determinant [14] [15], which is the wave function as a sum of products of one-electron wave functions of the occupied states, and solving the electronic Schrödinger equation with it will produce an upper bound energy which can be minimized by iterating over spin orbitals until a certain desired threshold of convergence is reached. The best wave function should give the lowest possible energy

$$E_0 = \langle \Psi_0 | \mathbf{H}_{elec} | \Psi_0 \rangle, \tag{9}$$

which is the ground state wave function [13]. This is the (summarized) idea behind the Hartree-Fock method.

2.2   Coupled Cluster method

Building upon the Hartree-Fock method, is the coupled cluster method. While HF essentially ignores the correlation between electrons, where the correlation energy is a measure of how much an electron's movement is influenced by the presence of all other electrons, CC aims to take it into account by including all corrections of a given type (S, D, T, Q, etc.) to infinite order. Different corrections are shown in Figure 2.
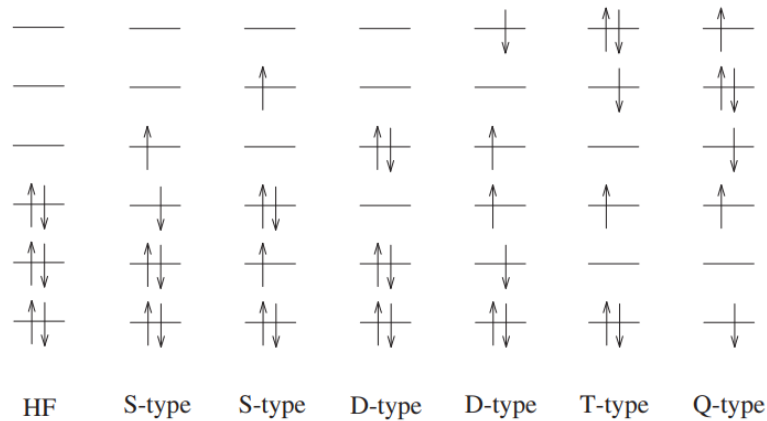

Figure 2: Different corrections generated from a HF ground state wave function. Obtained from [16].

In Figure 2, the HF reference wave function is the ground state, where all lowest energy levels are occupied by the available electrons. This is called the 'Fermi sea', shown schematically in Figure 3a. S-type corrections are single excitations. D-type corrections are double excitations, shown in two ways in Figure 3b and Figure 3c. Figure 3d shows triple excitations, or T-type corrections. Q-type corrections are quadruple excitations, not shown in Figure 3 nor relevant to our calculations.

Now we start by defining an excitation operator $\mathbf{T}$,

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \cdots + \mathbf{T}_{N_{elec}}. \qquad (10)$$

The excitation operator acts on a HF wave function Φ_0, generating excited Slater determinants of N types of excitations. The coupled cluster wave function reads

$$\Psi_{CC} = e^{\mathbf{T}}\Phi_0, \qquad (11)$$

where the exponential operator can be written as

$$e^{\mathbf{T}} = \mathbf{1} + \mathbf{T}_1 + \left(\mathbf{T}_2 + \frac{1}{2}\mathbf{T}_1^2\right)$$
$$+ \left(\mathbf{T}_3 + \mathbf{T}_2\mathbf{T}_1 + \frac{1}{6}\mathbf{T}_1^3\right) + \cdots . \qquad (12)$$

The first term is the HF reference wave function, the second term represents all single excitations. The third term represents all double excitations, from either a connected pair of electrons or two unconnected electrons (Figure 2b and 2c), the latter multiplied by a factor $\frac{1}{2}$ to avoid counting the same electrons twice. For the excitation of m independent pairs, the contribution to the amplitude of the wave function is [17]

$$\sum_{m=0}^{\infty} \frac{1}{m!}\mathbf{T}_2^m |\Phi\rangle = e^{\mathbf{T}_2} |\Phi\rangle . \qquad (13)$$

The third term in Eq. 12 represents triple excitations (Figure 2d), either from a triple excitation ($\mathbf{T}_3$), a combination of a double excitation and single excitation ($\mathbf{T}_2\mathbf{T}_1$), or three independent single excitations ($\frac{1}{6}\mathbf{T}_1$), the latter multiplied by a factor $\frac{1}{6}$ in order to once again avoid counting the same electrons multiple times. This leads to a contribution to the amplitude from n independent triplets of

$$\sum_{n=0}^{\infty} \frac{1}{n!}\mathbf{T}_3^n |\Phi\rangle = e^{\mathbf{T}_3} |\Phi\rangle . \qquad (14)$$
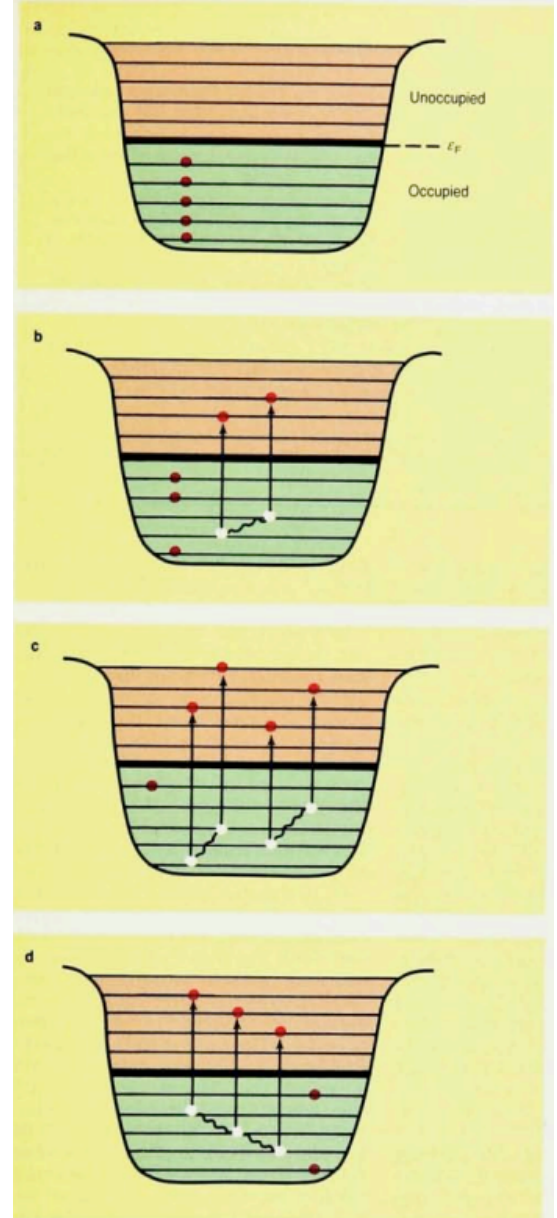

Figure 3: (**a**) - Filled Fermi sea; (**b**) - a correlated pair; (**c**) - two independent correlated pairs; (**d**) - a correlated triplet; excited out of the Fermi sea. Obtained from [17].

The possibility of double and triple excitations occurring at the same time must also be accounted for, with the total contribution being, for all n independent triplets and m independent pairs,

$$\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m!n!} \mathbf{T}_2^m \mathbf{T}_3^n |\Phi\rangle = e^{(\mathbf{T}_2 + \mathbf{T}_3)} |\Phi\rangle. \tag{15}$$

Extending the result from Eq. 15 to account for simultaneous excitations of N particles, we obtain the wave function

$$e^{(\mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \cdots + \mathbf{T}_N)} |\Phi\rangle, \tag{16}$$

which is the excitation operator written out in Eq. 10, and we arrive back at Eq. 10, the coupled cluster wave function. With Eq. 11, the Schrödinger equation (Eq. 4) becomes

$$\mathbf{H} e^{\mathbf{T}} \Phi_0 = E_{CC} e^{\mathbf{T}} \Phi_0, \tag{17}$$

which after a few manipulations becomes the energy equation, analogous to the one in Eq. 9 [16],

$$E_{CC} = \langle \Phi_0 | e^{-\mathbf{T}} \mathbf{H} e^{\mathbf{T}} | \Phi_0 \rangle. \tag{18}$$

In the framework of this paper, the CCSD(T) method is used, but CCSD energies are given as well. The CCSD method is the coupled cluster singles and doubles method, meaning the excitation operator is $\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2$, to only account for single and double excitations [18]. The CCSD(T) method adds a perturbative triple excitation [19], which is calculated non-iteratively using many body perturbation theory [20].

2.3   Relativity

The HF method and CC method discussed so far work with a non-relativistic Hamiltonian. But as the Z of heavier elements increases, the orbiting electrons are more strongly attracted to the core, so that the electrons move faster, leading to a mass increase of $m = m_0/[1 - (v/c)^2]^{1/2}$, where m_0 is the rest mass of the electron, v its velocity, and c the speed of light. A number of relativistic effects arise from the increase in velocity of electrons. The first concerns the contraction and stabilization of hydrogen-like s and $p_{1/2}$ electrons. This is visible in the calculation of the effective Bohr radius,

$$a_B = a_B^0 \sqrt{1 - (v/c)^2}, \tag{19}$$

which decreases for increasing velocity of the inner electrons, contracting the hydrogen-like electrons [21]. For example, the effect of the ns orbital contraction reaches its maximum in the 7th row for element 112, with a 31% contraction [22]. This is also the reason why Darmstadtium (and other transactinides) does not follow the electron configuration of row 6 elements, where the filling of the d shell takes place before the filling of the s shell. As such, the electron configuration of the transactinides follows the $d^m s^2$ configuration [23], where the s shell is filled up first due to the relativistic stabilization of the $7s$ atomic orbital. So Darmstadtium has a $6d^8 7s^2$ configuration, compared to its lighter homologue, Platinum, with a $5d^9 6s^1$ configuration [24]. The ionic configuration Ds$^+$ ($6d^7 7s^2$) also differs from the ionic configuration of Platinum, Pt$^+$ ($5d^9$) [1]. The anionic configurations are Ds$^-$ ($6d^9 7s^2$) and Pt$^-$ ($5d^{10} 6s^1$).

The contraction of *ns* orbitals also leads to a better shielding of the nuclear charge, resulting in the outer orbitals becoming more expanded and energetically destabilized [25]. The *d* and *f* orbitals experience a weaker attraction, an indirect relativistic effect.

Another effect is the spin-orbit (SO) splitting of $l > 0$ levels into $j = l \pm \frac{1}{2}$. The SO splitting is strongest for inner core shells than for outer shells, and it decreases for increasing l for the same principal quantum number *n*, meaning splitting in the *p* shell > splitting in the *d* shell > splitting in the *f* shell, and so forth [25].

It is clear that relativistic effects cannot be ignored in the calculation of atomic energies for heavy elements. While the non-relativistic Hamiltonian was used before, it is now imperative to use the relativistic Dirac-Coulomb (DC) Hamiltonian. The non-relativistic one-electron terms in Eq. 3 are replaced by the one-electron Dirac operator h_D,

$$\mathbf{H}_{DC} = \sum_i h_D(i) + \sum_{i<j} \frac{1}{r_{ij}}, \tag{20}$$

with

$$h_D(i) = c\alpha_i \cdot \mathbf{p}_i + c^2 \beta_i + V^n(i). \tag{21}$$

Here, α and β are four-dimensional Dirac matrices, V^n is the nuclear attraction operator, and $\mathbf{p}$ is the four-momentum of the electron [26]. The Dirac-Hartree-Fock (DHF) method uses the four component relativistic wave function (Ψ_{4c}), for which it is conventional to write as two-component wave functions

$$\Psi = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \\ \Psi_4 \end{pmatrix} = \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix} \tag{22}$$

where Ψ_L and Ψ_S are called the large and small components of the wave function. The first two degrees of freedom in the intermediate step in Eq. 22 are assigned to the spin of particles, the latter two are interpreted as the electron and positron [16]. The positronic solutions are shown in Figure 4, as a continuum of negative energy states, whereas electronic solutions are positive.

The large and small components are coupled by

$$\Psi_S = R\Psi_L$$
$$R(E) = \frac{c(\sigma \cdot \mathbf{p})}{2mc^2 - V + E^+} = \frac{1}{2mc} B(E)(\sigma \cdot \mathbf{p}). \tag{23}$$

In Eq. 23, σ represents Pauli spin matrices. For positive (E^+) and negative (E^-) energy solutions respectively, the factor $B(E)$ is

$$B(E) = \left[1 + \frac{E^+ - V}{2mc^2} \right]^{-1}; \quad B(E) = \frac{2mc^2}{E^- - V}. \tag{24}$$
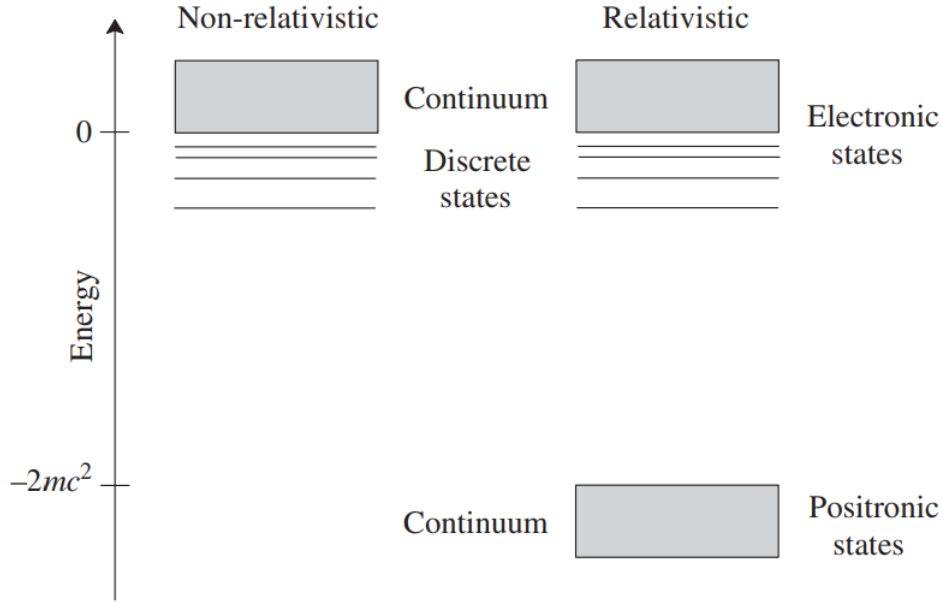
Figure 4: Non-relativistic and relativistic solutions of the Schrödinger equation. The energy scale of discrete states is exaggerated relative to continuum states. Obtained from [16].

The large component in Eq. 22 reduces down to the solutions of the non-relativistic Schrödinger equation when $\lambda c \to \infty$, where λ is a scaling parameter. The small component disappears for this limit. If the momentum goes to zero, the large component disappears and the small component represents the negative energy solutions. The positive and negative energy solutions are now decoupled, giving [27]

$$\tilde{\Psi}_L^+ = \sqrt{1 + \hat{R}^\dagger \hat{R}} \, \Psi_L^+, \quad \tilde{\Psi}_S^- = \sqrt{1 + \hat{R}\hat{R}^\dagger} \, \Psi_S^-. \tag{25}$$

$R^\dagger$ is the Hermitian conjugate of R. The two-component Hamiltonian drops the negative solutions (Ψ_S) and only takes into account the positive solution, essentially neglecting positronic contributions [28]. As such, the exact two-component Hamiltonian (X2C) acts on the two-component wave function

$$\Psi_{2c} = \sqrt{1 + \hat{R}^\dagger \hat{R}} \, \Psi_L^+. \tag{26}$$

The X2C Hamiltonian gives less accurate results than the four-component Hamiltonian, but can reliably reproduce relativistic results. Since the X2C Hamiltonian requires much less computational resources, resulting in a shorter run time, it may be beneficial to use it instead of the four-component Hamiltonian, if calculations are needed quicker or due to not having enough computational resources at one's disposal.

2.4   Basis sets

A basis set is a set of one-particle functions which are used to build atomic orbitals. A basis set can vary in size, with bigger basis sets generally producing more accurate results. There are two types of basis functions commonly used in electronic structure calculations, Slater-Type Orbitals (STOs and Gaussian-Type Orbitals (GTOs). Here, we will focus on GTOs. Gaussian type orbitals, in Cartesian coordinates, are written as

$$g_{ijk} = Nx^i y^j z^k e^{-\alpha r^2}, \tag{27}$$

where the sum of the non negative integers i, j, and k determines the orbital. N is a normalization constant and α is a positive orbital exponent. It is important to balance the choice of basis set with the computational method used. A number of different Dyall basis sets [29] are used to perform calculations with. The first three basis sets are double zeta (v2z), triple zeta (v3z), and quadruple zeta (v4z). A minimal basis set employs one basis function per occupied orbital. This will give a minimum description of the occupied orbitals of an atom. So for row 1 elements, a single zeta basis set will only have one basis function, whereas for row 2 elements, it will have two basis functions for the two s orbitals and 3 basis functions for the three p orbitals ($2x, 2y, 2z$). For row 3 elements, it will have 3 basis functions for each s orbital (1s, 2s, 3s) and 2 sets of 3 basis functions for each p orbital (2p, 3p), and so forth for other row x elements. Improving in accuracy, a double zeta basis set employs two functions per orbital, the triple zeta basis set employs three basis functions per orbital, and the quadruple basis set employs 4 basis functions per orbital. It is evident that with an increasing number of basis functions per orbital, the description of occupied orbitals will become more accurate. Two other basis sets are cv3z and cv4z. The 'c' prefix denotes functions describing core correlation, which is used if core electrons are not frozen in the computations. Other than functions describing core correlation, the number of basis functions follows the same trend of v3z and v4z, as for cv3z and cv4z respectively. Another two basis sets used in this paper are s-aug-v3z and s-aug-v4z. The 's-aug' prefix denotes the use of diffuse basis functions. These basis sets add an automatic single augmentation function, meaning that one set of diffuse functions is added for every angular momentum present in the basis. Computations on anions should be done with augmented basis sets. Added electrons occupy diffuse orbitals, which in turn occupy a larger region of space, so a diffuse function should be used to account for this [30]. Consequently, d-aug-v4z and t-aug-v4z basis functions are also used for Darmstadtium, adding automatic double and triple augmentation functions, respectively.
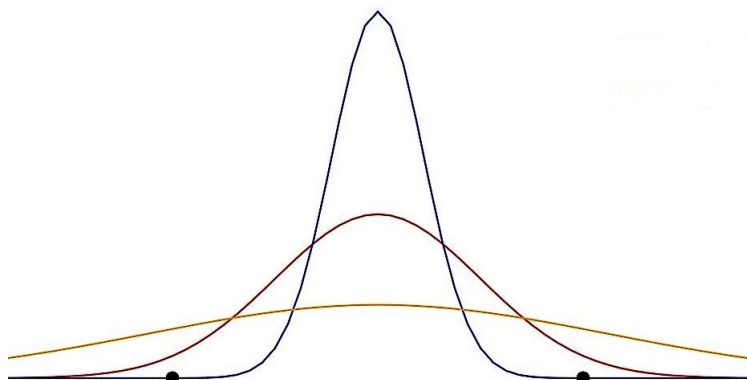

Figure 5: Diffuse orbitals (yellow, red) occupy more space than regular orbitals (blue). Obtained from [31].

3   Results

Computations are done in the DIRAC19 program [11]. Atomic energies are calculated for an ion, a neutral atom, and an anion of an element. The ionization potential (IP) is the difference in energy between the ion and the neutral atom. The electron affinity (EA) is the difference in energy between the neutral atom and anion. Calculations are given in Hartree atomic units and converted to electron volts, where 1 hartree (E_h) = 27,2113... eV [32]. Calculated values for IP and EA are compared to experimental values if possible. In hartree atomic units, the speed of light $c = 1/\alpha \approx 137\ E_h$ [33], where α is the fine-structure constant [32]. Non-relativistic (NR) solutions can then be obtained by setting the speed of light to an arbitrarily large number ($c = 10000\ E_h$ is used), such that the large component in Eq. 21 produces the NR solutions. The X2C Hamiltonian is also used to see if the trade off in less accuracy for less computational resources is worth it. Calculations are done with a -30/30 a.u. cutoff for the occupied and virtual orbitals respectively for all basis sets except the cvnz basis sets, where no orbitals are cut off at all.

3.1   Platinum

The IP and EA for Platinum are calculated with nearly all basis sets mentioned in section 2.4, in order to check which combination of method and basis set will give the best possible results for the calculations with Darmstadtium. First, DHF, CCSD, and CCSD(T) values will be given for a v2z basis set for Pt in Table 1, since it is already clear at this level of accuracy which method is the best.

Table 1: DHF, CCSD, CCSD(T) values for a v2z basis set for the IP and EA of Platinum, compared to experimental values. Values in eV, rounded to 4 decimals.

v2z	IP	Error	*Experiment*	EA	Error	*Experiment*
DHF	7,443	-16,93%	8,95883 [34]	-0,034	-101,61%	2,125104 [35]
CCSD	8.693	-2,97%	"	1,517	-28,61%	"
CCSD(T)	8,836	-1,37%	"	1,732	-18,48%	"

The smallest errors compared to experiment are for the CCSD(T) method, which is in accordance with literature, since CCSD(T) is supposed to be the most accurate of the three methods. As such, for the other basis sets, only the CCSD(T) values will be given.

Table 2: CCSD(T) IPs and EAs for Platinum for different basis sets, compared to experimental values. Values in eV, rounded to 4 decimals.

CCSD(T)	IP	(Δ)	Error	*Experiment*	EA	(Δ)	Error	*Experiment*
v2z	8,836		-1,37%	8,95883 [34]	1,732		-18,48%	2,125104 [35]
v3z	8,999	+0,163	0,44%	"	-		-	"
s-aug-v3z	9,007	+0,008	0,54%	"	-		-	"
cv3z	9,035	+0,028	0,85%	"	-		-	"
v4z	9,048	+0,013	0,99%	"	2,123	+0,391	-0,10%	"
s-aug-v4z	9,050	+0,002	1,02%	"	2,151	+0,028	1,20%	"
cv4z	9,066	+ 0,016	1,20%	"	2,136	-0,015	0,53%	"

Due to time constraints, no basis sets bigger than cv4z were used for Pt. Despite raising the IP, sufficient calculations could not be done with cv4z (meaning the addition of augmentation functions to cv4z, e.g. s-, d-, t-aug-cv4z) for Ds such that results converged. Therefore, convergence is reached for s-aug-v4z for the IP. The obtained values for the EA for triple zeta basis sets did not make any sense, so these values are omitted from the tables.

Calculations for Platinum with the X2C Hamiltonian were done as well. Table 3 shows these results for a v3z basis set. Included are the non-relativistic solutions as well, for a v4z basis set.

Table 3: CCSD(T) X2C Hamiltonian (v3z) and non-relativistic (v4z) results. Values in eV, rounded to 4 decimals.

CCSD(T)	IP	Error	*Experiment*	EA	Error	*Experiment*
X2C (v3z)	8,984	0,28%	8,95883 [34]	-	-	2,125104 [35]
NR (v4z)	7,102	-20,73%	"	1,132	-46,72%	"

While the X2C calculation does produce accurate results, the triple zeta basis set is not suitable for the EA calculation here. For the non-relativistic solutions, values differ by a large margin from the relativistic solutions. The *s* electron is removed from the atom for ionized Platinum. This electron, in the relativistic treatment of Platinum, is stabilized significantly, thus needing more energy to be removed. The non-relativistic treatment does not take this stabilization into account, leading to a lower IP. This result shows that relativistic effects already play a significant role in Platinum and will play an even more important role in Darmstadtium.

3.2   Darmstadtium

For Darmstadtium, the effect of augmentation on a basis set is shown. Again only CCSD(T) results are given. Values are rounded to 4 decimals.

Table 4: Calculated IP and EA of Darmstadtium in eV.

CCSD(T)	IP	(Δ)	EA	(Δ)
v2z	9,3777	-	0,4486	-
v3z	9,5948	+0,2171	1,5810	+1,1324
v4z	9,6994	+0,1046	1,7238	+0,1428
cv4z	9,7026	+0,032	1,7246	+0,0008
s-aug-v4z	9,7007	-0,019	1,7488	+0,0242
d-aug-v4z	9,7007		1,7494	+0,0006
t-aug-v4z	9,7007		1,7491	-0,0003
s-aug-vNz	9,7651	+0,0644	1,7763	+0,0272

In this project, meV accuracy is sought after, that is, we want the results to converge to within single meV, and Table 4 shows that this happens for the singly augmented basis set. Here, the third decimal no longer changes (after rounding) for further calculations. The cv4z basis set does raise the IP in the deV range (convergence is reached for EA), but due to time restraints, no further calculations could be done with cv4z and adding augmentation functions. For this reason, the final calculated values for the IP and EA of Darmstadtium are, rounded to meV, 9,701 eV and 1,749 eV, respectively. Consequently, the CBS limit is taken for the singly augmented N zeta basis set, with N an integer. More explanation on the CBS limit is given in the final paragraph of the discussion.

The non-relativistic EA for Darmstadtium has a value of 4,948 eV. The IP is not reported as the calculations did not work out. The NR EA is three times as large as the relativistic solutions, showing that relativistic effects play a big role in the chemical properties of heavier elements.

4   Discussion of results

There is not a lot of literature on IP calculations for Darmstadtium. One review paper [23], reports an expectation value for the IP of 9,6 eV, by means of DFS calculations, similar to the values in this report. Published in 1975, the result might be outdated, given that since then computational algorithms have improved significantly, and more accurate calculations could be done in recent years. Another paper [36], using the random-phase approximation reports an IP of 11,2(7) eV, which is a lot higher than the calculated values in this report. An IP of 9,739 eV is reported in [37] with an all electron quadruple zeta basis set and the CCSD(T) method. [37] also reports an IP of 10,755 eV, taking into account the full triple and QED effects, but not the Breit correction. QED effects lower the IP in the deV range [38], but the full triple increases [37]'s IP by almost a full eV. This is an interesting result, since the perturbative triple already accounts for most of the contributions from triple excitations, and as such the full triple is not expected to increase the IP by that much. An explanation is not given, and therefore more research is needed, which is out of the scope of this paper. [37] also reports an EA of 1,015 eV, using the CCSD(T) method and a v4z basis set, correlating all electrons. This is the only other reported EA found, and a 700 meV discrepancy between the two values cannot be explained by the increase in active space, since the calculations in this paper use a smaller active space. Testing this for Platinum, correlating all electrons with the active space, the IP and EA only change by less than a tenth of a percent. The only explanation that could reasonably be given is that [37] used the DIRAC16 program, compared to the DIRAC19 calculations here. I have no access to the DIRAC16 program, however, and cannot check these results.

Multiple sources of error arise in the calculations of Darmstadtium. The first is the incomplete treatment of electron correlation. At the present level, the CCSD(T) method is used, with a perturbative triple. Compared to the CCSD method, the CCSD(T) gives more accurate IP and EA values, raising both values considerably. A more complete treatment takes the triple excitation as a whole, giving the CCSDT method. Taking the full triple is expected to give a higher IP, as stated earlier, and a higher EA as well. Moreover, the possibility of quadruple or more simultaneous excitations should be incorporated as well, giving rise to the CCSDT(Q) method with a perturbative quadruple or the full CCSDTQ, with even higher order treatments possible, to give even more complete results. Following the same trend of the full triple increasing the IP and EA, including higher order excitations will likely increase these properties as well.

In the derivation of the DC Hamiltonian, the Breit correction was left out, and in the final calculated values, the QED correction was omitted as well [26]. These corrections are expected to lower the IP and EA in the deV range [39, 40, 41, 38].

The incompleteness of the basis set is another error. The finite basis set is expanded towards an infinite set of functions, yielding an extrapolated result approaching the complete basis set limit [42]. For the IP of Darmstadtium, this value is 9,765 eV and for the EA, this value is 1,776 eV. These values are obtained using a a mixed Gaussian/exponential extrapolation scheme [43] [44]. The idea is that, using bigger basis sets, the IP and EA of Darmstadtium will asymptotically tend towards these values. The contributions from adding core valence functions (cv4z compared to v4z), for example, are negligible (+0,0032 for the IP and +0,0008 for the EA). It is expected that using bigger basis sets, like all electron basis sets, will have a more significant contribution. However, due to time constraints, it was not possible to use bigger basis sets for this project.

5   Conclusion

Calculations were performed for Darmstadtium and its lighter homologue Platinum. Calculations were performed in the DIRAC19 program, with the relativistic 4-component Dirac-Coulomb coupled cluster (CCSD(T)) method and large augmented basis sets. In the framework of this project, meV convergence was reached. For Platinum, calculations produce values less than a percent off of the experimental values. From these results, the singly augmented quadruple zeta basis set was taken as a benchmark to study Darmstadtium. Convergence was reached for Darmstadtium with this basis set as well. For Darmstadtium, an IP of 9,701 eV and EA of 1,749 eV were produced. The CBS limit gives an IP of 9,765 eV and EA of 1,776 eV. Future papers should seek to use bigger basis sets and include higher order excitations for increased correlation. Breit and QED effects should also be corrected for, yielding the most accurate possible results at the current level of theoretical chemistry.

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