Aromaticity and Antiaromaticity in Alkali Metal and Alkaline Earth Metal Small Clusters

This paper is on the aromaticity concept to small aromatic alkali metal and alkaline earth metal clusters. The scientists selected various groups of triatomic and tetratomic metal clusters. They used Li\(^+\) and Li\(^-\) ions to explain stability and their structure. They also choose various structures such as Li\(_3\)Cl to get energy and prove if Li\(^+\) or Li\(^-\) is more stable. Also they tested Li\(_2\)MG\(_2\) to prove that the cyclic aromatic structure is more stable than the linear structure. This shows the importance of the sigma aromaticity in metal clusters. These tests are important in the advancement of the aromaticity concept into metal clusters in understanding chemical bonding in these species. For this research they performed initial calculations of (B3LYP/6-331+G*, CCSD(T)/6-311+G* and CCSD(T)/6-311+G(2df). My purpose is to prove their theory, that Li\(_2\)MG\(_2\) is more stable in cyclic form then linear, and test their various calculations in their paper through Gaussian.

This paper discusses topics and concepts, which is confusing to the beginning chemistry major. First of all this paper involves the science of organic chemistry which has the largest amount of chemical compounds. This paper tests on alkali and alkaline earth metals. Alkali metals are in-group 1 of the periodic table. Alkali metals are highly reactive metals that do not occur freely in nature. These metals
have only one electron in their outer shells, which they give up when ionic bonding with other elements. Alkaline earth metals are metallic elements found in the second group with an oxidation number of +2. This makes them very reactive, but still not found freely in nature.

Another part of the paper discussed is the kekule structures. This theory from August Kekule says that carbon atoms can join to one another to form chains. The benzene structure is the one we used to today. This paper involves the resonance of these structures.

A big part of this paper involves organomettalic chemistry. This chemistry involves a carbon atom bonded to a metal. It also deals with compounds in which an organics group is attached through carbon to an atom, which is less electronegative than carbon.

Still another concept discussed is Wade’s rule, which goes along with organomettalic chemistry. The rule states that a cage molecule with a geometry based on a closed polyhedron constructed of triangles with n vertices will possess n+1 sketal bonding electron pairs. The rule has been successful in showing the structural interconnections between boranes, carbines, organomettallic complexes, and transition-metal cluster compounds.

Next, there is the Jahn-Teller Theorem that was published in 1937. It states that any non-linear molecular system in a degenerate electronic state will be
unstable and undergo distortion, to form a system of lower symmetry and lower energy thereby removing the degeneracy. The theorem predicts the distortions should occur for any degenerate state.

In the paper there is something about Robinson’s aromatic metal clusters and all I’ve found about is Robinson annulation is a synthesis of six membered rings. This could be in the same league because the paper deals six membered ring structures.

Antibonding involves two atoms repulsing each other. These two atoms will never combine to form one compound though it might happen in the orbital level.

Another topic of the paper involves aromaticity. This concept was created to account for the unusual stability of organic molecules. It was originally created for benzene. Now it’s used to describe cyclic, planar, and conjugated nonpossessing pi-electrons. It uses the expression of \((4n+2)\). The \((4n+2)\) expression is called Huckel’s rule, which involves the special degree of stability called aromaticity. The \((4n+2)\) means there must be a total of \((4n+2)\) pi electrons. This rule deals with organic molecules and involves molecular orbitals of molecules. One example is molecular orbital for rings containing five or six sp\(^2\) hybridized carbons. All contain a single orbital and four \(n\) degenerate pairs. It will take the \((4n+2)\) pi electrons to fill a set bonding orbitals, two for the lowest orbitals and four degenerate \(n\) pairs in these aromatic compounds. This is an example of the Huckel rule.
In this paper there are a lot of formulas for reactions where you can calculate the stability of the molecules, using the traditional formula of products-minus reactants. To get to these results I created the structures using WEBMO. I created the molecules by looking at what the paper showed for most of the molecules. Then I created them in WEBMO closest to what they asked for. To get answers, I used the optimized geometric structures using the geometry of CCSD(T)/6-311+G(2df). These reactions gave the answers in Hatree, put in the paper the answers were in kcal/mol. To reach the answers you have to use the conversion of 1 Hatree=627.5095 kcal/mol. In the paper there were formulas given to calculate various energies. There were four of them in the paper, and I tested their answers with my own calculations. My results were from figures they gave in the paper with energies below them. I tested them, though for this I had to find the correct products to use in the formula to get a close answer. The rest of the results are three versions of Li$_2$Mg$_2$ that I tested to see which is more stable the cyclic version or the linear version. Again the paper didn’t give an idea of all the structures needed to get that energy, though it did give hints in their tables. These hints made it possible for me to create the formula they used. Below is a Table of all my results of the ten formulas I the paper didn’t give one.
For reaction 1, the formula was Li₃Cl→Li₂+LiCl. For the LiCl₃ required that it looked like the picture above. It had a bond length of 2.77 angstroms from 3 to 4. From 1 to 4 and 1 to 3 had a bond length of 3.10. The bond between the lithium and Carbon, which is 1 to 2, had a bond length of 2.05. For the Li₂ and LiCl the paper did not give a length needed. So I created the molecules in WEBMO and let it clean up the molecules gave it a specific bond length. For the dilithium had a
bond length of 2.099 and the bond length between lithium and chloride was 2.22. I got an answer of 23 kcal/mol. This is answer is almost matches the answer they calculated in the paper of 23.4 kcal/mol.

For reaction 2 and 3 was comparing the atomization energy of Li₃⁻ and Li₃⁺. The Li₃⁻ had two bond lengths of 3.06. For the Li₃⁺ had bond lengths of 2.99 and is in a triangular form compared to the linear form of Li₃⁻. Using the formula of products minus reactants I got an answer of 44.9 for Li₃⁻ and –71 for Li₃⁺. One answer was close while the answer for Li₃⁺ was way off. I got an answer of negative making the reaction exothermic while the answer should have been endothermic. The real two answers are 42.2 and for Li₃⁺ the answer is 65. This shows that the atomization energy of Li₃⁻ is lower then the atomization energy of Li₃⁺.
For reaction 4 was part of a comparison of Li$_4^{+2}$ resonance energy. One problem is that I couldn’t do the first equation of Li$_4^{+2}$ because WEBMO wouldn’t let me. Also, another problem was that I couldn’t understand what they were comparing the two energies too and the ideas behind it. So for this part I just tested the formula of Li$_4$Cl$_2$→Li$_2$ + 2LiCl to see if I got the answer they got in the paper. For the structure the bond lengths from 2 to 3 and 1 to 2 should be 2.94 though for one of those bonds I had it at 2.938. The length between 3 and 1 should have been 3.1 though I got mine at 3.127. I had 3 and 4 and 1 and 6 at the length of 2.17. The lengths between 4 and 5 and 5 and 6 should be 2.16 though for one I had a length of 2.161. Also, the bond angle between 4,5, and 6 was at 140.8. Using this structure I got resonance energy of 87.2, which was pretty close to their result of 72.1.
These next two results are not formulas in the paper. The structure comes from figures I found in the paper. The structure of Mg$^4_4$ is a metal cluster and a tetraatomic structure. It has two structures one that is linear and the other is planar square geometry. In the paper they showed that the linear one is more stable. I tried to reproduce this though I found a problem. In the formula you need a Mg$_3$ molecule and they give an example in the paper, but it didn’t work well in

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matching my answers. In the table above I ran 5 tests with the same three molecules though with different charges, bond lengths and charge. The triangular version is the one they used in the paper. However none of the versions I worked out came close to their answer. So I used the one I originally did which was the linear of a charge of +2 and a bond length of 2.72, which was the closest answer to theirs. The first structure had a bond length of 3.14 for each one. Then doing it on WEBMO I got energy of 19.7. For the linear structure had a bond length of 3.01 from 4 to 3 and 1 to 2. It had a length of 2.91 from 1 to 3. I got an answer of 37 kcal/mol using WEBMO. My results did not prove that the linear structure is more stable than the cyclic. The linear should have an answer of 0 kcal/mol and I got 37. However it’s the closest answer I got using version 1 then all the other versions.

![Diagram of a molecule](image)

This test on this structure was to see if the Li$_3^+$ in the Li$_3$Cl was aromatic. If it were it would have a special stability relative to nonaromatic reference molecules, which would be expressed in the resonance energy. So they used this formula to calculate the resonance energy to test this theory. I didn’t really understand what was the importance of it though I tested to see if my answer matched their answer.
From this test I got resonance energy of 48.6 kcal/mol. This answer in the paper was higher than the dissociation energy of 35.7, which the paper calculated it at. The higher answer I obtained still proved that Li\(^{3+}\) is aromatic because it has a higher energy of Li\(_2\).

My final three results came from the abstract of the paper to predict to see if the cyclic or linear structure of Li\(_2\)Mg\(_2\) is more stable. The formula is Li\(_2\)Mg\(_2\)\(\rightarrow\)Li\(_2\)Mg + Mg and the paper required a special version of Li\(_2\)Mg. Figure 4 is Li\(_2\)Mg\(_2\) and is linear with bond lengths of 2.86. In figure one had bond lengths of 3.02 for all four sides. It bond angle for 1,4 and 3 was 62.801 which was close to 62.8 which was in the paper. The other angle of 1,2 and 3 is 62.8. The calculate result I obtained was 11.7kcal/mol which is close to the exact answer of 0 kcal/mol. For structure 2 the bond length of 1 and 2 was 2.87 where one and two are both lithium.
The length of 1 and 4 is 3.09 and for 2 to 3 are 3.08. The length of 3 to 4 is 3.12. The angle of 1,4 and 3 is 83.919 though the correct angle should be 89.98. The other angle of 2,1 and 4 is 88.059 though the correct angle is 89.60. From my calculation I got an answer of 6.4kcal/mol, which is very close to the answer of 5.6kcal/mol. The last structure is the linear version of Li$_2$Mg$_2$. It has a bond length of 2.85 from Li to Mg and a length of 3.05 for 1 to 2 which are the two magnesium atoms. The result I got after putting the molecule through WEBMO was 3.4. This answer is below the result of 11.3 kcal/mol. The purpose of testing these three structures was to show which was more stable which was discussed in the beginning of the paper. In the paper it shows that the one with the highest relative energy was the least stable according to the paper is the linear version of Li$_2$Mg$_2$. My results though proved that the linear was most stable this outcome was erroneous.

Doing the calculations was the simplest part of the paper the concepts are not explained clearly. One example is that they talk about a simple two-center two-electron bond model. I couldn’t find any information on it and I’m not sure what it is. All I know from the paper is that has to do something with Lewis Structure and aromatic molecules. Its important in organic chemistry and the paper is trying to use this concept for metal clusters. I understand the idea they are trying to show that metal clusters lack the electrons that organic compounds have. It’s just the part that I didn’t understand is the 2C-2E concept and the idea behind it. The thing I did understand is the 2C-2E concept is used in organic chemistry and this paper is trying to prove that it can be used in metallic chemistry. Another thing I tried to
understand is the idea of metal clusters. I couldn’t find the information to fully understand its concept. I understood that the paper I got the idea it’s a large groups of metal ions that form compounds. The paper disclosed the idea that one type of metal cluster is any metal like lithium, sodium, potassium and copper bonded to four or six aluminum molecules. They had other molecules like that, but I’m not sure they were metal clusters. Overall, I have an idea of metal clusters, but not a fully understandable knowledge of it. Still another theory I could not make sense of is the idea of Coulumb repulsion. I couldn’t totally understand the basic concept. It was mentioned in a calculation in the paper that I didn’t do. All I was able to understand is that it plays a part in the stability of the Li$_4^{2+}$ molecule. They used it to calculate the resonance energy. I was still unable to understand the manner of how they obtained their conclusion and its ramifications. I hope to follow this up in the future. The paper is really for scientists who have a lot more knowledge of the topic. So I feel satisfied with myself that I have a decent understanding of what they are saying and was able to try reproduce some of their numbers.

The article was written well and presented a good idea though it had many flaws in my mind. One thing was in the abstract it described how it would show which was more stable the cyclic Li$_2$Mg$_2$ or the linear Li$_2$Mg$_2$. I was expecting a good deal of information on it, but it wasn’t mentioned at all really until the last page as if it wasn’t really important. Why did they put it in the abstract at all if wasn’t that important? Also, in the abstract they talked about the (B3LYP/6-311+G* and CCSD(T)/6-311+G*) calculations they used on the metal clusters. The
problem was, for most of the calculation in my paper these weren’t used at all. I used CCSD(T)/6-311+G(2df) to get all my answers because you need the correlation energy to convert to kcal/mol. A question was, why didn’t they put this in the abstract since it’s important? Another dilemma is for one calculation they ask to show the energy of the reaction of Li₃Cl. The answer was 35.7 kcal/mol though for the same molecule in a figure had and energy of 0 kcal/mol. This could be a bit confusing to have two different energy levels for the same molecule. One mistake I found is an error for looking at a figure. They say to look at figure one to look at cyclic Mg₂Li₂ though it was at figure 4. This was a simple error, but for these papers I thought they would review these in detail because of its importance. The final thing I found annoying is some calculations had to be put together by myself because they didn’t explain it well. For one I made a better molecule to get a better answer. This should not of happened. Other than these problems the paper was put together well. Most of the time I could understand how they calculated the answers that I tried to reproduce. The paper signifies important ideas about bringing 2c-2e molecules from organic molecules into the world of metal clusters.

Overall, the results obtained in my paper were pretty close to the outcomes in the article. I came to understand how they computed these results. Some of these results showed the resonance energies of various molecules or compared atomization energies of Li₃. It showed that Li₃⁻ has less atomization energy then Li₃⁺. To get these results it was easy to get the correlation energy of the various molecules using WEBMO and then turning it into kcal/mol. The only problem I
found is that one of my molecules gave me a better answer than what they had. This could just be a freak accident or they did something they didn’t say in the article.

Finally, I tried to show what is more stable the cyclic version of Li₂Mg₂ or linear version. My results were off but it showed that the cyclic one was more stable because of the lower energy compared to the linear one. The purpose was to understand idea of how they got these answers and I believed I showed this. I hope I showed the clear process of how I reached these results and how much time and work is involved in the process.
Reference


