This homework is a little different. We will use the cool web base *ab initio* site by Perri at Sonoma State U. Download the following paper and review the concept (http://pubs.acs.org/doi/pdf/10.1021/ed5004228). Follow the directions on this tutorial (you will not need to install *Avogadro* for this HW). We will use this package multiple times in this class so make sure you can complete the online tutorial if you are confused.

To start the calculations

- click here: https://chemcompute.org
- sign in: Username: "Chem110A" and password: "Halloween"
- click on GAMESS at the top
- click on "submit" on top right

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**Binding (total) Electronic Energy**

Binding energy $E_{\text{tot}}$ is the total electronic energy for the system and it does not include nuclear energies (e.g., vibration and rotational). The "chemical" reaction associated with this energy for the $M$ atom with $n$ electrons is

$$ M \rightarrow ne^- + M^{n+} \quad \text{Label(Eq1)} $$

The expression for **Binding Energy** would be calculated from the energies $E$ of each species:

$$ E_{\text{tot}} = \underbrace{nE(e^-) + E(M^{n+})}_{\text{products}} - \underbrace{E(M)}_{\text{reactant}} $$

Since kinetic energy of any species is not included in this discussion, only the energy of the $M$ and $M^+$ species needs to be explicitly calculated.

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**First Ionization Energy**

The **First Ionization energy** is the energy necessary to remove the weakest bound electron. The "chemical" reaction associated with this energy for the $M$ atom with $n$ electrons is

$$ M \rightarrow e^- + M^+ \quad \text{Label(Eq2)} $$

The expression for **First Ionization Energy** would be calculated from the energies $E$ of each species:

$$ E_{I_1} = \underbrace{E(e^-) + E(M^+)}_{\text{products}} - \underbrace{E(M)}_{\text{reactant}} $$

Since kinetic energy is not included in this discussion, only the energy of the $M$ and $M^+$ species needs to be...
Second Ionization Energy

The second ionization energy is the energy required to remove the next weakest bound electron. The "chemical" reaction associated with this energy for the \( M \) atom with \( n \) electrons is

\[
M^+ \rightarrow e^- + M^{2+} \tag{Eq3}
\]

The expression for **Second Ionization Energy** would be calculated from the energies \( \langle E \rangle \) of each species:

\[
\langle E_{I_2} \rangle = \underbrace{E(e^-) + E(M^{2+})}_{\text{products}} - \underbrace{E(M^+)}_{\text{reactant}}
\]

Since kinetic energy is not included in this discussion, only the energy of the \( M^+ \) and \( M^{2+} \) species needs to be explicitly calculated.

Note: The binding energies and Ionization Energy are related. For an atom \( \langle M \rangle \) with \( n \) electrons, the binding energy is determined by

\[
\langle E_{\text{tot}} \rangle = \sum_{i=1}^{n} -E_{I_i} = -E_{I_1} - E_{I_2} - ... - E_{I_{n-1}} - E_{I_n}
\]

Electron Affinity

The **electron affinity** is the change of energy when a neutral atom acquires an electron to generate an anion. The "chemical" reaction associated with this energy for the \( M \) atom with \( n \) electrons is

\[
M + e^- \rightarrow M^- \tag{Eq4}
\]

The expression for **electron affinity** would be calculated from the energies \( \langle E \rangle \) of each species:

\[
\langle E_{EA} \rangle = \underbrace{E(M^-)}_{\text{products}} - \underbrace{E(M) + E(e^-)}_{\text{reactant}} \tag{EA2}
\]

Since kinetic energy is not included in this discussion, only the energy of the \( M^- \) and \( M \) species needs to be explicitly calculated.

Calculating electron affinities is harder to do than with ionization energies, especially for closed shell systems (all electrons paired). While Equation \ref{EA2} is correct, we will learn a simpler approximation in a different *ab initio* project to avoid these difficulties.

Building the first Two rows of the Periodic Table

Run the single-point calculations on the first 18 atoms of the periodic table (Hydrogen to Argon) and fill in the below table. You only need to extract the total energy (binding energy) of each system for the table, but you need to address the spin of the system explicitly (see previous *Dry Lab* for details on multiplicity in quantum calculations).
- If the spin multiplicity of the atom is not 1, then use the UHR (Unrestricted Hartree-Fock) method,
- If the spin multiplicity of the atom is 1, you can use either the RHF (Restricted Hartree-Fock) or UHR method (should give the same results).

Use the \textit{aug-cc-pvdz} basis set for both calculations. \textbf{If you select the RHF method and have a non-unity spin multiplicity, the program will give you an error. You may have to modify}

If the program crash

You'll may have to use HCORE to calculate the orbitals which provides an initial starting point by just diagonalizing the matrix of orbitals instead.

1. Click Do more calculations
2. Click Create Input File
3. Change: GUESS=HUCKEL
4. To: GUESS=HCORE
5. Click Submit Job

When you recalculate a new atom you will have to change the multiplicity for the molecule (from the table you are making below) and then you "create" the input file and swap to the next atom in the input (see arrow above) by changing these two aspects:

1. the name of the atom to the standard chemical abbreviation and
2. the number after that is the atomic number \( \lfloor Z \rfloor \).
<table>
<thead>
<tr>
<th>Atom</th>
<th>Nuclear Charge ((Z))</th>
<th>Electronic Configuration (\text{Spin Multiplicity} , (2S+1))</th>
<th>(E_{(\text{tot})})</th>
<th>(E_{(I_1)})</th>
<th>(E_{(EA)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1</td>
<td>(1s^1)</td>
<td>2</td>
<td>-313</td>
<td>313</td>
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<tr>
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<tr>
<td>Argon</td>
<td>18</td>
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</tr>
</tbody>
</table>

Submit for Credit the Following Items or Answers

Submit the above table filled out for the total binding electronic energy of each atom (do not copy from others as if we will compare tables)

- Plot up this binding energy, first ionization energy and electron affinity vs. Z on your favorite software (e.g., Excel or...
matlab or Plot2 for mac users)

- You should notice several periodic trends in each of the three plots. Explain the origin of the trends of each plot and be as specific as possible within the context of atomic theory.

- The general argument for octets is based on the special "stability" of full shell systems. Does that argument make sense within the context of the definitions above and the simulations you ran and tabulated above? For example is $E_{\text{tot}}$ for $Ne$ more stable (lower) than $E_{\text{tot}}$ for Na? Why or why not does this justify the octet rule?

- Compare the calculated Electron Affinities to the "correct" ones. What conclusion can be drawn from this comparison?