Calculate the Electronic properties (Ionisation Potential , Electron Affinity) of Helium Atom by DFT functionals using Open-source software ORCA and Avogadro.

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1 Introduction

Normally, an atom is electrically neutral. But it can either gain or lose electrons to form ions. The positively charged ions are called cations and the negatively charged ions are called anions. Helium is a noble element hence it has a stable electronic configuration ($1S^2$). In this study I am using Density functional method to calculate the electronic properties such as ionisation potential and electron affinity of a helium atom using some open-source software Avogadro (Version 1.2.0) and Orca (Version 5.0.4).

1.1 Ionisation potential

Ionization potential (also called ionisation energy) represents the amount of energy needed to remove an electron from the valence shell of an isolated gaseous atom. The valence shell is the outermost shell. When a neutral atom loses an electron, it forms a mono positive cation. The ionisation potential is classified as First ionisation potential , Second ionisation potential and so on.

First ionisation potential refers to the minimum energy required to remove an electron from the valence shell of the neutral gaseous atom. It can be represented by the following equation :

$$M + \Delta H_{1st} \rightarrow M^+ + e^- \; ; \; \Delta H_{1st} = \text{First ionization energy}$$

Now again the minimum amount of energy required to remove an electron from the M^+ cation to form M^{+2} cation is called the second ionisation potential. It can be represented by the following reaction:

$$M^+ + \Delta H_{2nd} \rightarrow M^{2+} + e^- \; ; \; \Delta H_{2nd} = \text{Second ionization energy, etc.,}$$

The atoms having complete valence shells will require a high amount of ionization energy. So, for the noble gases, they have a complete valence shell, they are very stable, do not tend to ionize easily, hence they require high energy for ionization. Among a given period the ionisation energy of noble gas is highest.

1.2 Electron Affinity

The amount of energy released when an electron is added to a neutral atom to form an anion is called electron affinity. The electron affinity is the potential energy change of an atom when an electron is added to a neutral gaseous atom to form a negative ion.
When an electron is added to a neutral atom (i.e., first electron affinity) energy is released; thus, the first electron affinities are **negative**. However, more energy is required to add an electron to a negative ion (i.e., second electron affinity) which overwhelms any the release of energy from the electron attachment process and hence, second electron affinities are **positive**.

- First Electron Affinity (negative energy because energy released):

$$X(g)+e^{-}\rightarrow X^{-}(g)$$

- Second Electron Affinity (positive energy because energy needed is more than gained):

$$X^{-}(g) + e^{-}\rightarrow X^{2-}(g)$$

Noble gases have a filled valence shell of electrons, which makes them very stable and unreactive. The valence shell of noble gases is completely filled with electrons, so there is no room for additional electrons to be added. Hence, Electron affinity of Noble gases is very low or almost near to zero.

1.3 Theoretical Calculation

- First Ionisation Energy =Total SCF Energy of Cation - Total SCF Energy of Neutral atom
- First Electron Affinity = Total SCF Energy of Neutral atom - Total SCF Energy of Anion

***SCF Energy** stands for Self-Consistent field which uses the Hartree Fock (HF) and DFT methodology to Compute the Energy of the species.

For **Hydrogen like species** the formula for Ionisation Energy (I.E) is (Bohr's Model)

$I.E = 13.6 \{ Z^2 / n^2 \}$ eV Z : Atomic Number
n : Shell Number of Valence electron

2. Objectives

- Draw the helium atom in the Avogadro interface.
- Do the Auto optimization of helium atom using the Auto optimization tool of Avogadro.
- Generate the orca input file using Avogadro for single point energy calculation using DFT functionals
- Run the calculation for neutral helium atom on Windows terminal to generate the orca output files.
- Run the calculation again, by changing charge value in the input file for generating single point energy of cation and anion using same DFT functionals.
- Use the given formula to calculate the ionisation potential and electron affinity of Helium atom
- Compare the values with the theoretical and experimental observations.

3. Methodology

Software required : **Avogadro (Version 1.2.0) , Orca (Version 5.0.4).**

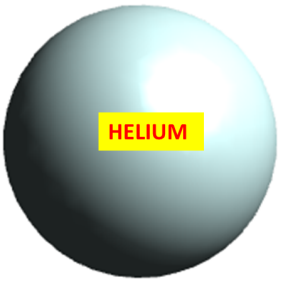
To download the software, go through the below mentioned video link of Spoken Tutorial Project , IIT Bombay.

Avogadro: Click here to Watch

Orca: https://youtu.be/KOa5HmmftWov

Now follow the steps to understand the process of running the calculation.

Step 1 : Open Avogadro and using the Draw tool , Select Helium to get the atom. It looks as shown in figure 1.



Step 2 : Now, Auto optimisation tool but since it is single atom there is no need of Optimising of its geometry.

Step 3: Go to the extension menu of Avogadro and select **Orca** Option. Then Click on Ge**nerate Orca Input** Option. A dialogue box appears. In the comment line write "**Single point Energy Calculation**" (you may leave it blank also).

Step 4: Now Edit the Input file Preview box shown below in **figure 2.**

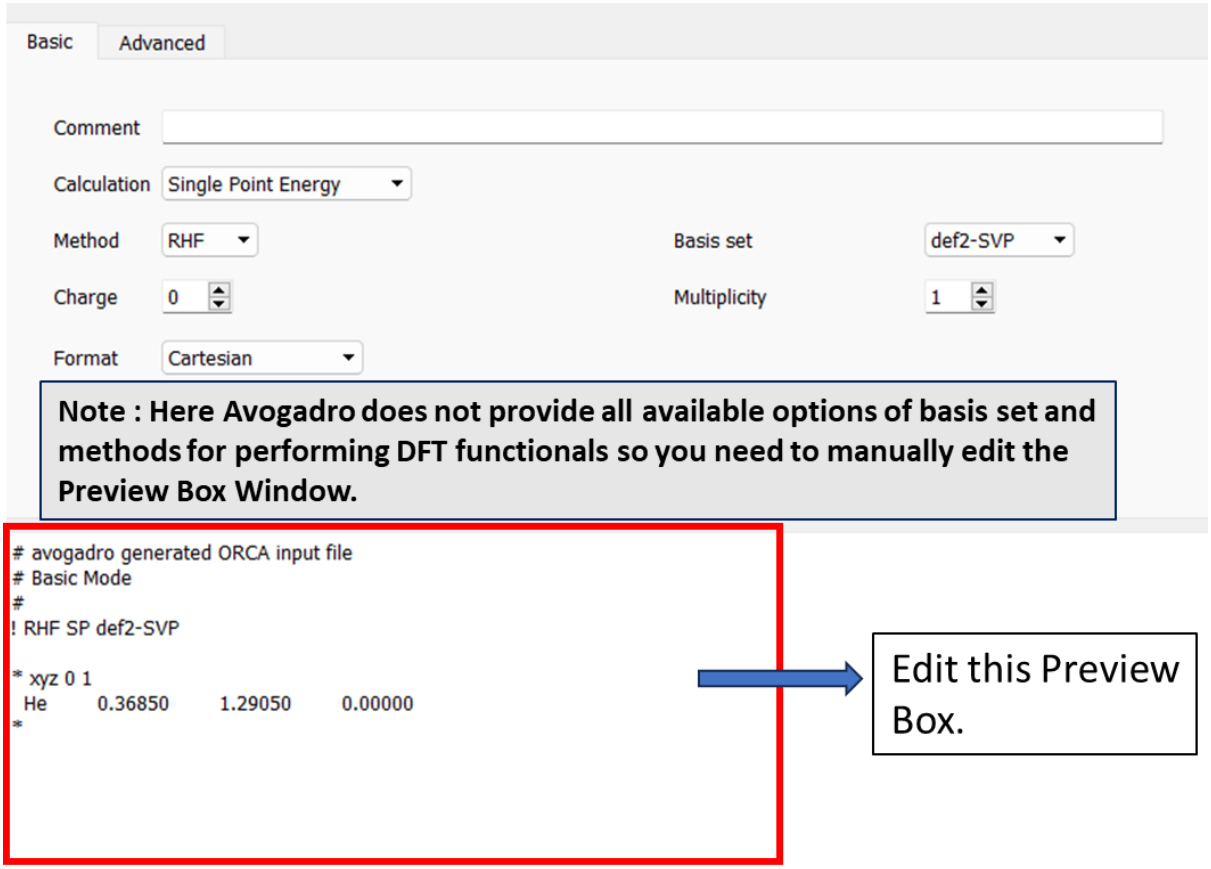


Figure 2

- Change the DFT functional RHF to **B3LYP**
- Change the basis set def2-SVP to **aug-cc-pVTZ**
- Change the Charge to 0 and Multiplicity to 1 for Neutral Helium atom
- Apply **TightSCF** Method to compute the result and hence **add %scf** block

```
%scf
MaxIter 125
CNVDIIS 1
CNVSOSCF 1
end
```

The final preview of the input files sample is shown below in fig 3:

```
## avogadro generated ORCA input file
# Advanced Mode
# Single point energy calculation
! B3LYP SP aug-cc-pVTZ TightSCF
%scf
        MaxIter 125
        CNVDIIS 1
        CNVSOSCF 1
end
* xyz 0 1
  He        0.36850        1.29050        0.00000
*
```

Figure 3

Note : The basis set with B3LYP must be chosen wisely as all basis sets do not produce the correct results for electron affinity and it might give some errors. (Refer here for information)

Step 5: Click on the Save button to save the input file (Say helium_neutral.inp) in the folder (Say Helium present in E drive). Make sure that the Orca executable files must be present in the same drive where you are running the calculation, (Here E drive)

Step 6: Open Command Prompt, as I am running on windows and bring the command to the E drive using basic commands as shown in **figure 4.**

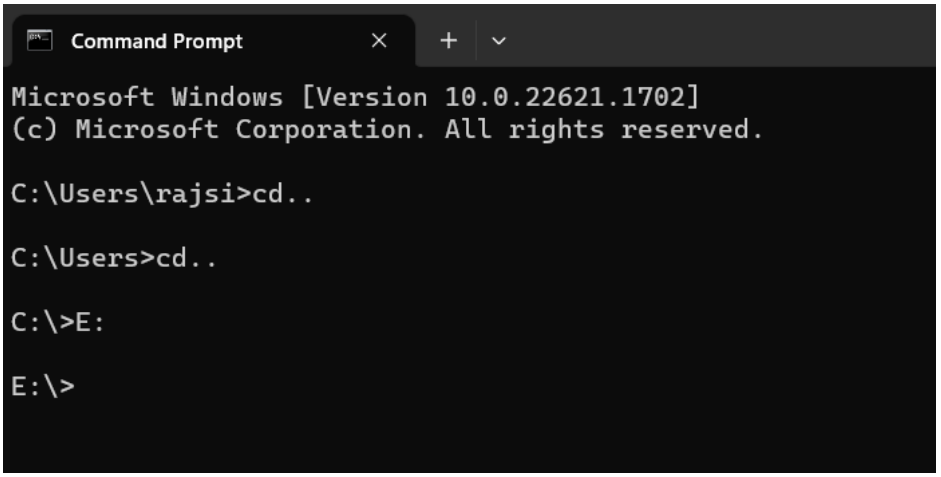


Figure 4

Step 7: Now run the following command to Run orca as shown in figure 5.

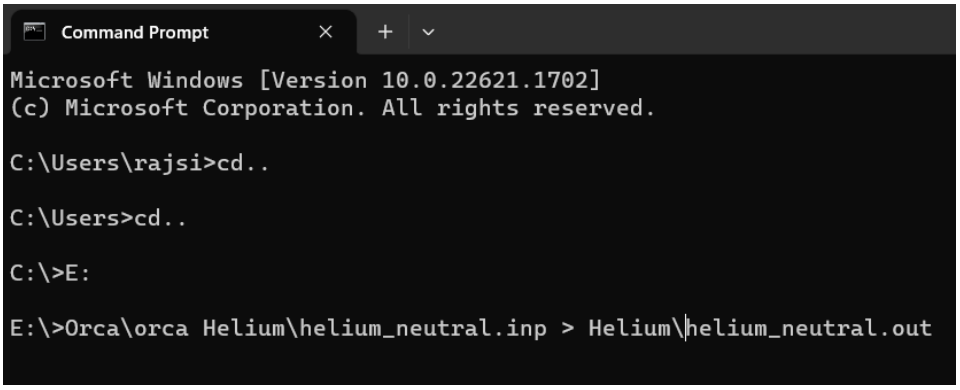


Figure 5

Here **Orca\orca** means the address of the orca executable file. The orca executable file is present in the folder Orca in E drive and Similarly the .inp file is present in Helium folder so it is **Helium\helium_neutral.inp** and the output is generated in Helium folder in the filename **helium_neutral.out** .

Step 8: After the calculation is completed the output file is generated in the Helium folder

Step 9: Now Save another copy of the helium_neutral.inp file in the helium folder and rename it as helium_cation. Open the file in the text editor and just change the value of charge to 1 and multiplicity to 2. Now the input file looks as shown in figure 6.

```
## avogadro generated ORCA input file
# Advanced Mode
# Single point energy calculation
! B3LYP SP aug-cc-pVTZ TightSCF
%scf
        MaxIter 125
        CNVDIIS 1
        CNVSOSCF 1
end
* xyz 1 2
  He        0.36850        1.29050        0.00000
```

Figure 6

Step 10 : Run the calculation similarly with this input file and generate the output result.

Step 11: Now Save another copy of the helium_neutral.inp file in the helium folder and rename it as helium_anion. Open the file in the text editor and just change the value of charge to -1 and multiplicity to 2. Now the input file looks as shown in figure 7.

```
## avogadro generated ORCA input file
# Advanced Mode
# Single point energy calculation
! B3LYP SP aug-cc-pVTZ TightSCF
%scf
        MaxIter 125
        CNVDIIS 1
        CNVSOSCF 1
end
* xyz -1 2
  He        0.36850        1.29050        0.00000
*
```

Figure 7

Step 12: Run the calculation similarly with this input file and generate the output result.

4. Results and Discussions

The .out file of the neutral, cation and anion of Helium gives the following Total SCF energy.

For Neutral:

```
----------------
TOTAL SCF ENERGY
----------------

Total Energy       :          -2.90758749 Eh            -79.11948 eV
```

For Cation:

```
----------------
TOTAL SCF ENERGY
----------------

Total Energy       :          -1.99422108 Eh            -54.26551 eV
```

For Anion:

```
----------------
TOTAL SCF ENERGY
----------------

Total Energy       :          -2.84245361 Eh            -77.34709 eV
```

Calculation of the Ionisation energy and Electron Affinity

Total SCF Energy of He (Neutral) = -79.11948 eV

Total SCF Energy of He (Cation) = -54.26551 eV

Total SCF Energy of He (Anion) = -77.34709 eV

Ionisation Energy = Total SCF Energy of He (Cation) - Total SCF Energy of He (Neutral)

= -54.26551 eV - (-79.11948 eV) = **24.85397 eV**

Electron Affinity = Total SCF Energy of He (Neutral) - Total SCF Energy of He (Anion)

= -79.11948 eV - (-77.34709 eV) = **-1.77239 eV**

4.1 Experimental Observations

According to the experimental results (**Cited** : Kramida, A.; Ralchenko, Yu.; Reader, J., and NIST ASD Team. "NIST Atomic Spectra Database Ionization Energies Data". Gaithersburg, MD: NIST.) The first ionisation energy of helium is **24.587389011** eV.

The electron affinity of Helium (**Cited** : NIST Computational Chemistry Comparison and Benchmark Database,NIST Standard Reference Database Number 101 Release 22, May 2022, Editor: Russell D. Johnson III http://cccbdb.nist.gov/) using B3LYP functional and basis set aug-cc-pVTZ gives the result **-2.682 eV** (near to zero and small negative value of electron affinity for noble gas as discussed earlier.)

4.2 Comparison of the Results

The table shown below compares the electronic properties of Helium.

Electronic Property	Experimental Value	Computational Value
Ionisation energy	**24.587389011**	**24.85397 eV**
Electron Affinity	**-2.682 eV**	**-1.77239 eV**

5. Conclusion

Helium has the highest value of Ionisation energy due to stable electronic configuration. It has two electrons attracted closely to the nucleus with low atomic radius. On the other hand, it has a very small negative value of electron affinity as it is difficult to add an electron to the stable Helium atom because of strong repulsions.