The Relationship Between Shape and Electronic Structure of Graphene Nanoflakes

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Introduction

Graphene nanoflakes and quantum dots are promising materials in nanotechnology due to graphene's unique electronic properties. Graphene systems are well-reported in literature[1,2], and are simple to build. Although graphene shows potential in semiconductor technology, its band gap provides limitations in its success. Graphene's band gaps, and furthermore its electronic structure are directly correlated with its atomic structure, and therefore understanding the role of molecular shape in creating electronic structures is a useful computational tool. Through the use of computational simulations, one is able to test a diverse array of potential graphene structures. There are two main categories that will affect electronic structure: size, and shape. There exists literature that researches both of these categories presently[1,2]. Wettstein et. al reports on the shape dependency present in large nanoflakes, and Shi et. al reports on size dependency when describing HOMO-LUMO gaps for various sized flakes, ranging from 16 carbon atoms to over 2,000 atoms. This project aims to examine the electronic properties of some of the smaller graphene nanoflakes (60 atoms being the largest) used in Shi et. al as a way to understand more in-depth the electronic structures of these small graphene nanoflakes[3].
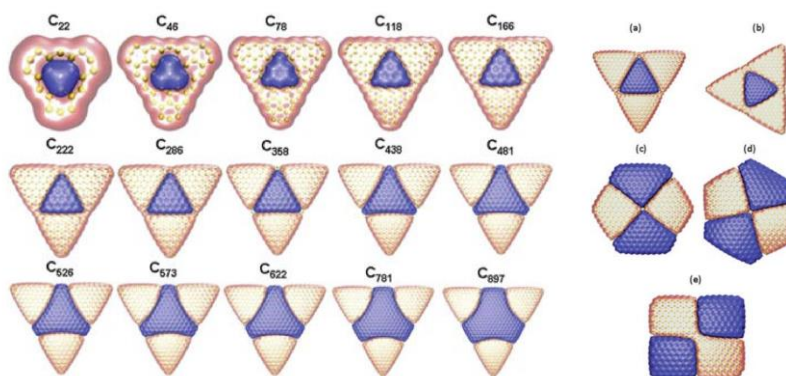

Figure 1. HOMO and LUMO representations for different sizes and shapes of graphene nanoflakes.[2]

Methods

The following calculations used the NEXMD[4] (Nonadiabatic Excited State Molecular Dynamics) program, QMFlows[5], a Python package, the CP2K software package[6], and Libra[7] a Python package. Specific parameters will be discussed in the below sections.

1. NEXMD Parameters

The AM1 Hamiltonian was used in all calculations. For geometry optimization, 300 cycles were used. For excited state calculations, 2 excited states were propagated, starting at the ground state at a temperature of 300K using the Langevin thermostat setting. A temperature of 300K was also used in molecular dynamics, along with a timestep of 0.5 fs due to the presence of hydrogen atoms for a total number of steps of 4,000 (simulation time of 2 picoseconds).

2. QMFlows Parameters

QMFlows was used to generate absorption spectra of the molecules through the CP2K software package. An active space of [10, 10] was used, along with the PBE functional and a constant 30x30x30 cell for all nanoflakes.

3. CP2K and Libra Parameters

CP2K was used to compute the absorption spectra through QMFlows as well as to calculate the projected density of states (pDOS). The parameters mentioned in the QMFlows section were used in all computations. Libra used a Gaussian wave function to plot the pDOS of each system, as well as calculate the band gap.

Results and Discussion

1. Rectangle Nanoflake

Two rectangle nanoflakes were used, both with the formula $C_{28}H_{14}$, and are shown in figure 2 below.
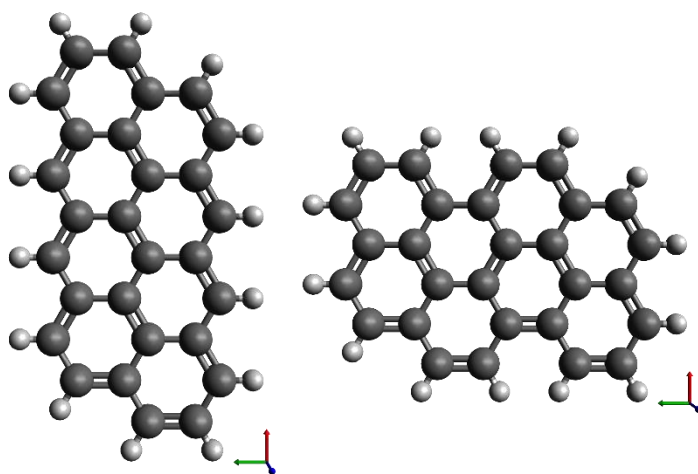

Figure 2. The rectangle graphene nanoflakes used in this project.

1.2 Single-Point Calculation & Excited State Calculation

A single-point ground state calculation and an excited state calculation were carried out using NEXMD. The results are summarized in figure 3.
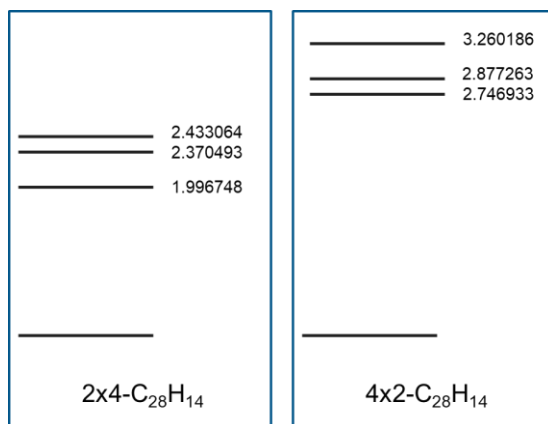

Figure 3. Qualitative representation of the excited states for the two rectangle graphene nanoflakes (energies in eV with the ground state at 0eV).

Although the two nanoflakes have the same chemical formula, their respective excited state energies are quite different. The second flake (figure 2b) has a much larger energy difference between the ground state and its first excited state as compared to the first flake (figure 2a). This shows the role that molecular structure plays in excited energy states, and furthermore electronic structure.

1.3 Absorption Spectrum

Wettstein et. al reports absorption spectra as evidence of differing structure equating to differing electronic properties, and so this was repeated for all of the structures in this project. The results are in figure 4 below for the rectangle nanoflakes.
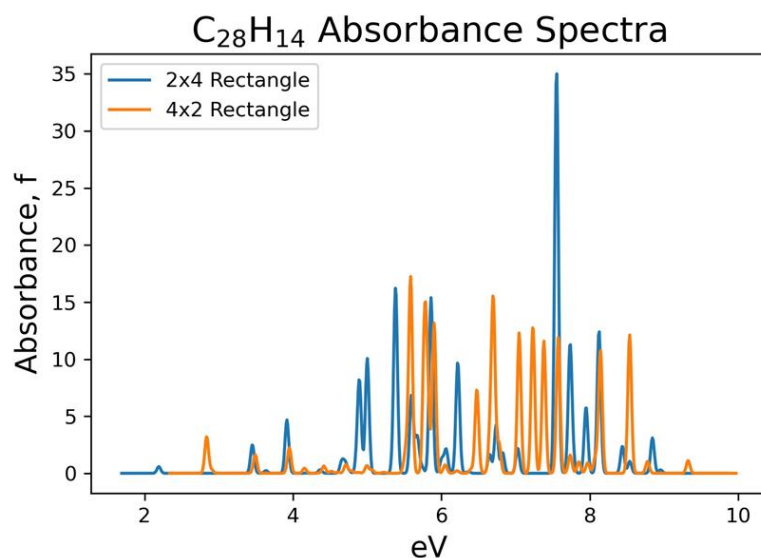

Figure 4. The absorption spectra for both rectangle graphene nanoflakes, labeled.

There are many peaks that do not shift (or shift negligibly) between the two nanoflakes, such as the peaks around 3.5 – 5 eV. However, there are large changes in the area between 6 and 8 eV. The 4x2 rectangle nanoflake does not have the large peak that the 2x4 nanoflake has at around 7.5eV, and the 4x2 nanoflake has four distinct peaks in that range compared to the smaller, more broad peaks present in the 2x4 nanoflake.

1.4 Projected Density of States

Again, following the data present in Wettstein et. al, the projected Density of States were calculated for all of the nanoflakes. The pDOS plots for the rectangle nanoflakes are shown in figure 5.
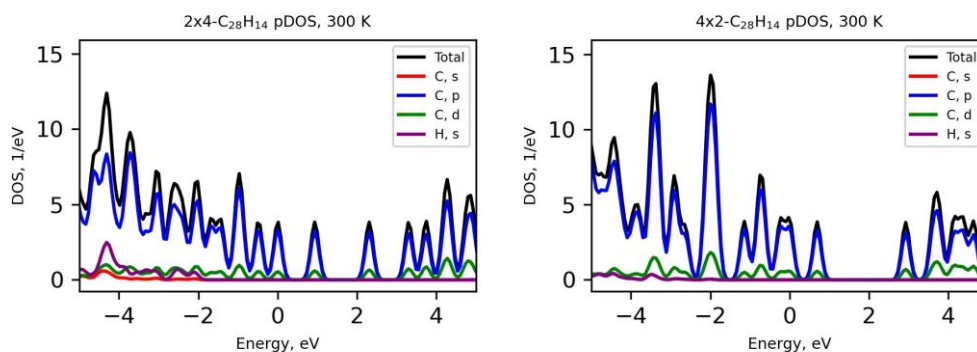

Figure 5. The pDOS for the rectangle nanoflakes.

The projected density of states establishes a relationship between structure and band gap, and therefore supports the potential of creating structures with finite or tunable band gaps for use in semiconductors.

2. Hexagon Nanoflake

The electronic properties of three hexagon-shaped graphene nanoflakes were studied, two with hydrogen passivation and one without, as shown in figure 6. Please note the nanoflakes are categorized by edge-type, either armchair (ac) or zigzag (zz).
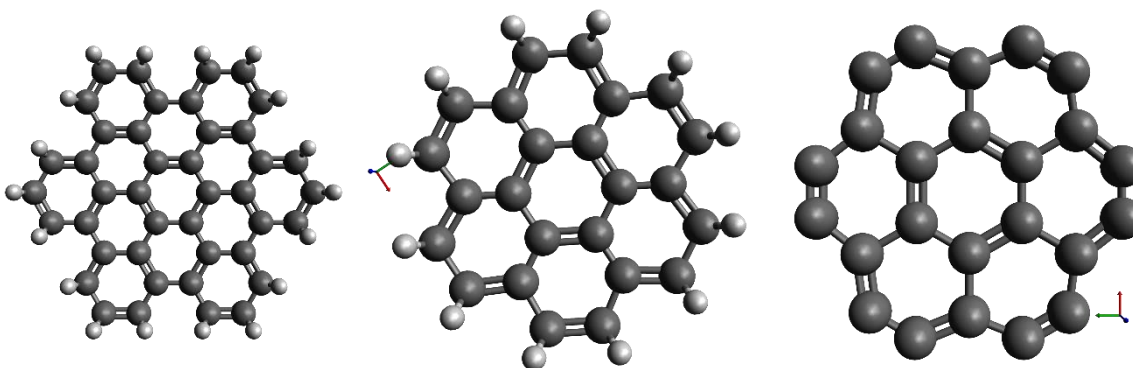
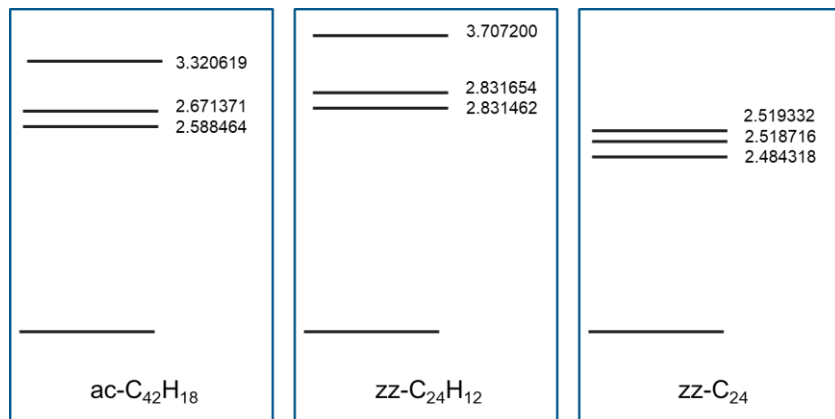## 2.1 Single-Point Calculation & Excited State Calculation

Figure 7. The excited states of the three hexagon-shaped nanoflakes, corresponding to figure 6a, 6b, and 6c respectively.

Hydrogen passivation seems to play a large role in the excited state energies of graphene nanoflakes. The excited states of the hexagon with hydrogens versus without ($C_{24}H_{12}$ vs C_{24}) support the theory that graphene nanoflakes without hydrogen atoms have lower-lying excited states compared to hydrogen passivated nanoflakes. There is also a possible trend between either edge-shape (armchair versus zigzag) or size, as the larger nanoflake (figure 7a) has excited states with lower energy than that of the smaller nanoflake with zigzag edges.

2.2 Absorption Spectrum

The absorption spectra were calculated for the larger nanoflake (figure 6a) and the nanoflake without hydrogens (figure 6c). However, for an unknown reason the absorption spectrum for the smaller nanoflake with hydrogen passivation (figure 6b) could not be calculated.
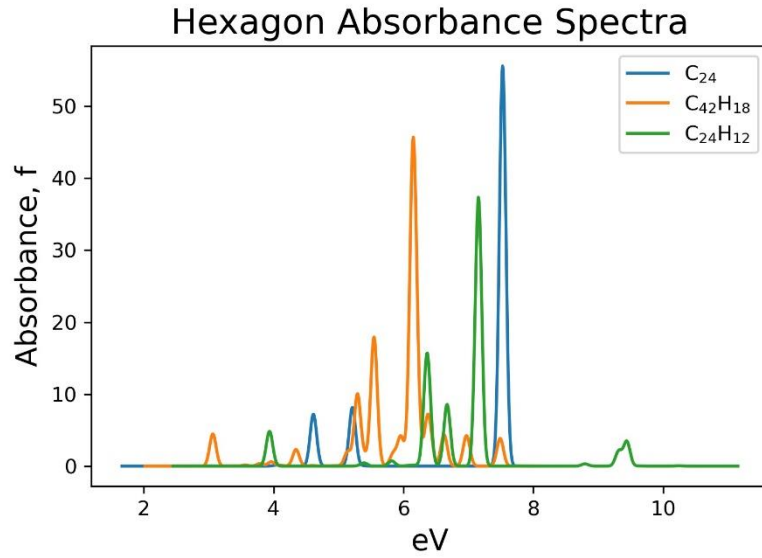
Figure 8. The absorption spectra for the hexagon nanoflakes.

Due to the differences in both edges and size, the two nanoflakes are not comparable to one another. However, we can compare the two smaller nanoflakes. By adding hydrogens, more peaks appear on the spectrum that have similar characteristics to peaks found in the larger nanoflake.

2.3 Projected Density of States

The projected density of states for the hexagon nanoflakes are shown in figure 9.
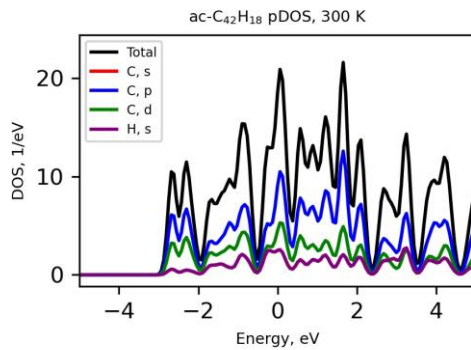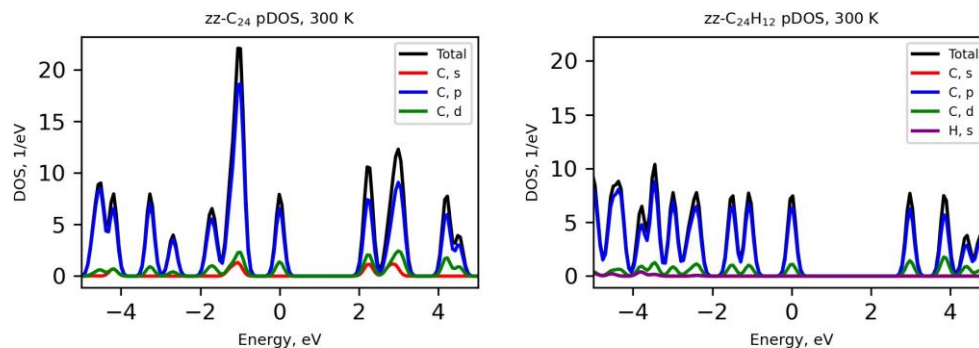
Figure 9. The pDOS of the three hexagon nanoflakes.

The pDOS plot for the larger nanoflake is unclear compared to the smaller, zigzag nanoflakes. This could either be due to size, or the armchair nature, or a combination of both. However, there is also evidence that spin may play a role in increasing the amounts of peaks as well as how close together they are, which may be a potential theory as to why it is so different as compared to the other two plots. The difference in band gaps between the two smaller nanoflakes is similar to that of the band gaps of the rectangle nanoflakes, which could show that at smaller size, the size of the system plays less of a role.

3. Trigon Nanoflake

There were some apparent issues with the trigon nanoflakes. I could not get the geometry to optimize on a number of the zigzag nanoflakes, and so currently I do not have data available for such a system. This also increases the difficulty at understanding and interpreting the data, since there is no other counterpart, although the data can still be compared to the previous geometries discussed. The trigon nanoflake used in this project is shown in figure 10.
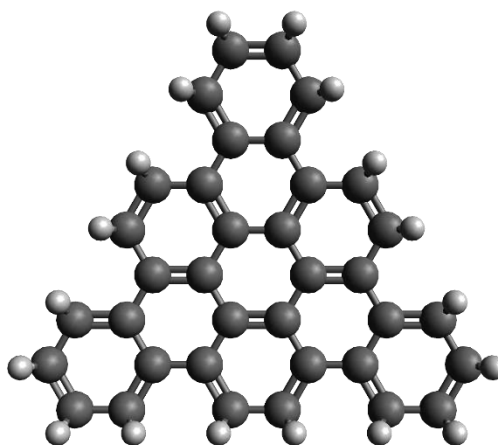

Figure 10. The trigon nanoflake used in this project.

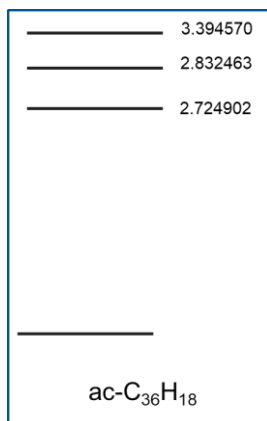*3.1 Single-Point Calculation & Excited State Calculation*

Figure 11. The first three excited states of the trigon nanoflake.

The excited state energies are quite similar to those reported earlier for the 4x2 rectangle graphene nanoflake. The complete results of the excited state calculations are summarized in the table below.

Table 1. Summarized excited state calculations results.

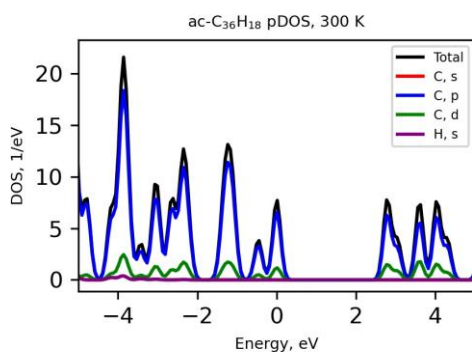|	2x4	4x2	ac-$C_{42}H_{18}$	zz-$C_{24}H_{12}$	zz-C_{24}	ac-$C_{36}H_{18}$
1st (eV)	1.996748	2.746933	2.588464	2.831462	2.484318	2.724902
2nd (eV)	2.370493	2.877263	2.671371	2.831654	2.518716	2.832463
3rd (eV)	2.433064	3.260186	3.320619	3.707200	2.519332	3.394570

3.2 Projected Density of States

Figure 12. The pDOS for the trigon nanoflake.

Again, due to issues with geometry, there is not another trigon nanoflake to compare it to. The band gaps calculated from the pDOS are summarized for all of the nanoflakes in table 2.

Table 2. Summarized band gaps calculated from the pDOS of each system.

	2x4	4x2	ac-$C_{42}H_{18}$	zz-$C_{24}H_{12}$	zz-C_{24}	ac-$C_{36}H_{18}$
Band Gap (eV)	1.37045	2.23307	0.00748	2.17394	2.98112	2.78466

The low band gap was not created by the armchair edges, as the trigon nanoflake did not have a similar trend with its bandgap. This is further evidence that something like spin is affecting the density of states and bandgap calculations.

Conclusions

1. Limitations

There were two main issues with this project: the first limitation was the issues that I faced with the trigon nanoflakes, as I tried different structures (both hydrogen passivated and not) and none of them worked. The second limitation was probably the most important: time. The paper that I based this project on[1] had tested multiple structures of different sizes to describe trends, whereas I did not have enough data to make solid trends from what I was seeing. That being said, the next section will describe what would be the next steps if I did have more time.

2. Possible Continuations

There are two main paths in my mind currently: the first being to use a wider array of systems, ranging from as small as this paper discusses to as large as 100 or 200 atoms, which would help to sort of "complete" the data from the Wettstein et. al paper that I used as a blueprint. The second thing I would do is compute the absorption spectra from a molecular dynamic trajectory, which I had completed the MD trajectories for all of the systems discussed but I came across space issues when I tried to compute the absorption with the QMFlows package (it ended up creating 4,000 directories, each containing a singular file that was not needed to compute the absorption spectrum anyway, and it would slow my terminal to almost a stop, not to mention the amount of space it took up). I would've looked into other options, and I wanted to try with the Columbus/newtonX interface that computed the absorption spectra, but I had no time, especially since we only learned about the interface over the last day or so. Below, however, are example outputs from the molecular dynamics simulations that I had run.
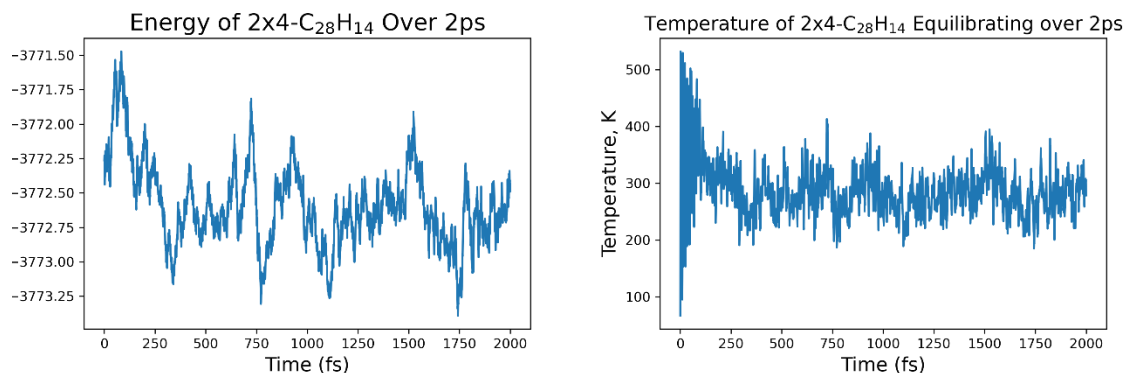
Figure 13. Energy vs. Time and Temperature vs. Time for the 2x4 rectangle nanoflake over 2ps.

References

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