

## Lab Week 4 – Experiment $\alpha_2$

### Delocalization: Optical and Electronic Properties of C-based Molecules

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#### OBJECTIVES

- Review the Linear Combination of Electronic Orbitals (LCAO) model of electronic structure
- Measure the optical absorption spectra of several carbon compounds
- Evaluate the anisotropic nature of the conductivity of graphite
- Make structure-property connections in terms of LCAO theory

#### QUESTIONS

At the end of your time working on this module, you should be able to answer the following questions:

- 1) How is LCAO related to the HOMO-LUMO gap?
- 2) How does this gap change as a function of molecule size?
- 3) What connections can be made between the optical and electronic properties of a material and the delocalization of electrons?

## INTRODUCTION

The intent of this lab module is to make connections between the LCAO model of electronic structure and measurable physical properties of a broad variety of carbonaceous compounds.

We will be using UV-vis spectroscopy to measure the absorption wavelengths of molecules of increasing size and structural complexity. You should observe what happens to the adsorption wavelength as molecular size changes, and relate it to concepts of electron delocalization and LCAO, which are discussed in brief below.

To complement these experiments, we will be measuring the conductivity of single crystalline, highly-ordered pyrolytic graphite (HOPG) as a function of crystal orientation. These measurements will again illustrate the connection between the atomic configuration, electronic structure, and physical properties of a material.

### LCAO Theory: A Brief Review

You have seen in lecture that a linear combination of atomic orbitals can be used as a means of approximating the orbitals of larger clusters of atoms. That is to say, the allowable electronic states of a cluster of atoms are determined by combining the wavefunctions of the individual atoms which constitute the cluster.

In planar systems, a matrix detailing the interactions of the atoms making up a molecule can be developed, with one matrix element,  $\alpha$ , describing the "coulombic integral", a value measuring the ability of a given atom to attract electron density. For a given atom in a molecule,  $\alpha$  is independent of any other atoms in the system [1]. The second matrix element,  $\beta$ , describes the extent to which an electron can be shared between neighboring atoms. In this model, known as the Hückel approach, it is assumed that atoms further away than nearest-neighbor positions do not contribute to this electron sharing. The result, for a compound with only one unique atom, is two Hamiltonians,  $H_{ij}$ , such that

$$H_{ij} = \alpha \text{ when } i = j$$

and

$$H_{ij} = \beta, \text{ when } i \text{ and } j \text{ are neighbors.}$$

Consider the case of the benzene ring, which is the building block of many of the compounds you will look at in this experiment. In benzene, the six carbon atoms cannot be differentiated from each other, resulting in the expression:

$$H_{11} = H_{22} = H_{33} = H_{44} = H_{55} = H_{66} = \alpha$$

$$H_{12} = H_{23} = H_{34} = H_{45} = H_{56} = H_{61} = \beta$$

Linear algebra tells us that nonzero solutions to the matrix derived from the above information exist when the determinant of the matrix (shown below) is zero [1].

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix}$$

The solution to the determinant (done in Matlab) is  $x^6 - 6x^4 + 9x^2 - 4$ , which results in the roots  $\alpha + 2\beta$ ,  $\alpha - 2\beta$ ,  $\alpha + \beta$  (twice), and  $\alpha - \beta$  (twice). With  $\beta > 0$  corresponding to a decrease in energy, this explains both the discretized energy levels (and the degeneracy of two of the levels) shown in Figure 1 (below), which is a slide taken from lecture 12.

Image removed due to copyright restrictions.

Source: 3.012 Fall 2005 lecture slides.

**Figure 1:** Formation of bonding and anti-bonding  $\pi$  orbitals as derived from Hückel's approach. Note that the two bonding orbitals  $\alpha + \beta$  and the antibonding  $\alpha - \beta$  appear twice because their roots do in the solution to the determinant. A physical rendition of their corresponding electron densities is shown at right. (From 3.012 Lecture Slides)

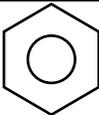
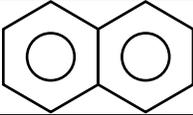
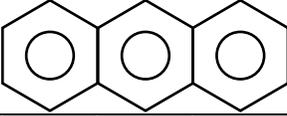
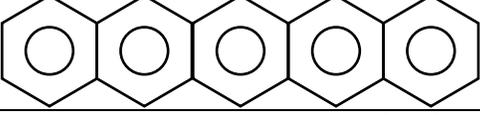
Rules for filling molecular orbitals dictate that electrons enter orbitals of the lowest available energy. Each of the six carbon atoms in benzene donates 1 electron to the delocalized  $\pi$  orbitals, resulting in the complete filling of the three bonding orbitals with no electrons free to enter the higher-energy antibonding orbitals. In general, the MO of the highest energy that is occupied by electrons is dubbed HOMO (Highest Occupied

Molecular Orbital), and the MO of lowest energy that is empty and available for electrons to be excited into is referred to as LUMO (Lowest Unoccupied Molecular Orbital). You might think of the energy difference between HOMO and LUMO, commonly referred to as the HOMO-LUMO gap, as the molecular equivalent of the band gap in a semiconductor or insulator.

What happens to the molecular orbitals as more atoms are introduced to a molecule? Each atom introduced into the system brings with it an additional bonding and anti-bonding orbital, with energies approaching  $\alpha$ . Increasing the number of atoms in a molecule therefore reduces the HOMO-LUMO gap.

Benzene derivatives are a choice set of systems to illustrate how increases in electron delocalization lead to changes in the HOMO-LUMO gap. As additional benzene rings are added to a system, so too are additional delocalized electrons. In this lab, you will first consider a class of benzene derivatives known as polycyclic aromatic hydrocarbons (PAHs). These consist of edge-sharing benzene rings. Like benzene, they are planar or near-planar molecules (Can you show why, knowing what you do about hybridization?), a structural feature that further helps facilitate the delocalization of electrons within the system, as  $\pi$ -bonds are known to delocalize above and below the plane of the molecule [2]. Simple structures are shown in Table 1; more complex compounds that you will also look at are shown in Table 2. For the compounds shown in Table 2, give some additional consideration to what impact various bonds in each molecule will have on the delocalization of  $\pi$  bonds.

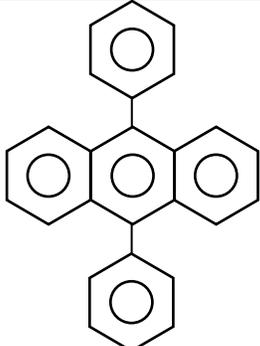
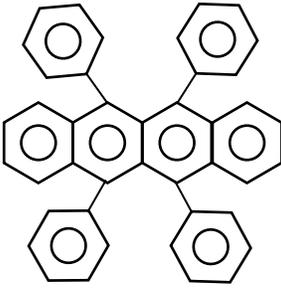
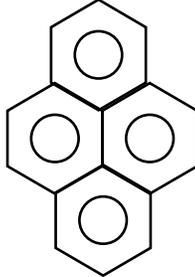
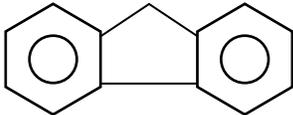
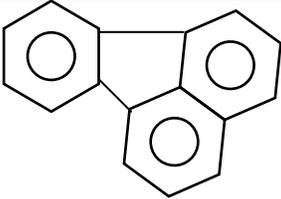
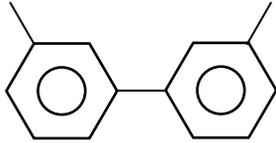
**Table 1: Simple Polycyclic Aromatic Hydrocarbons**

	<b>Benzene</b>
	<b>Napthalene</b>
	<b>Anthracene</b>
	<b>2,3-Benzanthracene</b>
	<b>Pentacene</b>

For an electron to cross the HOMO-LUMO gap, it requires some external excitation. It turns out that larger PAHs, starting with anthracene, have HOMO-LUMO gaps that are small enough that wavelengths on the order visible light can excite electrons from bonding to anti-bonding orbitals. Measuring the absorption spectra of these compounds

with a UV-vis spectrophotometer, therefore, is an effective means of demonstrating changes in the HOMO-LUMO gap as a function of molecular size and configuration.

**Table 2: Additional Compounds for Consideration**

		
<b>Diphenyl Anthracene</b>	<b>Rubrene</b>	<b>Pyrene</b>
		
<b>Fluorene</b>	<b>Fluoranthene</b>	<b>3,3'-Dimethylbiphenaline</b>

In addition to the hydrocarbons shown above, you will also look at the buckminsterfullerene molecule ( $C_{60}$ ), shown Figure 2, which has a geodesic icosohedral structure akin to that of a soccer ball. The hybridization of this molecule is a mix of the  $sp^2$  of graphite and  $sp^3$  of diamond.

**Figure 2:** The structure of  $C_{60}$ . (Image taken from [3].)

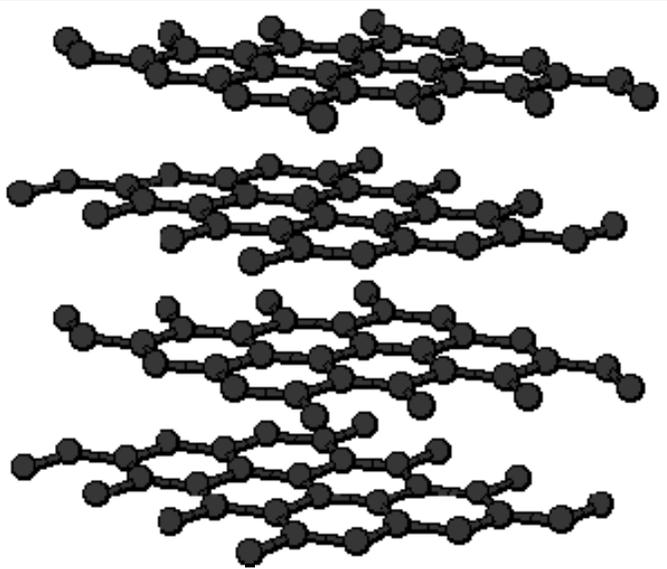
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## Delocalization in Graphite

To complement these experiments, consider also the structure of graphite. In this form, carbon atoms assume  $sp^2$  hybridization; the valence state is 4, indicating that three valence electrons of each carbon atom occupies each of the three  $sp^2$  orbitals, and the fourth electron is available to form a subsidiary  $\pi$  bond (derived from the remaining p orbitals). Hexagonal structure results from the  $\sigma$  bonds between  $sp^2$  orbitals of adjacent carbons in the basal sheet. The sheets are stacked in the -ABABAB- sequence above each other as shown in Figure 3 for the case of hexagonal graphite. The stacking sequence is -ABCABC- for rhombohedral graphite, a thermodynamically unstable form, which can be considered as an extended stacking fault of the hexagonal graphite [4].

The distance between carbon atoms in the sheet is 1.42 Å while the interlayer spacing between the sheets is 3.354 Å [5]. Since the sheets are weakly held together by van der Waals forces, the crystal can be sheared easily in a direction normal to the plane of the hexagonal network. The highest filled valence band overlaps with the lowest empty conduction band by approximately 36 meV. The de-localized p electron cloud above and below the hexagonal sheets forms a partially filled conduction band between the basal planes where electrons can be moved readily in a wave pattern in response to electric fields. This makes graphite a good conductor in the basal plane. The large spacing between planes in the direction normal to them, coupled with the absence of a viable mechanism for moving electrons results in poor conductivity in this direction. Thus graphite exhibits anisotropic conductivity, which you should be able to measure with the samples provided to you in the lab.

**Fig 3:** The atomic structure of graphite. The planar sheets of atoms permit high in-plane delocalization of electrons, allowing for dramatic differences in conductivity in-plane and out of plane [6].



Courtesy of Dr. Alan J. Jircitano. Used with permission.

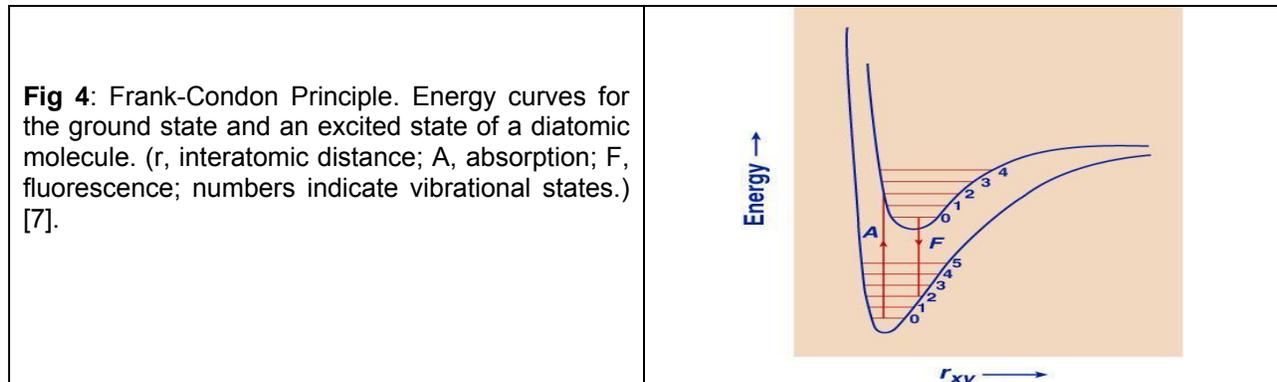
## Appendix 1: Frank Condon Principle

*The text of this appendix has been reproduced with some modifications from Source: [7]*

Absorption of UV/Visible radiation by a molecule excites it from a vibrational level in the electronic ground state to one of the many vibrational levels in the electronic excited state. A molecule in a high vibrational level of the excited state will quickly fall to the lowest vibrational level of this state by losing energy to other molecules through collision. The molecule will also partition the excess energy to other possible modes of vibration and rotation. Fluorescence occurs when the molecule returns to the *electronic* ground state, from the excited state, by emission of a photon. If a molecule which absorbs UV radiation does not fluoresce it means that it must have lost its energy some other way. These processes are called radiationless transfer of energy.

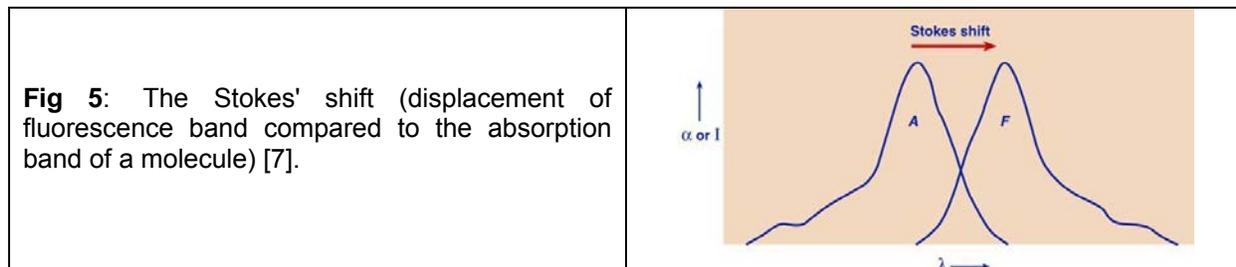
In a diatomic or polyatomic molecule, one or several series of (also quantized) vibrational and rotational states are superimposed on each electronic state. If the molecule is complex, the various vibrational and rotational states lie very close together.

When a photon is absorbed, the molecule usually is not merely transferred into an excited electronic state, but also acquires some vibrational energy. According to the so-called Frank-Condon principle [8], the absorption of a photon is a practically instantaneous process, since it involves only the rearrangement of practically inertia-free electrons.



Courtesy of Govindjee. Used with permission.

Approximate mirror symmetry of the two bands – absorbance and fluorescence exists when the shapes of the potential curves in the ground state and the excited state are similar. A small shift known as Stokes' Shift is observed in the spectrum (Fig 5).

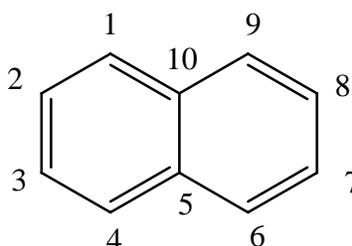


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## Appendix 2: Making a simple LCAO Calculation

Using MATLAB you can make LCAO calculations for each of the polycyclic aromatic hydrocarbons (PAHs) featured. From these calculations you can obtain the allowed energy values (eigenstates) for the p-orbital electrons in each compound. These energy values allow you to construct a simple energy hierarchy which can be used to estimate the HOMO-LUMO gap, which we can experimentally verify as the adsorption peak. It can be useful to make one of these calculations to compare the quantum model with reality.

As an example, we'll calculate the energy states for naphthalene. There are 10 carbons in the naphthalene molecule; all of them are in the  $sp^2$  hybridization. This implies that each carbon atom adds a single p-orbital electron to the conjugation (aromatic system). The figure below shows the chemical schematic of naphthalene with an arbitrary numbering of the carbons.



Just as in the benzene LCAO, we can approximate this system by defining two parameters:

$$H_{ij} = \langle j | H | i \rangle = \begin{array}{ll} \alpha & \text{if } i = j \\ \beta & \text{if } i \text{ and } j \text{ are nearest neighbors} \\ 0 & \text{for all other pairs} \end{array}$$

For naphthalene we need a 10x10 array to represent this energy system. We define, as before,  $x = (\alpha - E)/\beta$  to simplify the problem; thus our determinate becomes:

$$\begin{vmatrix}
 x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 & 1 \\
 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 \\
 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & x
 \end{vmatrix} = 0$$

Notice that for atoms 5 and 10 we have to take into account the fact that each carbon has three nearest neighbors.

You can obtain the polynomial of this determinate by hand using the method of minors and coefficients, however it can be obtained easily (and symbolically) using MATLAB. To do this in MATLAB you simply need to define a variable as symbolic using:

```
>>x = sym('x')
```

The **sym()** operator generates the symbolic character x. The ' ' denote x as a character. You then need to construct the naphthalene array. Arrays in MATLAB are defined using square brackets [ ]. A row is given by a sequence of numbers with each element separated by a space. Each row is separated by a semi colon ;. Thus for example

```
>> m = [1 2 3; 4 5 6; 7 8 9]
m =
     1     2     3
     4     5     6
     7     8     9
```

You can concatenate arrays to each other by simply redefining the array, like so:

```
>> m = [x 1 0 0 0 0 0 0 0 1]
m = [ x, 1, 0, 0, 0, 0, 0, 0, 0, 1]

>> m = [m; 1 x 1 0 0 0 0 0 0 0]
m = [ x, 1, 0, 0, 0, 0, 0, 0, 0, 1]
     [ 1, x, 1, 0, 0, 0, 0, 0, 0, 0]
```

This is how I build up arrays, but you can probably find an easier way. Whatever way you build the array, the final result for naphthalene should look like the array given

previously. You can correct an element by simply accessing the element and equating it to a new value; for instance if you want to change the element in row 2 and column 5 you would type:

```
>> m(2, 5) = 10;
```

Once you have your array, you need to find the determinate. This can be done with the **det()** operator.

```
>> D = det(m)
```

```
D = -9+43*x^2-65*x^4+41*x^6-11*x^8+x^10
```

This returns the symbolic polynomial of your determinate. From this you need to find the zeros of the polynomial, which give you the eigenvalues. You can do this by hand using the method of divisibles, or graphically by looking for zeros, or using a computer. In MATLAB, to find the zeros you need to first define a polynomial. You do this by generating a single row array. For our naphthalene model we have:

```
>> p = [1 0 -11 0 41 0 -65 0 43 0 9]
```

```
p = 1 0 -11 0 41 0 -65 0 43 0 9
```

Note that to define the polynomial correctly, you give the machine the highest order term *first* (in this case the  $x^{10}$  term). You then can use the function **roots()** to find the polynomial roots:

```
>> R = roots(p)
```

```
R =
```

```
2.2814  
1.8414  
1.2342 + 0.4890i  
1.2342 - 0.4890i  
-2.2814  
-1.8414  
-1.2342 + 0.4890i  
-1.2342 - 0.4890i  
0 + 0.4052i  
0 - 0.4052i
```

The roots of your polynomial give you the eigenvalues. These roots are actually given in terms of  $x$ , so to get the energy values just convert back to  $E$ . We have ten roots, which is correct, since we have ten electrons from the ten p-orbitals of the ten carbon atoms (there is always conservation of states in LCAO, and I think in quantum mechanics in general)

You should see something funny about the roots we obtain from naphthalene. First, there are the complex numbers; you can ignore the imaginary bit because its only used

for finding the mathematical values. However you'll see that two of the energy states have value  $E = 0$  which means that there is a certain wavestate in which the naphthalene has gained no stability by bonding the carbon orbitals together. If you fill the molecular orbitals using Pauli exclusion principle (i.e. only two electrons can occupy any energy level) and Hund's rules (lowest energy levels are filled first; all orbitals half filled with aligned spins first before pairing spins), you'll find that the naphthalene's HOMOs are at  $E = 0$ ! Even more interesting, you have a doubly degenerate HOMO, each with only one electron.

If you compare the HOMO-LUMO gap for benzene to naphthalene you find that:

$$\Delta E_{Benzene} = -2\beta$$

$$\Delta E_{Naphthalene} = -1.23\beta$$

We find that naphthalene has a smaller energy gap, which implies that it takes a lower energy photon to generate the first excited state. Lower energy photons have longer wavelengths, and thus we should see a red-shift in the absorption peak between benzene and naphthalene.

Notice that the gap energy is not a function of  $\alpha$ ; its important to consider why that might be, and to consider if this makes sense altogether. When we excite an electron from the HOMO to the LUMO, this means we are imbuing kinetic energy to the particle. This kinetic energy means the electron is more mobile and becomes more delocalized through space. If we were dealing with a single atom, then to set an electron into free space we must ionize the atom; this requires a lot of energy, in fact for our model it would require energy equal to  $\alpha$ .

Now, suppose there is another atom nearby, so that the electron has an electromagnetic attraction to this atom's nucleus. Now we have additional stabilizing energy, and it costs us less energy to liberate the electron. However, instead of sending the electron off into free space, the electron now becomes delocalized between the two atoms. Thus we can gain mobile electrons easier when we have more nucleids around. The energy costs now are associated with transferring an electron between the two atoms, which is exactly our  $\beta$  value. Another way of looking at this is to assume  $\beta = 0$ ; then there is no delocalization, all of the polycyclic aromatic hydrocarbons just look like individual atoms held together, with no interaction (which is somewhat what would see in non-aromatic hydrocarbons). In these systems there would be no HOMO or LUMO by our model; each electron on each atom would occupy its p-orbital with energy  $\alpha$ . The only excitation you could achieve then would be to ionize one of the atoms by using photons of energy  $\sim \alpha$ .

Okay, so this as far as we go with the model, but you're probably wondering why we don't use any real numbers for  $\alpha$  and  $\beta$ . These numbers, remember, represent the energy for binding an electron into the p-orbital of a carbon atom (that's  $\alpha$ ) and the energy of transferring an electron from one p-orbital to another (that's  $\beta$ ). We don't have these numbers readily; you could go and do a calculation using quantum mechanics to get the number. Alternatively (and more to my tastes) you can get these

numbers experimentally. One way to do this would be to find  $\beta$  based on your experimental value from benzene. Then, since your energy gaps are based on  $\beta$ , you can use this to predict the absorption peaks for the other PANs. But what about  $\alpha$ ? A rough estimate here would be to use the 1st ionization energy for carbon.

If you want to go even one step further you can go back and figure out the waveforms of each of your energy states by finding the eigenvectors. The challenge here is to find the absorption peak for fullerene, which has 60 carbon atoms and a high degree of connectivity!

## References

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