

# Investigating Atoms and Ions with Computers:

## The Aufbau Principle and Periodic Trends

### Overview

Every student who has ever taken a chemistry course is familiar with the periodic table and has learned how to read it. Elements are organized by increasing atomic number, and each group contains elements possessing similar chemical behavior. Various trends are also associated with the periodic table, and many of these trends, are often memorized rather than understood. This series of activity seeks to introduce computational chemistry by utilizing it to increase comprehension of electron configurations, the Aufbau principle and periodicity for first-year students. This exercise will be utilize the Open-Source Pseudopotential Interface/Unification Module (OPIUM) and Xmgrace to determine correct electron configurations, examine the relationships between quantum numbers and radial nodes, to question the Aufbau Principle and to inspect trends in periodicity.

### Installing on a Virtual Machine

Hyper-V is the virtual machine (VM) of choice at Hawkeye Community College as it allows for virtualizations of entire operating systems (OS) such as Linux. Therefore, if you plan on using a different VM on the lab computers, you may want to discuss what options are available with your IT department to ensure your machines are capable of supporting virtualization. To use Hyper-V, the machine should possess a 64-bit CPU with SLAT support, and be capable of VM Monitor Mode Extension, with a 4 GB of RAM minimum. Your institution's IT department should be able to help you get this info if you don't know it. Once Hyper-V is installed and enabled, it's time to create your virtual machine.

Some IT departments prefer to set up the switch portion rather than let the instructor do so. If this is the case at your institution, ask them to create an external one. If you're setting it up on your own, the next step is to open the Hyper-V manager from either the start menu or the desktop—wherever it appears, then, click on your system name (PC-name) and then click on the "Virtual Switch Manager." Select "New Virtual Network Switch", then "External." Using an internal switch makes it difficult to get software loaded on the machine as they usually don't connect to the internet, and private will allow only you to access it—not ideal in the lab setting. Then click "Create Virtual Switch."

At this point, you'll be asked to name the Switch—I went with Chemistry as that indicates to me this particular VM switch relates to—this is important for me as I share computers with Physics. Below the name section, there is another section called "Connection type", you'll need to select the external network connection that you would like to use. If you have more than one of them, reach out to your IT department to determine the best one to use. Once the external network connection has been selected, click "Apply" and "OK."

Once the external network connection is set up, it is time to install Ubuntu, or your chosen Linux OS. Download Ubuntu from the [official Ubuntu website](#). To do this, use the built-in wizard, and select Action, then New, then Virtual Machine. A new wizard will pop up, with a Before You Begin page, select

“Next” to be able to specify the name of the virtual machine, as well as the location where you wish to store it. Most computers will default to the C:\ drive. Ask your IT department if they want you to store it elsewhere so it’s easier for them to copy to other computers. The VM is named at this stage, and I’ve named mine Linux\_Chemistry, so I know which OS is going to be used. If I were going to have multiple VMs, I’d probably go with both OS and software in the name so students could easily identify which experiments it relates to. Then, it’s time to choose the generation. Select Generation 1, as Generation 2 requires some special firmware. Select the amount of memory you wish to allocate to the VM, Ubuntu and OPIUM can easily run with on just 1 GB, but ensure dynamic memory has been enabled for the VM. In the configure networking section, select the network interface previously created, then connect to a virtual hard disk—basically, select the location where the virtual hard disk is stored. Ubuntu has a size minimum of 25 GB, but I find that 50 GB works for both Ubuntu and the software necessary for this exercise—especially as IT resets my machines back to the original build each semester. However, choose what you’re comfortable with, or discuss with your IT to find out what their recommendations are. Then, choose the “Install an operating system from a bootable CD/DVD-Rom” and click on “Image File” and select the Ubuntu file previously downloaded from wherever it was saved. Then select “Next” to see the final summary of your choices. Carefully review them and select “Finish”

It’s now time to finish the install. Right-click on the new VM and click “Connect” to start the VM. Instructions will appear on the screen to complete installation. [Ubuntu on Windows](#) is a great website to follow along with step-by-step directions.

Once the VM is installed, it’s time to install OPIUM and grace. If you’re not familiar with using a command line prompt or Linux, it’s best to familiarize yourself with commands before you import OPIUM and Grace into your brand new VM. I recommend [linux command tutorials](#) as a good starting place or [Ubuntu tutorials](#). It’s important that you’re comfortable moving around in and using Linux before you start doing this lab with students. Once familiar with the commands, or with the aid of your cheat sheet, you are ready to install OPIUM and Grace. First, make sure you can connect to the internet using the new VM. I had to have help with this as IT created internal Virtual Switches—and I couldn’t pull the saved downloads into the Ubuntu VM from a flash drive. This is why I recommend setting up an external switch. Download [OPIUM](#) and its readme file into the VM, and follow the installation directions in the readme file. Make note of where you’re storing OPIUM so you or students can find it easily. I made a directory for it, by typing **mkdir opium** in the command line of a terminal I opened in the virtual machine. If you need to copy the tar file into the new directory, this can be done by finding where the file saved to under the file drawer image in the VM, and then copying it to this new opium directory by opening a new terminal in the file directory and typing **mv tarfilename destinationfolder** and clicking enter. [Grace](#) should be downloaded and copied into this same directory. Both files should be untarred, and the readme files read to install correctly. The opium runsript has quite a long name, depending on the version, so I recommend renaming the executable to just opium. This is done in a similar manner as moving files to a new directory, the command used in **mv originalname newname** and hitting the enter key.

## Pre-laboratory Questions Given to Students

Assign elements to students. 2-3, depending on class size, and if they're sharing computers. In classes where students share computers, I've found that 3 configurations for 2 assigned elements is what students have time to get through during a 2-hour lab period when students are rotating on the computer. Have them submit test configurations prior to the start of class—it helps with instructor prep of the class database if you know which configurations they plan on testing. It is also beneficial for students to have the atomic radii of their atoms written down and brought with them. For students assigned noble gases, have them use the radius of the preceding halogen.

Must be written in your lab notebook and turned in prior to the start of class.

1. What are the electron configurations for your assigned elements? How many total orbitals are in each configuration for each element?  
*Answers vary; by orbitals, the OPIUM code wants to know the total number of subshells the atom has.*
2. For one of your assigned elements with quantum number  $n=3$ , what other electron configurations are you planning on testing? Write the configurations for each of them. Why do you want to test these configurations?  
*Answers Vary*
3. For one of your transition metals, write the electron configurations for the neutral atom, the +1 cation, and the +2 cation. How many total electrons do each of these have?  
*Answers vary*
4. Find the literature values for the first and second ionization energies for the element you chose in number 3. Record these and your source.  
*Answers vary*
5. Determine the conversion factors to convert Ry/atom to kJ/mol. *Students may need help with this one—go over it at the start of class to make sure they have the appropriate conversion factor (1312.75 kJ/mol = 1 Ry/atom)*
6. What is the formula for determining percent error?

$$\frac{|literature\ value - calculated\ value|}{literature\ value} * 100 = \% error$$

## Objectives

In this experiment, students will

- Gain experience with open-source computational chemistry software.
- Identify relationships between quantum numbers, atomic orbital energies, and wavefunctions.
- Learn how quantitatively identify incorrect electron configurations.
- Determine if and where exceptions to the Aufbau Principle occur.
- Calculate ionization energies and compare with literature.
- Extract and plot trends from quantitative data.

As this activity will require 2 laboratory periods, it is broken into two parts: Investigating the Aufbau Principle and Periodic Trends

## Materials

Lab computers with OPIUM and Grace installed either in Linux or on a Virtual Machine

Periodic Table

Directions on how to use OPIUM ([OPIUM in VM--Carbon](#))

If using a different VM, it may be best to record your own video for your students. I've found that providing students with a video helps them better prepare for the activity.

## Example Input File

[Atom]

C                    Symbol for the element  
3                    Total number of subshells  
100 2.00 -        Sublevel in *n/m* notation, # of electrons, and the '-' tells the code to calculate the energy  
200 2.00 -        Repeat for each sublevel  
210 2.00 -        with desired # of electrons.

[Pseudo]

3 1.54 1.54 1.54        Total # of sublevels to plot, and a radius to use for each (use diameter of atom)  
opt                    Calculation method

[Optinfo]

7.07 10                Info for calculation method  
7.07 10                List these values for each sublevel to be plotted.  
7.07 10                No need to change values for this activity—we're not building pseudopotentials!

## Methods

Investigating the Aufbau Principle

1. Log in to the computer, then log in to the server or access the virtual machine as directed by the instructor.
2. Follow along with the instructor to work through the Carbon example as demonstrated by the video. Record data as directed. Some of the commands you'll use follow:

```
emacs C.param  
./opium C C.log ae plot wa  
emacs C.log
```

Shown below is the sample output file for Carbon. We're interested in the total energy, which is listed first under the total number of iterations, then the orbitals, their filling, and their related eigenvalues for this exercise.

```

=====
Begin AE calculation
=====
Performing non-relativistic AE calculation...
-----Eigenvalue guesses-----
1s      -36.00000000
2s      -2.25000000
2p      -2.25000000

iter      Etot          Ebs          Ehxc          de_max      dv_max
 1      -78.0101223   -46.1066343   -31.9034880   0.73E+00   0.20E+01
 2      -76.9630569   -44.6770656   -32.2859913   0.10E+00   0.10E+01
 3      -75.3373196   -42.8552064   -32.4821132   0.18E+00   0.14E+00
  :
25      -74.8485240   -42.5925070   -32.2560171   0.22E-07   0.57E-07
26      -74.8485240   -42.5925070   -32.2560171   0.11E-07   0.32E-07
27      -74.8485240   -42.5925069   -32.2560171   0.52E-08   0.18E-07

 27 iterations: (units are Ry and bohr)
Energy:   -74.84852399  Ebs:    -42.59250694  Ehxc:    -32.25601705
Eh       :   35.24955639  Exc:     -9.45350358

Orbital   Filling      Eigenvalues      Norm(rc->oo)      Peak
|100>     2.000        -19.895705
|200>     2.000        -1.001950        0.542895          1.224346
|210>     2.000        -0.398599        0.589443          1.192923

=====
End AE calculation
=====

```

- Take a picture or a screenshot of the plots created. [Let them use their phones if desired, it helps them rotate through faster to ensure everybody is able to get their configurations done.](#)
- Complete all-electron calculations for all assigned elements and record your data—all the places after the decimal should be recorded. When using the commands above, remember to change out the symbol for your elements! [Again, allowing them to take pictures and then record in their lab notebook is a timesaver!](#)
- To run different configurations of an element or ion, there are two approaches. If you want to change the entire configuration, create a new input file. If you want to test an ion of an existing configuration, the command **cp Sy.param Sy1.param** is your best option, where Sy is the symbol of your element. Use the emacs command to open the new file and modify as desired. [Watch for errors here, many of them may use Sy instead of the symbol of their assigned element, or they'll add extra space and will then need to recreate the file.](#)
- Run a variety of different configurations for one of your assigned elements in period 3. For the configurations you tested, **how can the correct electron configuration be identified?** (Data Analysis Question 1) **Explain your reasoning.** (Because the book says a particular configuration is correct is not a valid answer.) [This is a good topic to discuss with the class as a whole.](#)
- Create a graph for one of your non-transition metal elements showing the orbitals filling in increasing energy. The x-axis should be your orbitals in *n/m* notation, and your y-axis should be the energy of the orbitals in Ry. Label your graph. [I allow the use of bar or line graphs—it depends on your preference.](#)

8. Create a graph for one of your assigned transition metals. The graph should have the same axes used in 7. [These graphs get tricky to read due to the huge differences in energy which we start to notice. Bar graphs are generally a bit easier for this one compared to line graphs.](#)
9. Compare your graphs from 8 and 9. And, using the class data, create a plot of  $4s$  and  $3d$  orbital energies for the 3d transition metals. Label your graph. What happens as one moves from left to right across the period? Do all of these follow the diagram in the text? [Again, line or bar graph. I prefer a line graph, and I have my students label the x-axis with the element symbols for Sc-Zn.](#)

**Is the Aufbau Principle obeyed in all circumstances? (Question 2)**

At this point, you should be wrapping up week 1 of the lab. Next week will wrap up Part I by examining the relationship between quantum numbers and radial nodes, and will then continue on with Part II. Turn all data from Week 1 into the instructor so the class database can be completed and uploaded to Canvas. [\(Or LMS of your choice\)](#)

10. Examine the plot for your transition metal. How many times do the radial wavefunctions for the  $1s$ ,  $2s$ ,  $3s$  and  $4s$  orbitals cross zero? **How are quantum numbers and radial nodes related?** (Question 3) [If they edit their graphs to have different colors for each of the wavefunctions, this is easier for them to determine.](#)
11. Using the same graph as the previous step, examine the radial wavefunctions for the  $3s$ ,  $3p$ , and  $3d$  orbitals. **Within a particular quantum number, what is the relationship between radial nodes and type of orbital?** (Question 4) [Same note as above, different colors help make it easier to pick out lines—they can also increase line thickness if desired.](#)

Periodic Trends

12. To calculate the first ionization energies, run all-electron calculations for the neutral atom and for the +1 cation for one of your assigned metal atoms. Record the total energy for each.
13. Take the difference between the total energy of the +1 cation and the neutral atom. As all of the energies provided by the software are in Ry/atom (electron), unit conversions will be necessary to convert to the SI units students are familiar with. **How is ionization energy related to total energy?** (Question 5) [Students need to take the differences in total energy.](#)
14. Calculate your percent error. Literature values can be obtained from the textbook or from the NIST Chemistry Webbook.
15. To calculate the second ionization energy, run the all-electron calculation for the +2 cation. Take the difference between the +2 cation and the +1 cation's total energies. Convert to SI units. Calculate the percent error. **Using your results, can you explain why certain cations will form, but others won't? (Question 6)**
16. Make a table of containing the valence orbitals and their energies for the representative elements.
17. Examine the class data, **does the data explain why the noble gases are the most inert group of elements?** (Question 7) [What do they notice happens to the valence orbitals as the noble gases are approached?](#)
18. All tables and graphs must be in your typed, electronically submitted lab report.

## Data Analysis Questions

Investigating the Aufbau Principle:

1. How can the correct electron configuration be identified?
2. Is the Aufbau Principle obeyed in all circumstances?
3. How are quantum numbers and radial nodes related?
4. Within a particular quantum number, what is the relationship between radial nodes and type of orbital?

Periodic Trends:

5. How is ionization energy related to energy?
6. Does the data explain why the noble gases are the most inert group of elements?
7. Why can some cations form, but others cannot? Examples of  $\text{Na}^+$  vs  $\text{Na}^{2+}$ .

## Error Analysis

Discuss the percent error found from your ionization energies. What do these values tell you about the methods used by the software?

## Conclusion

How has your understanding of electron configurations changed after doing this lab? Were you able to meet all of the objectives? Are there any parts of the exercise you would like to spend more time on or that are still unclear?

These questions help gauge where students now feel they are on understanding the topic, and also help modify the lab to fit your needs based on student feedback.

## Teacher Information

### Sample Answers for Data Analysis Questions

1. How can a correct electron configuration be identified?

**The example here is for Chromium:** Test out various configurations—the easiest way to do this is through use of the [Configs] keyblock as only a single input file is needed. The total energy for the correct configuration is -2084.03498 Ry. For the  $[\text{Ar}] 4s^2 3d^4$  configuration, the total energy is -2084.02264 Ry. The correct configuration is the most stable one, will always have the lowest total energy.

2. Is the Aufbau Principle obeyed in all circumstances?

By examining a table of the energy (Ry) values of the  $4s$  and  $3d$  orbitals and by plotting them, we find that once one moves to Ti in the transition metals, the  $4s$  orbitals are higher in energy which makes them easier to remove. One can also hypothesize that the closer in energy the  $4s$  and  $3d$  orbitals are, the more likely the elements are to lose all the electrons contained in both orbitals.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	-0.3135	-0.3348	-0.3525	-0.2363	-0.3828	-0.3965	-0.4095	-0.4220	-0.3447	-0.4459
3d	-0.2619	-0.3397	-0.4089	-0.3016	-0.5327	-0.5897	-0.6215	-0.6969	-0.4044	-0.7974

Eigenvalue Comparison of 4s and 3d Orbitals for the 3d Transition Metals

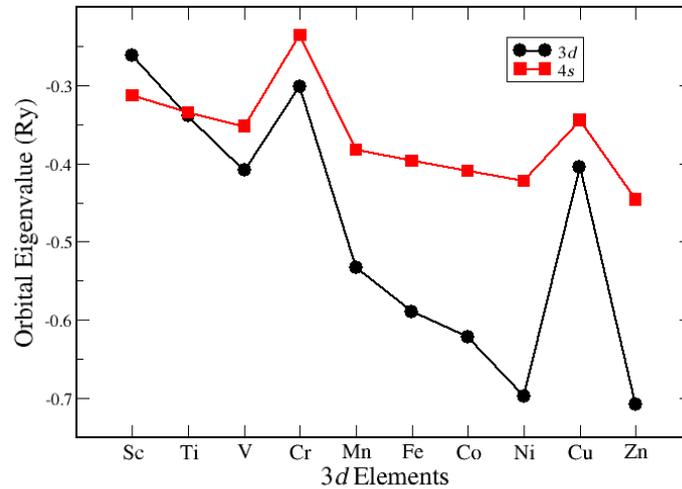


Figure 1. Plot of 4s and 3d orbital energies.

3. How are quantum numbers and radial nodes related?

## Radial Distributions for the $s$ Orbitals

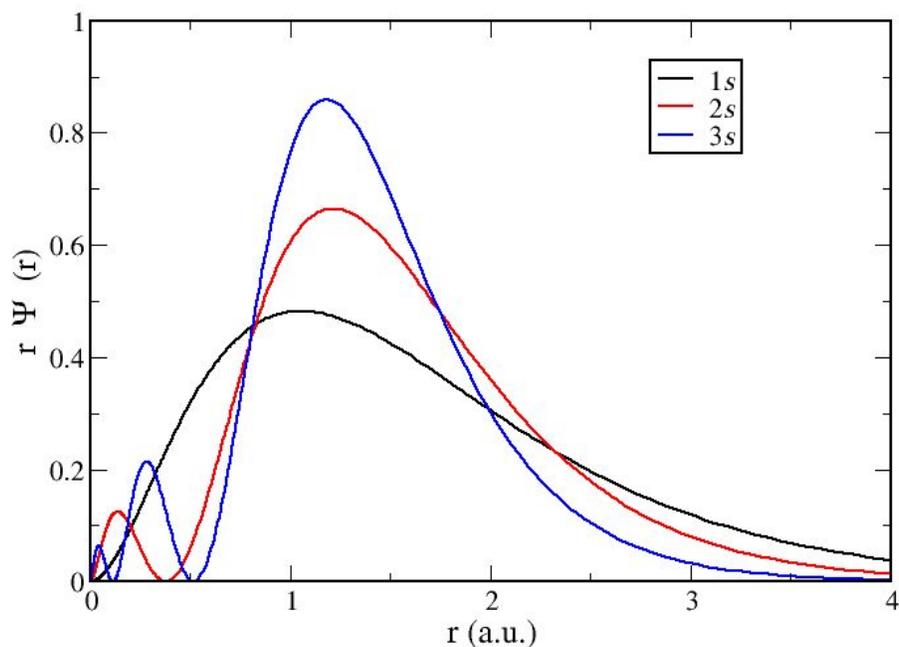


Figure 2. Radial Probability Distribution for  $n=1$  through  $n=3$ .

By plotting or comparing the wavefunctions for the  $s$  orbitals for the principle quantum number, we can see that the relationship between wavefunction (or radial probability distribution) and the number of nodes is

$nodes = n-1$ . We also can observe that the greater  $n$  is, the greater the probability that the bulk of the radial distribution of the electrons will be located further from the nucleus.

4. Within a particular quantum number, what is the relationship between radial nodes and type of orbital?

## Radial Probability Distribution for $n = 3$

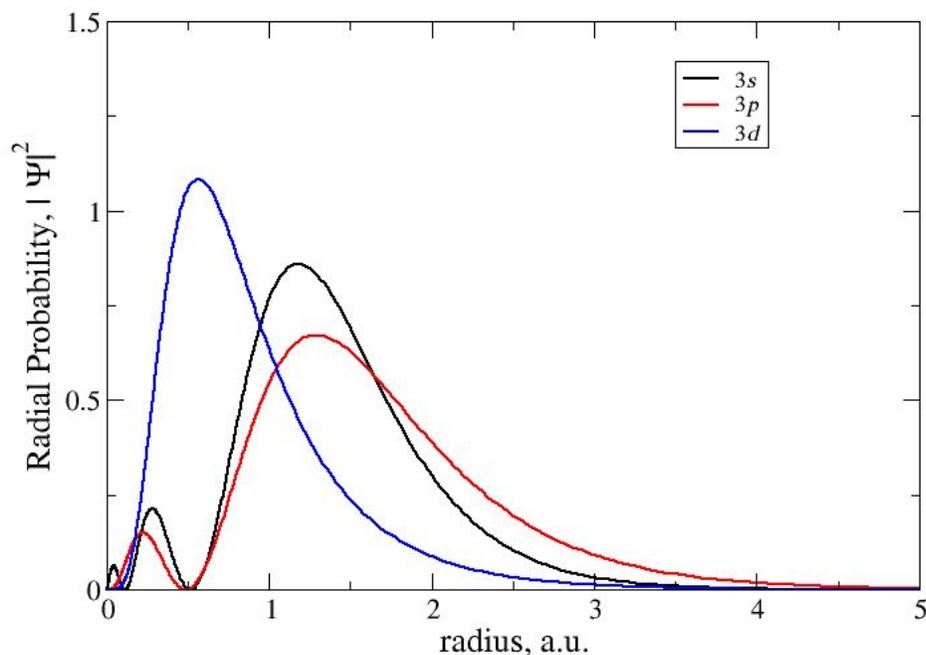


Figure 3. Radial probability distribution for all  $n=3$  wavefunctions.

If we examine the radial probability distribution of all  $n=3$  wavefunctions, we see the  $3s$  has 2 nodes, the  $3p$  has 1 node, and the  $3d$  has zero nodes. This means we can further clarify that nodes =  $n-1$  for the  $s$  orbitals,  $n-2$  for the  $p$  orbitals and we can hypothesize this trend will be  $n-3$  for the  $d$  orbitals and  $n-4$  for the  $f$  orbitals. More calculations would need to be computed and plotted to test this hypothesis.

### 5. How is ionization energy related to total energy?

By making a table of the valence atomic orbitals energies (Ry) we find that the higher the principle quantum number, the higher the energy (or the smaller the energy's magnitude), making it easier to remove an electron. This matches the trend that as one goes down a group, the ionization energy decreases. We also see the energy of the valence atomic orbitals becomes more negative (an increase in magnitude) as one goes left to right across the periodic table, requiring more energy to remove an electron. This again follows the trend for ionization energy.

Ionization energy for the formation of cations can easily be calculated using this software. By using the `cp` command, we can copy the initial file to one of the ion, and then make the necessary edits. We can make as many of these files as desired and use them to test a multitude of cations. **The example here is for copper.**

Start by obtaining the total energy for the neutral configuration. For neutral Cu with the configuration  $[\text{Ar}]4s^1 3d^{10}$ , the total energy is -3275.53914 Ry. The  $\text{Cu}^+$  cation was ran through as `Cu1.param` and a total energy of -3274.93714 Ry was obtained. Take the difference between the two total energies.

-3274.93714 Ry - 3275.53914 Ry = 0.60200 Ry.

However, SI units are in kJ/mol. Units need to be converted. This is the energy it takes to remove a single electron from a copper atom. How many atoms are in a mole? ( $6.022 \times 10^{23}$  atoms/mol). What is the conversion between Rydberg and kJ? ( $2.18 \times 10^{-21}$  kJ = 1 Ry) or (1 Ry = 1312.75 kJ/mol).

$$\frac{0.60200 \text{ Ry}}{1 \text{ atom}} * \frac{2.18 * 10^{-21} \text{ kJ}}{1 \text{ Ry}} * \frac{6.022 * 10^{23} \text{ atoms Cu}}{1 \text{ mol Cu}} = 790.31 \frac{\text{kJ}}{\text{mol}}$$

Literature value (obtained from NIST Chemistry Webbook) is 745.48 kJ/mol.

The percent error can be calculated, and is found to be 5.95 % for the first ionization energy.

This can be repeated for the removal of the second electron, where the difference would be taken between  $\text{Cu}^{2+}$  and  $\text{Cu}^+$ . The percent error for the second ionization energy of copper is 7.58 %. Students would be able to determine a trend in ionization energies.

6. Does the data explain why the noble gases are the most inert group of elements?

Orbitals in Kr	Orbital energies in Ry
1s	-1019.9700
2s	-132.5730
2p	-120.0360
3s	-18.6305
3p	-14.1734
4s	-1.6410
3d	-6.1483
4p	-0.6928

By creating a table of containing all the orbitals' energies (example shown is Kr), the data shows a large difference in energy each time electrons enter a new shell (higher  $n$ ). The higher the value of  $n$ , the smaller in magnitude the energy is. For example, there is a significant increase in energy as one moves from the  $2p$  orbital to the  $3s$  orbital. However, moving left to right across a particular quantum number show only a slight increase in energy (slight change in magnitude. If for example, we were to look only at the orbital energies for  $n=3$ , one finds that the  $s$  orbital is the lowest in energy, the  $p$  orbital falls in the middle, and the  $d$  orbital is the highest in energy. If the collected data is analyzed, one sees that by moving towards noble gas configuration, the valence shells energies become more negative, and therefore more stable. This can also be observed by examining the trend of the total energy for the elements.

7. Why can some cations form, but others cannot? Examples of  $\text{Na}^+$  vs  $\text{Na}^{2+}$ .

For cations, the ionization energies for removing multiple electrons can be determined, and the quantity of energy to remove each electron can be determined and the results analyzed to determine why some electrons can be removed and others cannot.

For example, the total energy for the Na<sup>+</sup> cation is -322.486965 Ry, for neutral Na, it is -322.866737 Ry. We can take the difference between these (Na<sup>+</sup> - Na), and then convert to kJ/mol to determine the ionization energy.

$$-322.486965 \text{ Ry} - -322.866737 \text{ Ry} = 0.3797722 \text{ Ry} * \frac{1312.75 \frac{\text{kJ}}{\text{mol}}}{\text{Ry}} = 498.54 \frac{\text{kJ}}{\text{mol}}$$

The total energy of the Na<sup>2+</sup> cation is -318.9290852 Ry. If the difference between the total energies for Na<sup>2+</sup> and Na<sup>+</sup> are taken, we find the second ionization energy as follows:

$$-318.9290852 \text{ Ry} - -322.486965 \text{ Ry} = 3.5578798 \text{ Ry} * \frac{1312.75 \frac{\text{kJ}}{\text{mol}}}{\text{Ry}} = 4670.61 \frac{\text{kJ}}{\text{mol}}$$

Students can find these energies and discuss why multiple electrons are unlikely to be removed from some elements.

## References

1. Ubuntu download site. <https://ubuntu.com/download/desktop> Accessed May 2021.
2. Ubuntu on Windows. <https://geekflare.com/ubuntu-on-windows/> Accessed May 2021.
3. 35 Linux Basic Commands Every User Should Know. <https://www.hostinger.com/tutorials/linux-commands> Accessed May 2021.
4. Ubuntu Tutorials. <https://ubuntu.com/tutorials/command-line-for-beginners#1-overview> Accessed May 2021.
5. OPIUM download site. <https://sourceforge.net/projects/opium/> Accessed May 2021.
6. Grace site. <https://plasma-gate.weizmann.ac.il/Grace/> Accessed May 2021.
7. OPIUM tutorial in a VM. <https://hcc.hosted.panopto.com/Panopto/Pages/Embed.aspx?id=dd43f166-73d7-405b-8c40-aa63012679a2> Accessed May 2021.