



First-Principles Study of Solar Cell Power Conversion Efficiency of Organic Molecules

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Background

Organic molecules make ideal photovoltaic materials due to their inexpensive and environmentally friendly manufacturing process. Certain molecules reached a 17% Power Conversion Efficiency (PCE) September 2018 [1], making them competitive with already commercialized silicon based solar cells if scientists can continue finding high performing organics. The experimental search for other molecules with a high enough PCEs can be aided by theoretical methods. The Scharber model is used to predict the PCE of a set of molecules to prioritize ones for experiment [2-3]. The model uses the energy of the highest occupied molecular orbital (HOMO) and that of the lowest unoccupied molecular orbital (LUMO) and the same values for fullerenes derivatives and assumes a quantum yield to predict the compound's PCE.

In this ongoing study, we want to find the Quantum Yield (QY) for each molecule using the overlap between the solar spectrum and the optical absorption obtained from TD-DFT [4-5] calculations. The molecules in this study were chosen for their semiconducting properties and available literature on electronic properties [6-17]. In the future, we will investigate the accuracy this calculated quantum yield predicts molecular PCE's in comparison to the Scharber Model.

For this poster, we show the time consuming set up for the project, where we model each molecule's geometry and electronic structure.

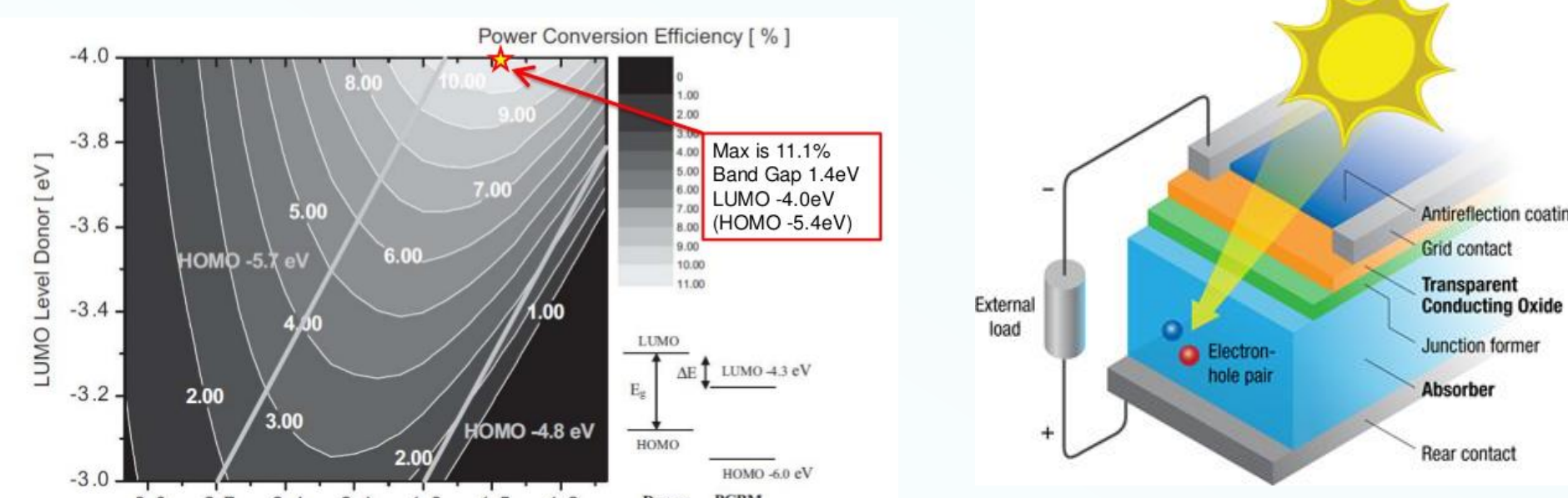


Figure 1: The Scharber Model
Scharber, Heeger et al. *Adv. Mater.* 2006, 18, 789

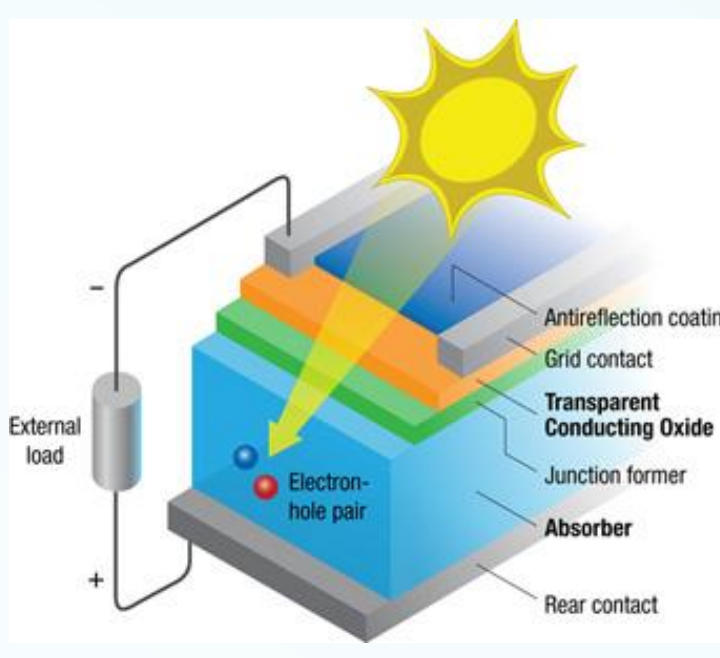
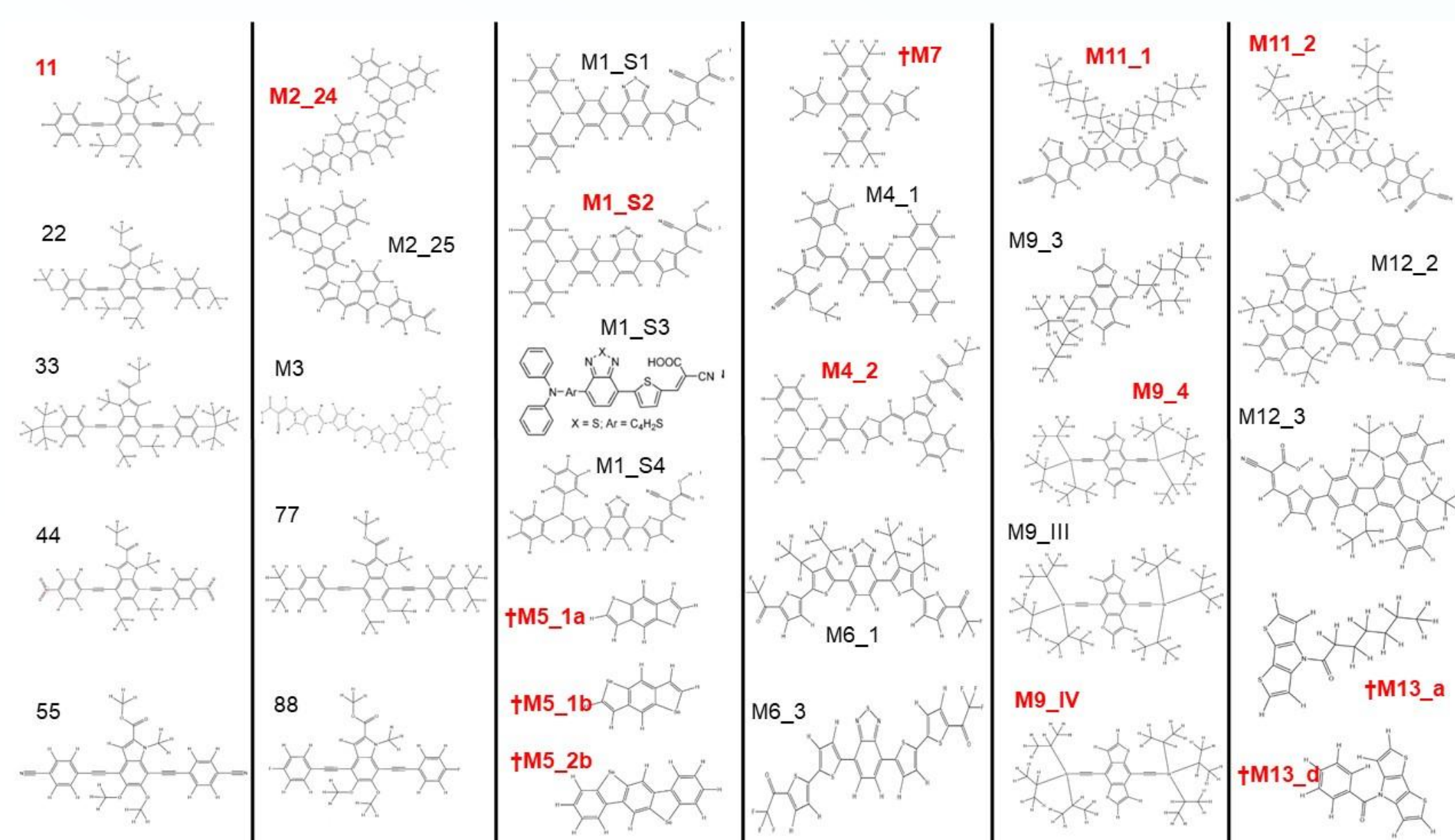


Figure 2: Organic Solar Cell Structure
National Renewable Energy Labs, 2019

Molecule Set

From 12 different published articles [6-17], we found 32 semi-conductive molecules to base our study on. We chose them because of the published data on their absorption spectrums and photo-electric properties. Then we compared the published data to what our theory generated. This method of comparing quantum theory to already published data is very similar to the methods of Zhang and Musgrave [18]. The goal of our methods differ from theirs because our focus was on optimizing the software we had before performing the appropriate theoretical calculations.

Figure 3: Molecules used for this project



Methodology

Figure 4: Project Steps

1. Build molecules in set using Avogadro
1 week (completed)

2. First Geometry Optimization Attempt
26 months (discarded)

3. Hardware Optimization
1 week (completed)

4. Second Geometry Optimization Attempt
7 months (in progress)

5. Absorption Spectrum Calculations
1 month (in progress)

6. Calculate Quantum Yield of each molecules

7. Use generated QY value to calculate molecular PCEs

8. Compare calculations to experiment and Scharber Model

Step 1: We manually constructed a model of each molecule from the papers in Avogadro [19]. We next used the "optimize geometry" feature to optimize the molecule's structure using molecular mechanics. This was a way to reduce the amount of time for subsequent calculations.

Step 2*: We initially tried to use the Octopus Software Suite [20] for DFT calculations to obtain the relaxed molecular geometry and followed this with a calculation of the molecular orbitals using an LDA pseudopotential. LDA was chosen due to its lower computing time and for the amount of literature available evaluating its performance. However, there were lots of bugs (Figure 8) creating inaccurate data and only the six smallest molecules converging (shown by † in Figure 3).

Convergence Criteria:

- 0.01 eV/Angstrom maximum force

Step 3: We split the molecules into three sets based on size, to better allocate computing resources. For each set, we optimized the wall time limits, system spacing, and hardware usage for the use of the Quantum Espresso Software Suite (QE) [21].

Set 1: 18 to 45 Atoms

- WTL: .5 to 2 days
- System Size: +10 Angstrom in x, y, z
- Hardware: 1 node (32 GB RAM), 12 processors

Set 2: 46 to 63 Atoms

- WTL: 3 to 5 days
- System Size: +15 Angstrom in x, y, z
- Hardware: 2 nodes (64 GB RAM), 24 processors

Set 3: 64 to 99 Atoms

- WTL: between 1 and 5 days
- System Size: +20 Angstrom in x, y, z
- Hardware: 1 BigMem node (256 GB RAM), 12 processors

Step 4*: We applied the findings from step 3 to the second attempt at geometry optimizations. This time, 14 out of 32 have converged (shown in red text in Figure 4). The other 18 molecules are steadily moving towards convergence. We can tell that by the decrease in maximum force values every calculation.

Convergence Criteria:

- Maximum Force: 0.0005 Ry/Bohr = 0.0125 eV/Angstrom

Step 5: The last step consists of exciting the system with a delta-kick that excites the system and we follow the dynamics using TD-DFT. The optical absorption spectrum is obtained by extracting the frequencies at which the molecule oscillates.

Next Steps (6-8): Once the geometry optimization and absorption spectrum calculations are complete for each molecule, we will calculate the QYs and PCEs for each molecule by integrating the absorption and emissions curves, then applying the appropriate formulas. We will then compare those results to experiment and the Scharber Model.



Figure 5: Avogadro logo

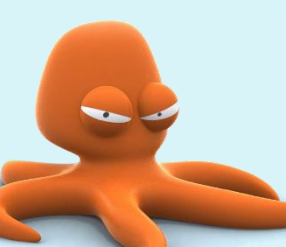


Figure 6: Octopus logo



Figure 7: Quantum Espresso logo

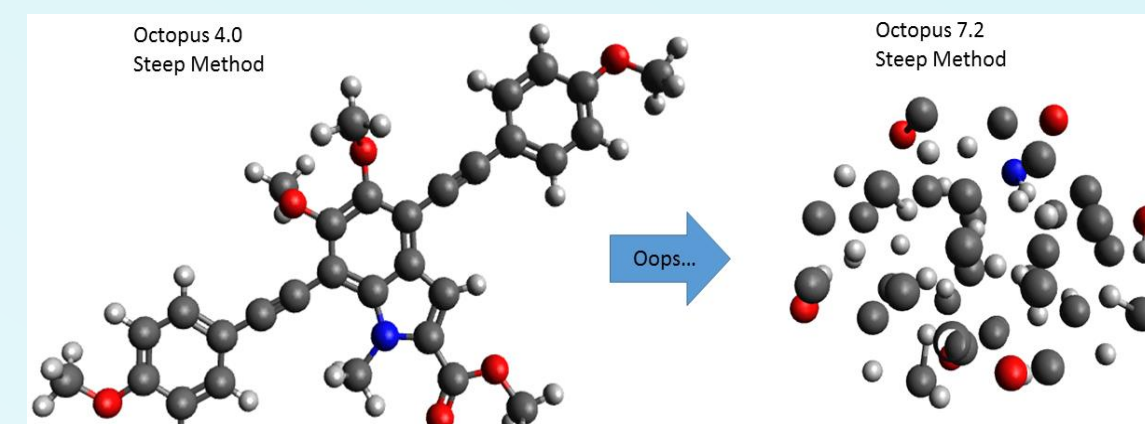


Figure 8: One of the errors encountered with Octopus Geometry optimizations

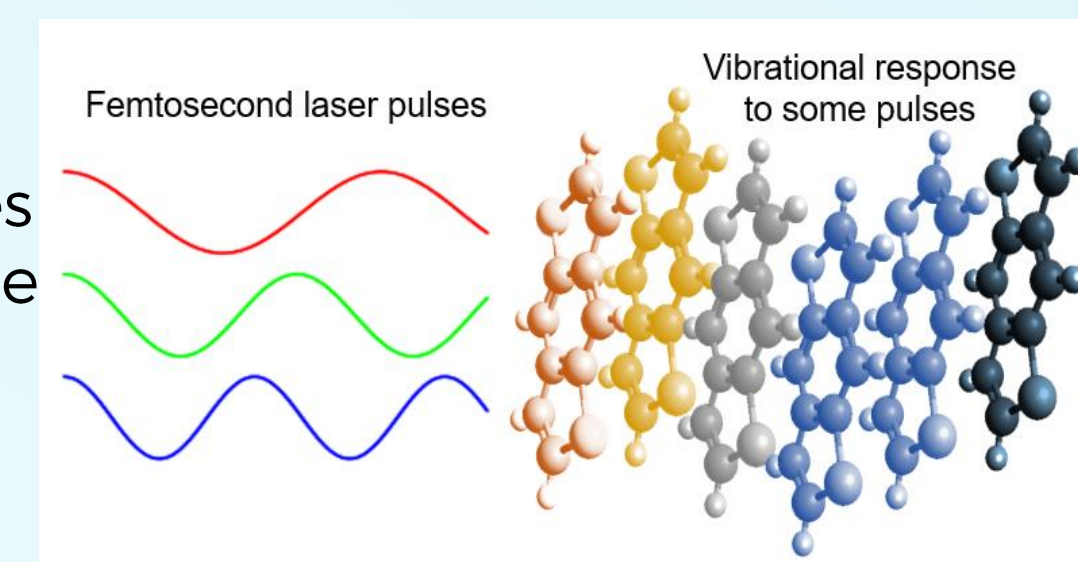
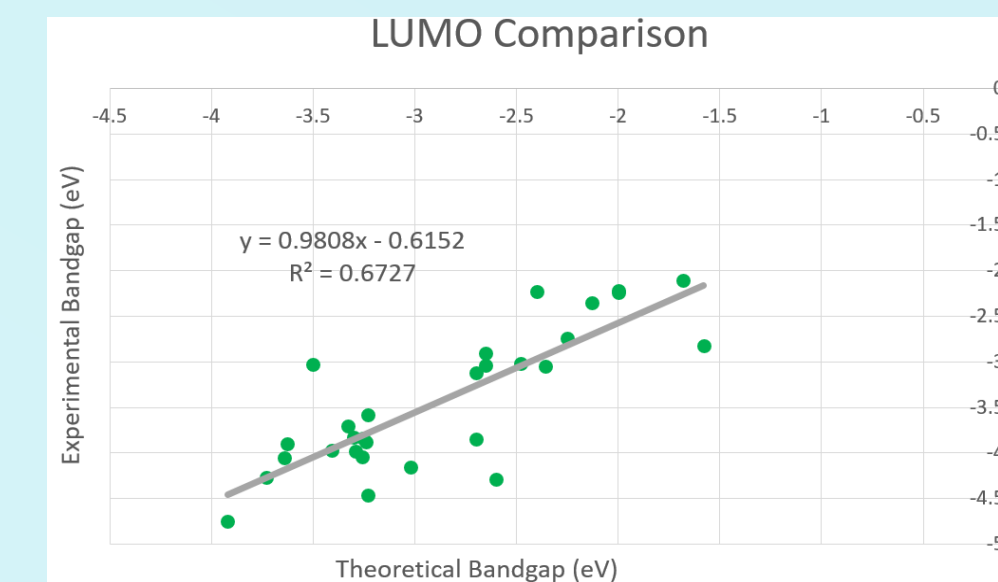
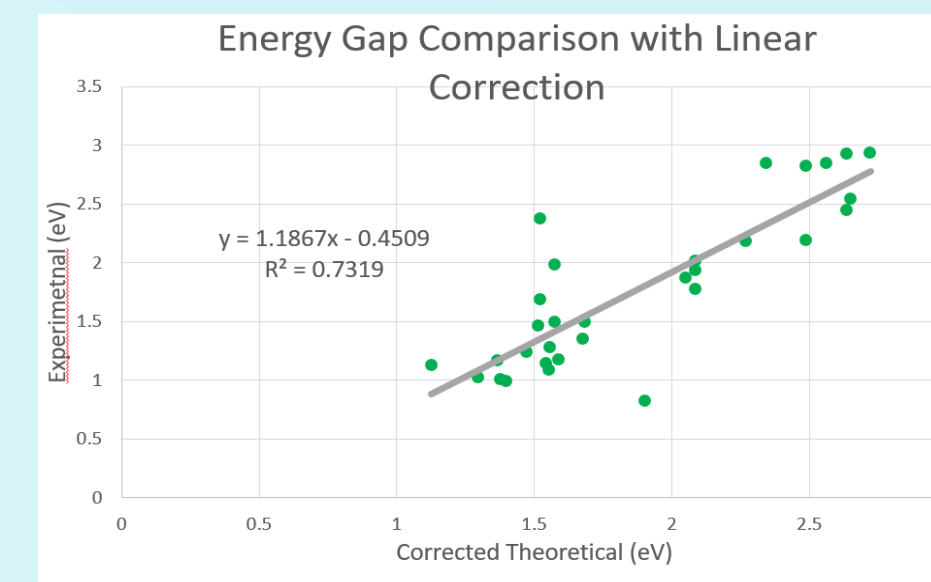


Figure 9: Illustration of TD-DFT Optical Absorption calculations

Results



Figures 11 & 12: Energy Gap Data from Octopus Geometry Optimizations

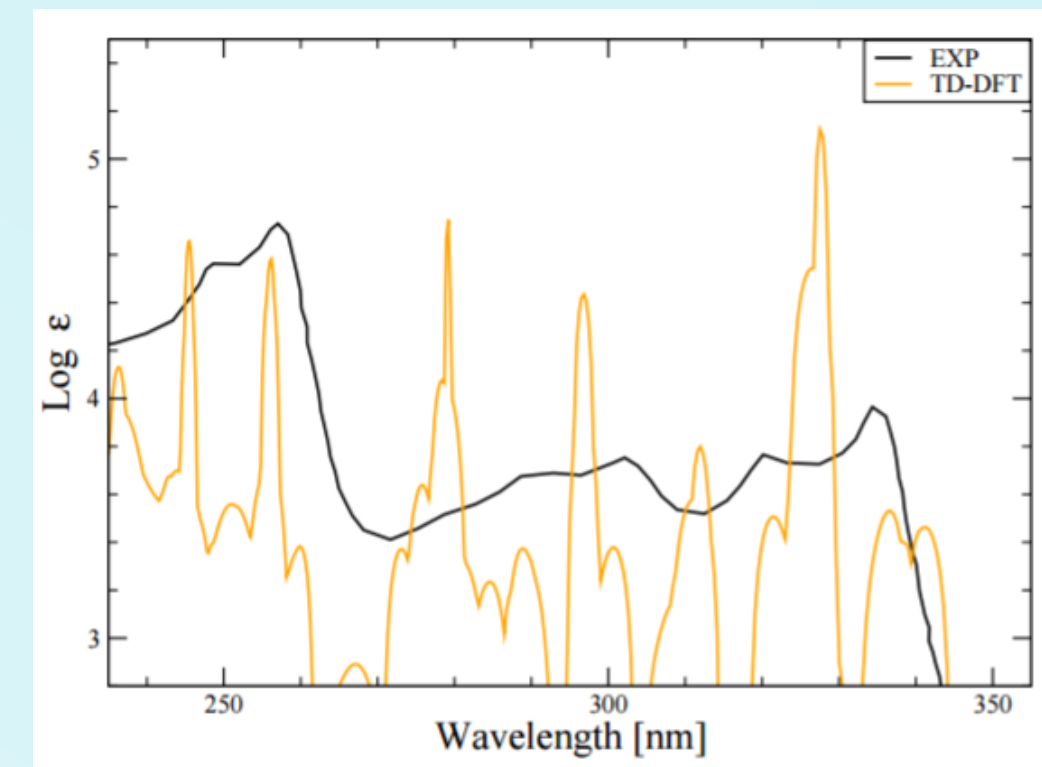


Figure 13: M5_1a Optical Absorption Spectrums

Discussion

The trend of our data in Figures 11 and 12 indicate that DFT-LDA is underestimating the LUMOs and overestimating the HOMOs. Our band gap results show a linear correlation between experiment and theory, once we have applied a linear correction. This indicates that the theory is consistent in its over and underestimations. To increase the accuracy of our band gap calculations, we can further optimize our molecular geometry calculations.

In figure 13, the experimental data came from a crystal of molecules, whereas the theoretical data came from a system of one molecule. The absorption spectrum of the experimental data shows then the average energy of multiple molecules interacting in a system. That of the theoretical data shows for only one molecule. If we were to place multiple molecules in the 1a system, we might see a closer correlation between the two results. However, for the purposes of this study, we will only continue to use one molecule. For future calculations plan to decrease the oscillation discrepancy between experiment and theory by matching temperatures of the systems.

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Figure 10: Convergence Time Comparison

Molecule	Octopus Convergence Time	QE Convergence Time
M5_1a	~150 hours	~1 hour
M5_1b	~175 hours	~1.5 hours
M5_2b	~200 hours	~4 hours
M7	200+ hours	~17 hours
M13_a	200+ hours	~5 hours
M13_d	200+ hours	~26 hours

Factors contributing to QE being faster

- Bugs in Octopus program affecting units and data management
- Use of parallel computing when made transition to Quantum Espresso
- Newer supercomputer hardware at time of transition
- Last set of coordinates from Octopus runs for each molecule was used as starting point for Quantum Espresso calculations

Similar trends between programs

- Smallest molecules converged first
- Some larger ones did as well
- Larger molecules containing Fluorine, Sulfur, and Silicon have not converged

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