# Crystal Structure of Graphite, Graphene and Silicon 

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#### Abstract

We analyze graphene and some of the carbon allotropes for which graphene sheets form the basis. The real-space and reciprocal crystalline structures are analyzed. Theoretical X-ray diffraction (XRD) patterns are obtained from this analysis and compared with experimental results. We show that staggered two-dimensional hexagonal lattices of graphite have XRD patterns that differ significantly from silicon standards.


The wide-variety of carbon allotropes and their associated physical properties are largely due to the flexibility of carbon's valence electrons and resulting dimensionality of its bonding structures. Amongst carbon-only systems, two-dimensional hexagonal sheets-graphene-forms of the basis of other important carbon structures such as graphite and carbon nanotubes. (:: Say something about interesting band structure here)

In the following, we will examine the planar lattice structure of graphene and its extension to higherdimensional lattice structures, such as hexagonal graphite. We first analyze the lattice and reciprocalspace structures of two-dimensional hexagonal lattices of carbon, and use the resulting structure factors to estimate the x-ray diffraction (XRD) intensities of graphite. We conclude by comparing its calculated XRD spectra to experimental spectra of graphene and crystalline silicon.

## 1. PRELIMINARY QUESTIONS

### 1.1. Lattice Structure

Our discussion of the crystal structure of graphite follows partially from D.D.L. Chung's review of graphite [1]. When multiple graphene sheets are layered on top of each other, van der Walls bonding occurs and the three dimensional structure of graphite is formed with a lattice


FIG. 1: In-plane structure of graphite and reciprocal lattice vectors [1].

[^0]spacing between sheets $c=6.71 \AA$. The sheets align such that their two-dimensional hexagonal lattices are staggered, either in an $A B A B$ pattern or an $A B C A B C$ pattern. The ABAB alignment is shown in Figure 1, which indicates four atoms per unit cell labeled A, B, A', and B', respectively. The primed atoms A-B on one graphene layer are separated by half the orthogonal lattice spacing from the A'-B' layer; BB' atomic pairs differ from their corresponding AA' pairs in their absence of neighboring atoms in adjacent layering planes. The coordinates of these atoms forming the basis are given by:
\[

$$
\begin{array}{ll}
\rho_{A}=(0,0,0) & \rho_{A^{\prime}}=\left(0,0, \frac{c}{2}\right) \\
\rho_{B}=\frac{a}{2}\left(\frac{1}{\sqrt{3}}, 1,0\right) & \rho_{B^{\prime}}=\left(\frac{-a}{2 \sqrt{3}}, \frac{-a}{2}, \frac{c}{2}\right)
\end{array}
$$
\]

With respect to an orthonormal basis, the primitive lattice vectors are given by,

$$
\begin{array}{ll}
\mathbf{a}_{1}=a(\sqrt{3} / 2,-1 / 2,0) & \left|\mathbf{a}_{1}\right|=a=2.46 \AA \\
\mathbf{a}_{2}=a(\sqrt{3} / 2,1 / 2,0) & \left|\mathbf{a}_{2}\right|=a=2.46 \AA \\
\mathbf{a}_{3}=c(0,0,1) & \left|\mathbf{a}_{3}\right|=c=6.71 \AA . \tag{1.2}
\end{array}
$$

The magnitudes of the primitive lattice vectors correspond to the lattice constants parallel and perpendicular to the graphene sheet. The corresponding ABCABC layer forms a rhombohedral structure with identical lattice spacing parallel and orthogonal to the layer.

### 1.2. Reciprocal Lattice Structure

Recall that the reciprocal lattice vectors $\mathbf{b}_{i}$ are defined as a function of the primitive lattice vectors $\mathbf{a}_{i}$ such that

$$
\begin{align*}
& \mathbf{b}_{1}=2 \pi \frac{\mathbf{a}_{2} \times \mathbf{a}_{3}}{\mathbf{a}_{1} \cdot \mathbf{a}_{3} \times \mathbf{a}_{3}} \\
& \mathbf{b}_{2}=2 \pi \frac{\mathbf{a}_{3} \times \mathbf{a}_{1}}{\mathbf{a}_{2} \cdot \mathbf{a}_{3} \times \mathbf{a}_{1}} \\
& \mathbf{b}_{3}=2 \pi \frac{\mathbf{a}_{1} \times \mathbf{a}_{2}}{\mathbf{a}_{3} \cdot \mathbf{a}_{1} \times \mathbf{a}_{2}} \tag{1.3}
\end{align*}
$$

The reciprocal lattice vectors for graphite are then


FIG. 2: Reciprocal lattice planes [001], [110], and [111]. given by,

$$
\begin{array}{ll}
\mathbf{b}_{1}=\frac{2 \pi}{a}\left(\frac{1}{\sqrt{3}},-1,0\right) & \left|\mathbf{b}_{1}\right|=\frac{2 \pi}{a} \frac{2}{\sqrt{3}} \\
\mathbf{b}_{2}=\frac{2 \pi}{a}\left(\frac{1}{\sqrt{3}}, 1,0\right) & \left|\mathbf{b}_{2}\right|=\frac{2 \pi}{a} \frac{2}{\sqrt{3}} \\
\mathbf{b}_{3}=\frac{2 \pi}{c}(0,0,1) & \left|\mathbf{b}_{3}\right|=\frac{2 \pi}{c} .
\end{array}
$$

The reciprocal lattice plane generated by the $b_{1}$ and $b_{2}$ vectors forms the outline of the first Brillouin zone, as depicted in Figure 1. The intersection of the the planes $k_{z}= \pm 2 \pi / c$ with the plane forms a hexagonal prism of height $4 \pi / c$.

### 1.3. Atomic form factors

As carbon is the only element present in graphene and graphite, the atomic form factor is uniform across the entire crystal, and thus can be factored out when calculating the structure factor. Thus the atomic form factor has no effect on the relative intensities of x-ray diffraction occuring in different planes of graphite. According to the NIST Physics Laboratory, the atomic form factor of carbon varies from 6.00 to $6.15 \mathrm{e} /$ atom with incident radiation ranging from 2 to 433 KeV [2].

## 2. X-RAY DIFFRACTION

### 2.1. Planes in the Reciprocal Lattice

Provide pictures of the crystal and of the reciprocal lattice in the [100], [110], and [111] planes. Indicate the vertical positions of atoms with respect to the plane.

Pictures of the crystal and of the reciprocal lattice in the [100], [110], and [111] planes are included in Figure 2. In MATLAB, the crystal was represented as a set
of points in space using the specified lattice vectors and atom bases. Normals generated from lattice vector sums were used to extract planes and display them. Varying colors were used to depict vertical spacing between adjacent planes.

### 2.2. Structure Factors and X-Ray Diffraction Intensities

Calculate the structure factor for all the reciprocal lattice vectors $\mathbf{K}_{l}<16(2 \pi / a)^{2}$.

The structure factor is calculated as

$$
M_{p}\left(\mathbf{K}_{i}\right)=f_{c} \sum_{j=1}^{n}\left(\mathbf{K}_{i}\right) e^{-i \mathbf{K}_{i} \cdot \rho_{i}}
$$

where $f_{c}$ is the structure factor of Carbon and $\rho_{i}$ are the basis vectors of our lattice. We find that only four unique, non-zero values of $M_{p}\left(\mathbf{K}_{i}\right)$ occur in the reciprocal lattice. Each of these corresponds to the height of a diffraction intensity peak and their relative values are referenced in Table I.

Calculate the ratio of the intensities expected for the following lines of the diffraction pattern with respect to the [111] line: [100], [200], [220], [311], and [400].

Including the structure factor, there are other several factors contributing to the intensities of the diffraction peaks [3]:

1. The Lorenz correction is a geometric relation altering the intensity of an x-ray beam for different scattering angles $\theta$.
2. The multiplicity factor $p$ is defined as the number of different planes having the same spacing through the unit cell. Systems with high symmetries will have different planes contributing to the same diffraction, thereby increasing the measured intensity.
3. Temperature, absorption, polarization each contribute higher-order corrections ultimately ignored in our calculation. These include Doppler broadening from thermal vibrations in the material, absorption of x-rays, and the polarization of initially unpolarized x-rays upon elastic scattering.

These factors all contribute to the relative intensity of a [ $h k l]$ diffraction peak given by

$$
\begin{equation*}
I_{[h k l]}(\theta)=p\left|M_{a}\left(\mathbf{K}_{m}\right)\right|^{2}\left(\frac{1+\cos ^{2} 2 \theta}{\sin ^{2} \theta \cos \theta}\right) \tag{2.1}
\end{equation*}
$$

Using the formula from the previous question to calculate the ratios of the structure factors in the given planes,


FIG. 3: Crystal structure of silicon.

TABLE I: X-Ray diffraction intensities for graphite and silicon $[4,5]$. Structure factors are included in parentheses.

|  | Si |  | C (Graphite) |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
|  | $2 \theta\left(^{\circ}\right)$ | Exp. | $2 \theta\left({ }^{\circ}\right)$ | Calc. | Exp. |
| $[111]$ | 28.47 | 100.00 | - | $(3)$ | - |
| $[100]$ | - | - | 42.77 | $4(3)$ | 3.45 |
| $[200]$ | - | - | - | $(1)$ | - |
| $[002]$ | - | - | 26.74 | $106(16)$ | 100 |
| $[220]$ | 47.35 | 64.31 | - | $(1)$ | - |
| $[311]$ | 37.31 | 37.31 | - | $(3)$ | - |
| $[400]$ | 69.21 | 9.58 | - | $(1)$ | - |

we obtain the following results presented in Table I. Calculations show that planes [100], [200], [220] and [400] exhibit relative diffraction intensities $1 / 3$ that of the [111] and [311] planes. The [002] plane exhibits the highest intensity diffraction, $16 / 3$ that of the [111] and [311] planes. We also found several non-zero structure factors that are not present in the experimental data.

### 2.3. Crystal Structure of Silicon

What are the ratios if the material were Si? How could you use this information to distinguish Si from your material by x-ray

## diffraction?

The crystal structure of another common semiconductor material, silicon (Si) is featured in Figure 3. Silicon forms a diamond cubic crystal structure with a lattice spacing of $5.42 \AA$. This crystal structure corresponds to a face-centered cubic Bravais lattice whose unit-cell basis contains 8 atoms located at vector positions,

$$
\begin{array}{ll}
d_{0}=\overrightarrow{0} & d_{4}=\frac{a}{4}(1,3,3) \\
d_{1}=\frac{a}{4}(1,1,1) & d_{5}=\frac{a}{4}(2,2,0) \\
d_{2}=\frac{a}{4}(3,3,1) & d_{6}=\frac{a}{4}(2,0,2) \\
d_{3} & =\frac{a}{4}(3,1,3)
\end{array}
$$

The structure factor contributing to its X-ray diffraction pattern is given by

$$
\begin{align*}
M_{a}\left(\mathbf{K}_{m}\right)= & \sum_{j=1}^{n} f_{a}^{(j)}\left(\mathbf{K}_{m}\right) e^{-i \mathbf{K}_{m} \cdot \mathbf{d}_{j}} \\
= & f\left(1+(-1)^{h+k}+(-1)^{k+l}+(-1)^{h+l}\right. \\
& +(-1)^{h+k+l}+(-i)^{3 h+k+l}+(-i)^{3 h+3 k+1} \\
& \left.+(-i)^{h+3 k+1}\right) \\
= & f\left(1+(-1)^{h+k}+(-1)^{k+l}+(-1)^{h+l}\right) \\
& \cdot\left(1+(-i)^{h+k+l}\right) . \tag{2.3}
\end{align*}
$$

This term undergoes a number of simplifications based on the parity of its Miller indices. If $[h k l]$ are all even and are divisible by 4 , then $M_{a}\left(\mathbf{K}_{m}\right)=8 f$. If they are not divisible by 4 or have mixed even and odd values, then $M_{a}\left(\mathbf{K}_{m}\right)=8 f$. Lastly if $[h k l]$ are all odd, then $M_{a}\left(\mathbf{K}_{m}\right)=4 f(1 \pm i)$.

The experimental X-ray diffraction intensities from these contributions are listed in Table I. The intensity values for silicon were measured with respect to a reference value $I / I_{0}=4.7$, which is a direct ratio of the strongest line of the sample to the strongest line of a reference sample $\alpha-\mathrm{Al}_{2} \mathrm{O}_{3}$. The number of visible peaks and the relative intensities between them suggest that silicon and graphite can be easily distinguished from each other using an x-ray diffraction experiment.
[1] D. Chung, Journal of Material Science 37, 1475 (2002).
[2] (????), URL http://physics.nist.gov/PhysRefData/.
[3] B. Cullity, Elements of X-Ray Diffraction (AddisonWesley, 1978).
[4] E. E. B. P. J. d. G. C. H. S. C. M. Morris, H. McMurdie, Standard X-ray Diffraction Powder Patterns, vol. Monograph 25, Section 13 (National Bureau of Standards, 1976).
[5] (????), URL http://rruff.info/graphite/display= default/.

# Phonon Spectra of Graphene 

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#### Abstract

We use a Born model to calculate the phonon dispersion of graphene by accounting for stretching $\left(\alpha_{s}\right)$ and bending $\left(\alpha_{\phi}\right)$ interactions between nearest neighbors. Our model describes four in-plane vibrational modes to whose dispersion relations we fit experimental lattice mode frequencies, yielding force constants $\alpha_{s}=445 \mathrm{~N} / \mathrm{m}$ and $\alpha_{\phi}=102 \mathrm{~N} / \mathrm{m}$. Our model also reasonably accounts for graphene's macroscopic properties, particularly sound speeds and elastic constants.


The lattice dynamical properties of graphene form the basis of understanding the vibrational spectra of carbonbased allotropes of various geometries, such as graphite or carbon nanotubes. We can use an analytical descriptions of micromechanical behavior to better understand the acoustic and optical properties of these materials.

In the following, we calculate the in-plane vibrational spectrum of graphene and its contributions to macroscopic elastic and thermodynamic quantities. We first discuss the force parameters of our Born model and derive a general potential to calculate the dynamical matrix of a primitive cell. Using our dispersion relations at high-symmetry points, we can determine the vibrational density of states, in-plane sound velocity, and elastic constants. We will briefly touch upon weak out-of-plane vibrational modes and its contributions to graphene's macroscopic properties.

## 1. BACKGROUND FOR THE BOHR MODEL

### 1.1. Parameters of Bohr Model

How many force constants are required for each bond? Why?

Two force constants, $\alpha_{s}$ and $\alpha_{\phi}$, are required to model each bond. Let $\alpha_{s}$ represent the restoring force seen when a bond is stretched and let $\alpha_{\phi}$ represent the restoring force seen when a bond is bent away from the axis along which it is normally aligned.

## What is the energy of a single bond in the Born model?

The energy in a single bond is the sum of the stretching and bending energies, $E_{s}$ and $E_{\phi}$. If $p$ is a vector along which the bond is aligned in equilibrium and $R$ is a lattice vector, then the energy contained in a bond between the

[^1]atom at $R$ and the atom at $R+p$ is
\[

$$
\begin{align*}
\mathbf{E}[R, R+p] & =E_{s}+E_{\phi} \\
& =\frac{1}{2} \alpha_{s}|p \cdot(u[R+p]-u[R])|^{2} \\
+ & \frac{1}{2} \alpha_{\phi}\left(|u[R+p]-u[R]|^{2}-|p \cdot(u[R+a]-u[R])|^{2}\right) . \tag{1.1}
\end{align*}
$$
\]

The model assumes that the bond is only slightly displaced from equilibrium. How would you modify the model to make the bond energy more realistically dependent on displacement from equilibrium - what order would the corrections be, and of what sign? Justify your answer physically; include sketches if appropriate.

The energy in the bond between the atom at lattice vector $R_{i}$ and the atom at lattice vector $R_{i}+a$ is generally estimated using a Taylor expansion to the second order as

$$
\begin{align*}
& \left.\mathbf{V}\left(u\left[R_{i}, t\right]\right)\right)= \\
& \quad \mathbf{V}_{0}+\sum_{n} \sum_{m}\left(\frac{\partial^{2} \mathbf{V}}{\partial u_{n}\left[R_{i}, t\right] \partial u_{m}\left[R_{i}+a, t\right]}\right)_{\mathbf{e q}} u_{n}\left[R_{i}, t\right], \tag{1.2}
\end{align*}
$$

where the position of the atom at $R_{i}+a$ is fixed, $n$ and $m$ index all dimensions being considered, $\mathbf{V}_{0}$ is the bond energy seen with zero displacement and $\mathbf{V}$ is the potential defined as the sum of all bond energies in the entire lattice

$$
\begin{equation*}
\mathbf{V}=\cdots+\sum_{n}\left(\mathbf{E}\left[R, R+a_{n}\right]+\mathbf{E}\left[R, R-a_{n}\right]\right)+\cdots \tag{1.3}
\end{equation*}
$$

where this is the slice of the lattice potential related to an atom at $R$ and the number of different vectors $a_{n}$ between the atom at R and atoms coupled to it depends on which $n^{\text {th }}$ nearest neighbor model is used to model the lattice.

Note that there is no first order term in this expansion. A first derivative of potential energy would imply a net force, so this term must equal zero as the Taylor coefficients are evaluated at equilibrium.

To make the Born model more accurate, we would need to take into account higher order terms from the Taylor
expansion of the potential. We know that the third order term is non-zero because the curve we are attempting to fit is not even around the equilibrium point. Based on the fact that the function has higher curvature to the left of the equilibrium point than it does to the right, it seems that the sign of the third order term would be negative.

### 1.2. Nearest Neighbor Couplings

If you use the only nearest neighbor couplings, how many force constants will your model require for your material? How large will the dynamical matrix be? What if you used nearest neighbor and next-nearest neighbor couplings?

Two force constants are needed to model graphene whether a nearest neighbor coupling or nearest and next nearest neighbor model is used, as long as the model is two-dimensional. As mentioned before, these are $\alpha_{s}$ and $\alpha_{\phi}$, representing restoring forces due to bond stretching and bond bending respectively. As graphene is a two dimensional material with a two atom basis, the dynamical matrix will be four-by-four. A third force constant $\alpha_{z}$ is required to account for out-of-plane phonon modes. The size of the dynamical matrix is not affected by the number of force constants used in our model, however if a third dimension is added to account for out of plane vibrations then the dynamical matrix will be six-by-six.

### 1.3. Elastic Properties

How many independent elastic constants does your material possess? What are they (give numbers)? Why will a nearest neighbor approach not provide the most general solution for a cubic material?

Graphene has two elastic constants, $\lambda$ and $\mu$. The measured values of transverse and longitudinal phonon velocities in graphene are $v_{t}=14 \cdot 10^{3} \mathrm{~ms}^{-1}$ and $v_{l}=$ $21.7 \cdot 10^{3} \mathrm{~ms}^{-1}$ respectively [1]. Given the density $\rho=$ $2 M_{C}\left[\frac{3 \sqrt{3} a^{2}}{2}\right]^{-1}=7.6 \cdot 10^{-7} \mathrm{kgm}^{-2}$, where the mass of carbon $M_{C}=1.99 \cdot 10^{-26} \mathrm{~kg}$ and the lattice constant $a=1.42 \cdot 10^{-10} m$, the Lamé coefficients are calculated using that $v_{t}=\sqrt{\mu / \rho}$ and $v_{l}=\sqrt{(\lambda+2 \mu) / \rho}$ to be $\mu \simeq$ $29.3 \mathrm{~N} / \mathrm{m}$ and $\lambda \simeq 72.2 \mathrm{~N} / \mathrm{m}$. It is worth noting that these macroscopic elastic constants are not usually calculated or measured for graphene because it is a two-dimensional material with single atom thickness.

## 2. CONSTRUCTION OF THE DYNAMICAL MATRIX

We will first determine the phonon dispersion relations of the in-plane vibrational modes in the context of the


FIG. 1: Hexagonal crystal structure of a graphene primitive cell and its neighbors; First Brillouin zone of graphene and its symmetry points.

Born force model and, and then briefly discuss the out-of-plane vibrational modes.

### 2.1. Lattice and Reciprocal Space Structures

[Label] all the atoms in the basis and all their nearest neighbors. For each atom labeled $A$ $H$, [verify] the lattice vectors $\mathbf{R}_{p}$ to each unit cell.

A graphene sheet forms a two-dimensional hexagonal crystal lattice with a primitive cell containing two atoms (A and B), depicted in Figure 1. Based on our previous discussion of the Born model, let us assume that the primitive cell interacts with nearest neighbors and next-nearest neighbors with spring constants $\alpha_{s}$ and $\alpha_{\phi}$, respectively, and that atoms of the primitive cell have a lattice spacing given by $a=1.42 \AA$ and a primitive lattice constant $2.46 \AA$. Figure 1 also depicts graphene's first Brillouin zone and its symmetry points located at $\mathbf{k}_{\Gamma}=$ $(0,0), \mathbf{k}_{M}=(2 \pi / a \sqrt{3}, 0)$, and $\mathbf{k}_{K}=(2 \pi / a \sqrt{3}, 2 \pi / 3 a)$.

The lattice contains two sublattices 0 and 1 , which differ by their bond orientations. The first atom $A$ in the primitive cell has three first neighbors in the other sublattice 1 with relative unit vectors

$$
\begin{equation*}
\mathbf{e}_{B}=(1,0) \quad \mathbf{e}_{C}=\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \quad \mathbf{e}_{D}=\left(-\frac{1}{2},-\frac{\sqrt{3}}{2}\right) \tag{2.1}
\end{equation*}
$$

and six next-nearest neighbors in the same sublattice 0 with relative unit vectors

$$
\begin{align*}
& \mathbf{e}_{E}=\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \quad \mathbf{e}_{F}=\left(\frac{\sqrt{3}}{2},-\frac{1}{2}\right) \quad \mathbf{e}_{G}=(0,1) \\
& \mathbf{e}_{H}=\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \quad \mathbf{e}_{I}=\left(-\frac{\sqrt{3}}{2},-\frac{1}{2}\right) \quad \mathbf{e}_{J}=(0,-1) . \tag{2.2}
\end{align*}
$$

### 2.2. Born Force Model

[Using a Born force model, find] a general expression for the potential energy of all the

TABLE I: Calculated nearest neighbor and next-nearest neighbor forces for graphene. The first (second) row of a given planar index specifies the force interaction between the A (B) atom and one of its neighbors.

|  | A | B | C | D | E | F | G | H | I | J |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $x x$ | $3 \alpha_{s} / 2+3 \alpha_{\phi}$ | $-\alpha_{s}$ | $-\alpha_{s} / 4$ | $-\alpha_{s} / 4$ | $-3 \alpha_{s} / 4$ | $-3 \alpha_{s} / 4$ | 0 | $-3 \alpha_{\phi} / 4$ | $-3 \alpha_{\phi} / 4$ | 0 |
|  | $-\alpha_{s}$ | $3 \alpha_{s} / 2+3 \alpha_{\phi}$ | - | - | $-\alpha_{s} / 4$ | $-\alpha_{s} / 4$ | - | - | - | - |
| $x y, y x$ | 0 | 0 | $\sqrt{3} \alpha_{s} / 4$ | $-\sqrt{3} \alpha_{s} / 4$ | $-\sqrt{3} \alpha_{\phi} / 4$ | $\sqrt{3} \alpha_{\phi} / 4$ | 0 | $\sqrt{3} \alpha_{\phi} / 4$ | $-\sqrt{3} \alpha_{\phi} / 4$ | 0 |
|  | 0 | 0 | - | - | $-\sqrt{3} \alpha_{s} / 4$ | $\sqrt{3} \alpha_{s} / 4$ | - | - | - | - |
| $y y$ | $3 \alpha_{s} / 2+3 \alpha_{\phi}$ | 0 | $-3 \alpha_{s} / 4$ | $-3 \alpha_{s} / 4$ | $-\alpha_{\phi} / 4$ | $-\alpha_{\phi} / 4$ | $-\alpha_{\phi}$ | $-\alpha_{\phi} / 4$ | $-\alpha_{\phi} / 4$ | $-\alpha_{\phi}$ |
|  | 0 | $3 \alpha_{s} / 2+3 \alpha_{\phi}$ | - | - | $-3 \alpha_{s} / 4$ | $-3 \alpha_{s} / 4$ | - | - | - | - |

atoms in the crystal in terms of their displacement from equilibrium.

The total elastic potential energy for the all the atoms in the crystal in terms of their displacements from equilibrium is given by summing the nearest-neighbor stretching interactions,

$$
\begin{align*}
V_{s}(R) & =\frac{1}{2} \alpha_{s}\left|\mathbf{e}_{B} \cdot\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{B}}\right]\right)\right|^{2} \\
& +\frac{1}{2} \alpha_{s}\left|\mathbf{e}_{C} \cdot\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{C}}\right]\right)\right|^{2} \\
& +\frac{1}{2} \alpha_{s}\left|\mathbf{e}_{D} \cdot\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{D}}\right]\right)\right|^{2} \tag{2.3}
\end{align*}
$$

with the nearest neighbor bending interactions

In this explanation, $V_{i j}^{\prime \prime}$ are second-partial derivatives of our Born model potential at equilibrium, $\mathbf{R}_{p}$ are the relative lattice vectors described in Equations 2.1 and 2.2, and $\mathbf{u}=\left(u_{x}^{1}, u_{y}^{2}, u_{x}^{1}, u_{y}^{2}\right)^{T}$. The force constants from taking the appropriate second derivatives is given in Table I.

The dynamical matrix is then given by

$$
D(\mathbf{k})=\left(\begin{array}{cccc}
A_{0} & B_{0} & C & D  \tag{2.7}\\
B_{0} & A_{1} & D & B_{1} \\
C^{*} & D^{*} & A_{0} & B_{0} \\
D^{*} & B_{1}^{*} & B_{0} & A_{1}
\end{array}\right)
$$

If we let $(A A)$ and $(B B)$ represent the 0 and 1 sublattices, respectively, these matrix elements represent
$=\frac{1}{2} \alpha_{\phi}\left(\left.\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{B}}\right]\right)\right|^{2}-\left|\mathbf{e}_{B} \cdot\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{B}}\right]\right)\right|^{2}\right)^{\mathrm{r}}$
$+\frac{1}{2} \alpha_{\phi}\left(\left|\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{C}}\right]\right)\right|^{2}-\left|\mathbf{e}_{C} \cdot\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{C}}\right]\right)\right|^{2}\right)_{0} A_{0}=D_{x x}(A A)=D_{x x}(B B)$
$+\frac{1}{2} \alpha_{\phi}\left(\left|\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{D}}\right]\right)\right|-\left|\mathbf{e}_{D} \cdot\left(u_{1}[\mathbf{R}]-u_{2}\left[\mathbf{R}+\mathbf{e}_{\mathbf{D}}\right]\right)\right|^{2}\right) C_{0}=D_{x x}(A B)=D_{x x}^{*}(B A)$

### 2.3. Dynamical Matrix

Use the expression for the potential energy to determine the force on a given atom in the crystal in terms of its displacement and its neighbors displacements. Check your answer by directly calculating the force from the spring constants and displacements.
Verify from the potential, by explicitly taking the derivatives, the factors in the matrix.

From the potential energy, the force on a given atom in the crystal is given in terms of a harmonic oscillator force expression

$$
\begin{equation*}
f_{i}=D_{i j}(\mathbf{k}) u_{j}, \tag{2.5}
\end{equation*}
$$

where $D_{i j}$ is the dynamical matrix is given by

$$
\begin{equation*}
D_{i j}(\mathbf{k})=\sum_{\mathbf{R}_{p}} \tilde{D}_{i j}\left(\mathbf{R}_{p}\right) e^{-i \mathbf{k} \cdot \mathbf{R}_{p}}=\sum_{\mathbf{R}_{p}} V_{i j}^{\prime \prime}\left(\mathbf{R}_{p}\right) e^{-i \mathbf{k} \cdot \mathbf{R}_{p}} \tag{2.6}
\end{equation*}
$$

$$
\begin{align*}
D_{0} & =D_{x y}(A B)=D_{y x}(A B)=D_{x y}^{*}(B A)=D_{y x}^{*}(B A) \\
A_{1} & =D_{y y}(A A)=D_{y y}(B B) \\
B_{1} & =D_{y y}(A B)=D_{y y}^{*}(B A) . \tag{2.8}
\end{align*}
$$

As a sample calculation, consider the element $D_{x x}$ given by $A_{0}$,

$$
\begin{align*}
A_{0}= & V_{x x}^{\prime \prime}(A A)+V_{x x}^{\prime \prime}(A E) e^{-i\left(\frac{\sqrt{3}}{2} k_{x} a+\frac{k_{y} a}{2}\right)} \\
& +V_{x x}^{\prime \prime}(A F) e^{-i\left(\frac{\sqrt{3}}{2} k_{x} a-\frac{k_{y} a}{2}\right)}+V_{x x}^{\prime \prime}(A G) e^{-i k_{y} a} \\
& +V_{x x}^{\prime \prime}(A H) e^{i\left(\frac{\sqrt{3}}{2} k_{x} a-\frac{k_{y} a}{2}\right)}+V_{x x}^{\prime \prime}(A I) e^{i\left(\frac{\sqrt{3}}{2} k_{x} a+\frac{k_{y} a}{2}\right)} \\
& +V_{x x}^{\prime \prime}(A J) e^{i k_{y} a} \\
= & \frac{3 \alpha_{s}}{2}+3 \alpha_{\phi}-\frac{3 \alpha_{s}}{4} e^{-i\left(\frac{\sqrt{3}}{2} k_{x} a+\frac{k_{y} a}{2}\right)}-\frac{3 \alpha_{s}}{4} e^{-i\left(\frac{\sqrt{3}}{2} k_{x} a-\frac{k_{y} a}{2}\right)} \\
& +0-\frac{3 \alpha_{\phi}}{4} e^{i\left(\frac{\sqrt{3}}{2} k_{x} a-\frac{k_{y} a}{2}\right)}-\frac{3 \alpha_{\phi}}{4} e^{i\left(\frac{\sqrt{3}}{2} k_{x} a+\frac{k_{y} a}{2}\right)}+0 \\
= & \frac{3}{2} \alpha_{s}+3 \alpha_{\phi}\left[1-\cos \left(\frac{\sqrt{3}}{2} k_{x} a\right) \cos \left(\frac{1}{2} k_{y} a\right)\right] \tag{2.9}
\end{align*}
$$

TABLE II: Calculated and measured [2] macroscopic properties of graphene.

| Quantity | Measured |  |  | Calculated |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Lattice Mode Frequencies (meV) |  |  |  |  |  |
|  | $\Gamma$ | M | K | $\Gamma$ | M | K |
| $\omega_{\text {LO }}$ | 194.8 | 175.1 | 155.36 | 170.3 | 182.9 | 197.4 |
| $\omega_{\text {LA }}$ | 0 | 169.84 | 155.36 | 0 | 151.5 | 156.4 |
| $\omega_{\text {TO }}$ | 194.8 | 169.84 | 155.36 | 170.3 | 180.6 | 156.4 |
| $\omega_{\text {TA }}$ | 0 | 50.03 | 125.07 | 0 | 66.5 | 99.8 |
| $\omega_{\text {ZO }}$ | 0 | 75 | 60 | - | - | - |
| $\omega_{\mathrm{ZA}}$ | 110 | 52 | 60 | - | - | - |
| Sound Velocities (km/s) |  |  |  |  |  |  |
| $v_{\text {LA }}$ |  | 21.7 |  |  | 13.12 |  |
| $v_{\text {TA }}$ |  | 14 |  |  | 6.21 |  |
| $v_{\text {ZA }}$ |  | - |  |  | - |  |
|  | Elastic Constants (10 GPa) |  |  |  |  |  |
| $C_{11}$ |  | $106 \pm 2$ |  |  | 131.0 |  |
| $C_{12}$ |  | $28 \pm 2$ |  |  | 72.3 |  |
| $C_{44}$ |  | $0.43 \pm 0.05$ |  |  | - |  |

A similar calculation for the remainder of the matrix elements gives us

$$
\begin{align*}
A_{0} & =\frac{3}{2} \alpha_{s}+3 \alpha_{\phi}\left[1-\cos \left(\frac{\sqrt{3}}{2} k_{x} a\right) \cos \left(\frac{1}{2} k_{y} a\right)\right] \\
B_{0} & =-\alpha_{\phi} \sqrt{3} \sin \left(\frac{\sqrt{3}}{2} k_{x} a\right) \sin \left(\frac{k_{y} a}{2}\right) \\
C & =-\alpha_{s}\left[e^{-i\left(\frac{k_{x} a}{\sqrt{3}}\right)}+\frac{1}{2} e^{i\left(\frac{k_{x} a}{2 \sqrt{3}}\right)} \cos \left(\frac{k_{y} a}{2}\right)\right] \\
D & =-i \frac{\sqrt{3}}{2} \alpha_{s} e^{i\left(\frac{k_{x} a}{2 \sqrt{3}}\right)} \sin \left(\frac{k_{y} a}{2}\right) \\
A_{1} & =\frac{3}{2} \alpha_{s}+\alpha_{\phi}\left[3-2 \cos \left(k_{y} a\right)-\cos \left(\frac{\sqrt{3}}{2} k_{x} a\right) \cos \left(\frac{1}{2} k_{y} a\right)\right. \\
B_{1} & =-\frac{3}{2} \alpha_{s} e^{i\left(\frac{k_{x} a}{2 \sqrt{3}}\right)} \cos \left(\frac{k_{y} a}{2}\right) . \tag{2.10}
\end{align*}
$$

## 3. MODEL OPTIMIZATION AND COMPARISON TO MACROSCOPIC PROPERTIES

### 3.1. Comparison with Published Theoretical and Experimental Data

Plot the phonon dispersion in appropriate units along the $\Gamma-X, X-L$, and $\Gamma-L$ directions.

For these values of force constants and masses, determine the atomic displacements for all the modes at $\Gamma$, and for the highest




FIG. 2: Calculated and experimental phonon dispersion curves for graphene. (a) Fitted experimental dispersion curves using inelastic x-ray scattering in graphite [2]; (b) (c) calculated dispersion relations using our fitted force constants ( $\alpha_{s}=445 \mathrm{~N} / \mathrm{m}$ and $\alpha_{\phi}=102 \mathrm{~N} / \mathrm{m}$ ) and suggested force constants ( $\alpha_{s}=1$ and $\left.\alpha_{\phi}=0.25\right)$.
optic and lowest acoustic modes at $X$ and L. Provide drawings of the atomic motion of these modes. How many modes are there at $\Gamma$ ?

### 3.2. Phonon Dispersion Relations

The phonon dispersion relation $\omega=\omega(\mathbf{k})$ is determined from the eigenvalue equation

$$
\begin{equation*}
\left(\mathbf{M}^{-1} \mathbf{D}(\mathbf{k})\right) \epsilon=\omega^{2} \epsilon . \tag{3.1}
\end{equation*}
$$

Note additionally, that while graphene is twodimensional, it possesses miniscule elastic movement in the vertical direction, leading to a very small, but nonzero elastic constant $C_{44}$. We can define force constants $\beta_{s}$ and $\beta_{\phi}$ for the nearest and next-nearest interactions of the out-of-plane vibrational modes. It has been shown [3] that the phonon dispersion relations for the out-of-plane optical and acoustic vibrational modes are

$$
\begin{equation*}
\omega_{Z O, Z A}=\sqrt{u \pm v} \tag{3.2}
\end{equation*}
$$

where
$u=2 \beta_{\phi}\left[\cos \left(\sqrt{3} k_{y} a\right)+2 \cos \left(\frac{3 k_{x} a}{2}\right) \cos \left(\frac{\sqrt{3} k_{y} a}{2}\right)\right]-3 \beta_{s} \mathrm{wh}$
$v=\beta_{s}\left[1+4 \cos ^{2}\left(\frac{\sqrt{3} k_{y} a}{2}\right)+4 \cos \left(\frac{3 k_{x} a}{2}\right) \cos \frac{\sqrt{3} k_{y} a}{2}\right]^{1 / 2}$,
where the out-of-plane spring constants are given by $\beta_{s}=-1.176$ and $\beta_{s}=0.190$. These dispersion relations are decoupled from the in-plane vibrational modes. By diagonalizing the Hermitian dynamical matrix in Equation 2.7 , we can add these dispersion relations a subspace. From empirical data (see II), we know that elastic out-of-plane motion is several orders of magnitude less than the in-plane motion. Our own plots of Equation 3.3 yielded high lattice mode frequencies, contradicting this intuition. As such, we have omitted its inclusion in our determination of macroscopic elastic constants.

Figure 2 compares the measured dispersion relation of graphene against our calculated dispersion relations using the suggested force constants ( $\alpha_{s}=1$ and $\alpha_{\phi}=$ 0.25 ) and our fitted force constants ( $\alpha_{s}=445 \mathrm{~N} / \mathrm{m}$ and $\alpha_{\phi}=102 \mathrm{~N} / \mathrm{m}$ ). The optimum force constants are found for our model by parameterizing the force constants and comparing the results of $\omega$ at the relevant zone edges. Two force constants are chosen, and $\omega$ is calculated for each of the three zone edges, $\Gamma, M$, and $K$. An RMS error is generated by subtracting the experimental values from the calculated values, and iteratively the optimum values for the force constants are found by searching for the lowest RMS error value.

The relative atomic displacements for the acoustic and optical modes at the $\Gamma, K$, and $M$ symmetry points is shown in Figure 5.There are a total of four in-plane modes (acoustical and optical, transverse and longitudinal) present at $\Gamma$, however both the optical and acoustical pairs are degenerate. The atomic displacement patterns associated with the various eigenmodes at different points of high symmetry in K space are shown in Figure
4. Many qualitative features of our calculated dispersion relations are consistent with the experimental and ab initio data in Figure 2 [4]. Note degeneracies at the $\Gamma$ point and linear dispersion relations for small displacements from $\Gamma$. Hexagonal symmetry of the graphene lattice also accounts for the measured and calculated degeneracies at the $M$ and $K$ points. The largest discrepancies between experimental data and our Born model are for the TO and LO modes, which require accounting of electron-phonon interactions in ab initio models for accurate prediction [5].
Theoretical sound velocities for both longitudinal and optical polarizations are estimated by calculating the slopes of the acoustical phonon dispersion curves of both polarizations near $\Gamma$ and taking $c=\frac{\delta \omega}{\delta k}$. The elastic constants $C_{11}$ and $C_{12}$ are determined from the phonon sound velocities as

$$
\begin{equation*}
v_{\mathrm{LA}}=\sqrt{C_{11} / \rho} \quad v_{\mathrm{TA}}=\sqrt{\left(C_{11}-C_{12}\right) / \rho}, \tag{3.4}
\end{equation*}
$$

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### 3.3. Density of States

Plot the total density of states (histogram method, include all modes) versus frequency.

Figure 3 shows the overall density of states and those for individual modes. Experimental data for graphene is unavailable, although the our calculation seemed qualitatively consistent with experimental data for graphite [4]

### 3.4. Specific Heat

> Calculate the specific heat of your material versus temperature using (a) your calculated density of states, (b) a Debye model, and (c) a combined Debye-Einstein model (Debye for acoustic modes, Einstein for optical modes). Plot your results for temperatures between $0 K$ and $3 \Theta_{D}$ Comment on the strengths and weaknesses of your model.

The specific heat for graphene is calculated using the combined density of states (3), Debye model, and combined Density of States (optical branches) and Debye model (acoustic branches). The two models result in radically different specific heats, perhaps because the Debye model does not account for the optical modes, upon which the specific heat significantly depends. The plots for the specific heats in these models is given in Figure 4.

In the Debye model calculation, the longitudinal acoustic velocity is used as the speed of sound instead of the inverse addition of longitudinal and tranverse velocities, because in the calculated phonon dispersion relation the transverse acoustic line is by far the most deviant from experimental value. In addition, it should be noted that



FIG. 3: Calculated total and individual-mode density of
[1] J. Hone, Book Series Topics in Applied Physics 80, 273 (2001).
[2] V. K. Tewary and B. Yang, Physical Review B (Condensed Matter and Materials Physics) 79, 075442 (pages 9) (2009), URL http://link.aps.org/abstract/PRB/v79/ e075442.
[3] L. A. Falkovsky, Soviet Journal of Experimental and Theoretical Physics 105, 397 (2007), arXiv:condmat/0702409.
[4] M. Mohr, J. Maultzsch, E. Dobardžić, S. Reich, I. Milošević, M. Damnjanović, A. Bosak, M. Krisch, and C. Thomsen, Physical Review B (Condensed Matter and Materials Physics) 76, 035439 (pages 7) (2007), URL http://link.aps.org/abstract/PRB/v76/e035439.
use of the longitudinal acoustic velocity provides a reasonably accurate $\Theta_{D}$ of 2200 K (with experimental data suggesting a $\Theta_{D}$ of $2400 \mathrm{~K}[6]$.
states.
[5] L. M. Woods and G. D. Mahan, Phys. Rev. B 61, 10651 (2000).
[6] W. DeSorbo and W. W. Tyler, The Journal of Chemical Physics 21, 1660 (1953), URL http://link. aip.org/ link/?JCP/21/1660/1.


FIG. 4: Calculated specific heats using calculated density of states, Debye model, and combined Debye-Einstein model.


FIG. 5: Atomic displacements for the eigenmodes of graphene at the 5(a) $\Gamma, 5$ (b) $K$, and $5(\mathrm{c}) M$ points [4]

# Electronic Band Structure of Graphene 

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The band structure properties of graphene form the basis of understanding the electronic spectra of carbonbased allotropes of various geometries, such as graphite or carbon nanotubes. We can use an analytical and numerical descriptions of carbon's valence electrons to better understand the conduction and semiconductor properties of these materials.

## 1. BAND STRUCTURE BACKGROUND QUESTIONS

How many extended orbital basis functions will you have for your material? Why?

A graphene sheet forms a two-dimensional hexagonal crystal lattice with a primitive cell containing two atoms (A and B); its lattice structure of graphene and its first Brillouin zone is shown in Figure 1. The electron configuration of free carbon atoms is $1 s^{2} 2 s^{2} 2 p^{2}$. For the two atoms in the basis, there are four valence orbitals, yielding eight extended orbital basis functions for our material. Because of its planar structure, atoms undergo bonding with four hybridized $s p^{2}$-wave functions of the form

$$
\begin{equation*}
\frac{1}{\sqrt{3}}\left(|2 s\rangle+\sqrt{2}\left|2 p_{i}\right\rangle\right) \quad(i=x, y, z) \tag{1.1}
\end{equation*}
$$

Conceivably one could also construct the LCAO wave function out of core orbitals as well as valence orbitals. How many extended orbital basis functions would you have to use for your material? How large would your Hamiltonian matrix be in this case? How do you expect your results would differ from those you would get with just valence orbitals? What if we used higher (totally unoccupied) orbitals, too? How many orbitals per atom would we have to use to get an exact band structure? Why?

If we were to add the $1 s$ orbital to our LCAO basis set, we would have five orbitals per atom in a two atom basis, yielding 10 LCAO wavefunctions and a $10 \times 10$ Hamiltonian matrix. The additional of this orbital to our basis has a negligible effect due to the statistically insignificant

[^2]

FIG. 1: Hexagonal crystal structure of a graphene primitive cell and its neighbors; First Brillouin zone of graphene and its symmetry points.
interactions between the $1 s$ and $2 s / 2 p_{i}$ orbitals. Being independent of the valence orbitals, the two extra rows of the Hamiltonian are block diagonalized from other eight rows.

## 2. CONSTRUCTION OF HAMILTONIAN MATRIX

What are the atomic configurations of the two atoms in your material? Which orbitals do you expect to play a significant role in bonding?

The electron configuration of free carbon atoms is $1 s^{2} 2 s^{2} 2 p^{2}$. The valence electrons in the $2 s, 2 p_{x}, 2 p_{y}$, and $2 p_{z}$ orbits play a significant role in bonding.

Draw all the atoms in the basis and all their nearest neighbors with appropriate orbitals on each atom. Label the orbitals according to their lattice vector, basis vector, orbital type, and the type atom they are associated with (cation or anion).

The lattice structure of graphene and its first Brillouin zone is shown in Figure 1. The lattice contains two sublattices 0 and 1 , which differ by their bond orientations. The first atom $A$ in the primitive cell has three first neighbors in the other sublattice 1 with relative unit vectors

$$
\begin{equation*}
\mathbf{e}_{B}=(1,0) \quad \mathbf{e}_{C}=\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \quad \mathbf{e}_{D}=\left(-\frac{1}{2},-\frac{\sqrt{3}}{2}\right) . \tag{2.1}
\end{equation*}
$$

and six next-nearest neighbors in the same sublattice 0
with relative unit vectors

$$
\begin{align*}
& \mathbf{e}_{E}=\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \quad \mathbf{e}_{F}=\left(\frac{\sqrt{3}}{2},-\frac{1}{2}\right) \quad \mathbf{e}_{G}=(0,1) \\
& \mathbf{e}_{H}=\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right) \quad \mathbf{e}_{I}=\left(-\frac{\sqrt{3}}{2},-\frac{1}{2}\right) \quad \mathbf{e}_{J}=(0,-1) . \tag{2.2}
\end{align*}
$$

The carbon basis atom $A$ at cell vector $R$ has orbitals $|2 s(\mathbf{R})\rangle$ and $\left|2 p_{i}(\mathbf{R})\right\rangle(i=x, y, z)$, and orbitals from three nearest neighbors shown in Figure 1,

$$
\begin{align*}
& B:\left|2 s^{A}\left(\mathbf{R}+\mathbf{e}_{\mathbf{B}}\right)\right\rangle \text { and }\left|2 p_{i}^{A}\left(\mathbf{R}+\mathbf{e}_{\mathbf{B}}\right)\right\rangle  \tag{2.3}\\
& C:\left|2 s^{A}\left(\mathbf{R}+\mathbf{e}_{\mathbf{C}}\right)\right\rangle \text { and }\left|2 p_{i}^{A}\left(\mathbf{R}+\mathbf{e}_{\mathbf{C}}\right)\right\rangle  \tag{2.4}\\
& D:\left|2 s^{A}\left(\mathbf{R}+\mathbf{e}_{\mathbf{D}}\right)\right\rangle \text { and }\left|2 p_{i}^{A}\left(\mathbf{R}+\mathbf{e}_{\mathbf{D}}\right)\right\rangle, \tag{2.5}
\end{align*}
$$

and the carbon basis atom $B$ at cell vector $R$ has orbitals $|2 s(\mathbf{R})\rangle$ and $\left|2 p_{i}(\mathbf{R})\right\rangle(i=x, y, z)$, and orbitals from three nearest neighbors,

$$
\begin{align*}
& A:\left|2 s^{B}\left(\mathbf{R}-\mathbf{e}_{\mathbf{B}}\right)\right\rangle \text { and }\left|2 p_{i}^{B}\left(\mathbf{R}-\mathbf{e}_{\mathbf{B}}\right)\right\rangle  \tag{2.6}\\
& E:\left|2 s^{B}\left(\mathbf{R}-\mathbf{e}_{\mathbf{C}}\right)\right\rangle \text { and }\left|2 p_{i}^{B}\left(\mathbf{R}-\mathbf{e}_{\mathbf{C}}\right)\right\rangle  \tag{2.7}\\
& F:\left|2 s^{B}\left(\mathbf{R}-\mathbf{e}_{\mathbf{D}}\right)\right\rangle \text { and }\left|2 p_{i}^{B}\left(\mathbf{R}-\mathbf{e}_{\mathbf{D}}\right)\right\rangle . \tag{2.8}
\end{align*}
$$

[...] approximate all the nearest neighbor interactions. Is this approximation reasonable? Calculate values for $E_{s s}, E_{s p}, E_{x x}$, and $E_{x y}$ in terms of $V_{s s \sigma}, V_{s p \sigma}$, etc

In examining the orbital interactions contributing to the matrix elements of the Hamiltonian, we will refer to several figures taken from Saito and Dresselhaus that depict carbon's valence orbital overlaps [1]. The hybridized orbitals contributing to the LCAO approximation are given by the $s p^{2}$ orbitals,

$$
\begin{align*}
\left|\phi_{1}^{A, B}\right\rangle & =\frac{1}{\sqrt{3}}\left|2 s^{A, B}\right\rangle \pm \sqrt{\frac{2}{3}}\left|2 p_{x}^{A, B}\right\rangle \\
\left|\phi_{2}^{A, B}\right\rangle & =\frac{1}{\sqrt{3}}\left|2 s^{A, B}\right\rangle \mp \frac{1}{\sqrt{6}}\left|2 p_{x}^{A, B}\right\rangle \pm \frac{1}{\sqrt{2}}\left|2 p_{y}^{A, B}\right\rangle \\
\left|\phi_{3}^{A, B}\right\rangle & =\frac{1}{\sqrt{3}}\left|2 s^{A, B}\right\rangle \mp \frac{1}{\sqrt{6}}\left|2 p_{x}^{A, B}\right\rangle \pm \frac{1}{\sqrt{2}}\left|2 p_{y}^{A, B}\right\rangle \\
\left|\phi_{4}^{A, B}\right\rangle & =\left|2 p^{A, B}\right\rangle \tag{2.9}
\end{align*}
$$

Figure 2 shows that all nearest neighbor bonding interactions are described by each of

$$
\begin{align*}
E_{s s} & =\left\langle 2 s^{A}(0)\right| \hat{H}\left|2 s^{B}\left(\mathbf{e}_{B}\right)\right\rangle \\
E_{s p} & =\left\langle 2 s^{A}(0)\right| \hat{H}\left|2 p_{x}^{B}\left(\mathbf{e}_{B}\right)\right\rangle \\
E_{x x} & =\left\langle 2 p_{x}^{A}(0)\right| \hat{H}\left|2 p_{x}^{B}\left(\mathbf{e}_{B}\right)\right\rangle \\
E_{x y} & =\left\langle 2 p_{x}^{A}(0)\right| \hat{H}\left|2 p_{y}^{B}\left(\mathbf{e}_{B}\right)\right\rangle, \tag{2.10}
\end{align*}
$$

where all remaining orbital overlaps going to zero.

(a)Four $s p^{2}$ hybridized orbitals in carbon bonding.


(b)The rotation of $2 p_{x}$ and $\sigma$-bond band parameter overlaps for the $2 s$ and $2 p_{i}(i=x, y, z)$ orbitals.

FIG. 2: Orbital overlaps in graphene. Figure 2(b) shows how to project $2 p_{x}$ along the $\sigma$ and $\pi$ components, and the nonvanishing (1-4) and vanishing (5-8) elements of the Hamiltonian matrix. Figure 2(c) shows examples of Hamiltonian matrix elements for $\sigma$ orbitals $\left\langle 2 s^{A}\right| \hat{H}\left|2 p_{x}^{B}\right\rangle$ and $\left\langle 2 p_{x}^{A}\right| \hat{H}\left|2 p_{y}^{B}\right\rangle$, respectively. Figures taken from [1].

The matrix elements for the Bloch orbitals between the $A$ and $B$ atoms of the basis are obtained by taking the components of the $2 p_{x}$ and $2 p_{y}$ orbitals in the $\sigma$ and $\pi$ basis. From rotating the orbitals, we have one of eight overlap configurations given by Figure 2. For example, the wavefunction $\left|2 p_{x}\right\rangle$ is determined by projecting it onto the $\sigma$ and $\pi$ basis such that

$$
\begin{equation*}
\left|2 p_{x}\right\rangle=\cos \left(\frac{\pi}{3}\right)\left|2 p_{\sigma}\right\rangle+\sin \left(\frac{\pi}{3}\right)\left|2 p_{\pi}\right\rangle . \tag{2.11}
\end{equation*}
$$

Using these rotation transformations, we can determine the energies given in Equation 2.10 in terms of $V_{i j k}$ overlap terms. For example, the third energy overlap term shown in Figure 2(b) is given by

$$
\begin{align*}
\left\langle 2 p_{x}^{A}\right| \hat{H}\left|2 p_{y}^{B}\right\rangle= & \frac{3}{4}\left(V_{p p \sigma}+V_{p p \pi}\right) e^{-i k_{x} a / 2 \sqrt{3}} e^{i k_{y} a / 2} \\
& -\frac{3}{4}\left(V_{p p \sigma}+V_{p p \pi}\right) e^{-i k_{x} a / 2 \sqrt{3}} e^{-i k_{y} a / 2} \\
= & i \frac{\sqrt{3}}{2}\left(V_{p p \sigma}+V_{p p \pi}\right) e^{-i k_{x} a / 2 \sqrt{3}} \sin \frac{k_{y} a}{2} . \tag{2.12}
\end{align*}
$$

The remaining overlap terms are summarized in Equation 2 in the next section of this paper.

Finally, in our LCAO approximation, note that

$$
\begin{align*}
\left\langle 2 s^{A}(0)\right| \hat{H}\left|2 p_{x}^{B}\left(\mathbf{e}_{B}\right)\right\rangle & =\left\langle 2 s^{B}(0)\right| \hat{H}\left|2 p_{x}^{A}\left(\mathbf{e}_{B}\right)\right\rangle \\
\left\langle 2 s^{A}(0)\right| \hat{H}\left|2 s^{A}(0)\right\rangle & =\left\langle 2 s^{B}\left(\mathbf{e}_{B}\right)\right| \hat{H}\left|2 s^{B}\left(\mathbf{e}_{B}\right)\right\rangle . \tag{2.13}
\end{align*}
$$

The first is valid because of the uniformity of our medium: valence orbitals will be the same regardless of where the electrons are located. Permutations of orbitals leave energy overlaps invariant because of the symmetry of the interactions. The latter expression is also valid, as orbital self-interactions will remain the same amongst identical atoms. In the case, both basis atoms are carbon.

Construct a set of extended atomic orbitals. Be explicit about your choice of phase factors. Write your trial wave function as a linear combination of these extended orbitals.

Recall that for the tight-binding solution that we use the trial wave function

$$
\begin{equation*}
|\psi(r)\rangle=\sum_{\alpha} \sum_{\mathbf{R}_{l}} c_{\alpha}\left[\mathbf{R}_{l}\right]\left|\phi_{\alpha}\left(\mathbf{r}-\mathbf{R}_{l}\right)\right\rangle, \tag{2.14}
\end{equation*}
$$

where $\alpha$ denotes both each type of wave function for each atom and also the type of atom in the basis, and $\mathbf{R}_{l}$ denotes the direct lattice vectors. Therefore, our LCAO trial wave function is given by hybridized wave functions for the atoms in the primitive basis

$$
\begin{align*}
|\psi\rangle=a_{A} & \left|2 s^{A}(\mathbf{R})\right\rangle+\sum_{i=x, y, z} b_{A}^{i}\left|2 p_{i}^{A}(\mathbf{R})\right\rangle \\
& +a_{B}\left|2 s^{B}\left(\mathbf{R}+\mathbf{e}_{\mathbf{B}}\right)\right\rangle+\sum_{i=x, y, z} b_{B}^{i}\left|2 p_{i}^{B}\left(\mathbf{R}+\mathbf{e}_{\mathbf{B}}\right)\right\rangle \tag{2.15}
\end{align*}
$$

Find the Hamiltonian matrix for the nearest neighbor approximation.
For a systems Hamiltonian operator $\hat{H}$, the Hamiltonian matrix in the LCAO method is

$$
\begin{equation*}
\mathbf{H}(\mathbf{k})=\sum_{\mathbf{R}_{p}} \tilde{\mathbf{H}}\left(\mathbf{R}_{p}\right) e^{-i \mathbf{k} \cdot \mathbf{R}_{p}}, \tag{2.15}
\end{equation*}
$$

where the matrix elements in right side of the equality are

$$
\begin{equation*}
\tilde{\mathbf{H}}_{\beta, \alpha}\left(\mathbf{R}_{n}, \mathbf{R}_{m}\right)=\left|\phi_{\beta}\left(\mathbf{r}-\mathbf{R}_{n}\right)\right\rangle \hat{H}\left|\phi_{\alpha}\left(\mathbf{r}-\mathbf{R}_{m}\right)\right\rangle . \tag{2.15}
\end{equation*}
$$

Assuming only nearest neighbor interactions and that $\mathbf{S}(\mathbf{k})$, the Hamiltonian matrix of a two-dimensional hexagonal crystal of carbon atoms is given by a block diagonal matrix

$$
H_{3 D}=\left[\begin{array}{ll}
A_{2 \times 2} & B_{2 \times 2}  \tag{2.15}\\
B_{2 \times 2}^{\dagger} & A_{2 \times 2}
\end{array}\right]
$$



FIG. 3: The energy dispersion relations for graphene are shown through the whole region of the Brillouin zone. The lower and the upper surfaces denote the valence $\pi$ and the conduction $\pi^{*}$ energy bands, respectively. The coordinates of high symmetry points are $\Gamma=(0,0), \mathrm{K}=(0,2 \pi / 3 a)$, and $\mathrm{M}=(2 \pi / \sqrt{3} a, 0)$. The energy values at the $\mathrm{K}, \mathrm{M}$, and $\Gamma$ points are $0, t$, and $3 t$, respectively (http://www.iue.tuwien. ac.at/phd/pourfath/node18.html).
with

$$
\begin{equation*}
A_{2 \times 2}=\operatorname{diag}\left(E_{s}, E_{p}, E_{p}, E_{p}\right), \tag{2.15}
\end{equation*}
$$

and
$B_{2 \times 2}=\left[\begin{array}{cccc}V_{s s \sigma} g_{0} & V_{s p \sigma} g_{1} & V_{s p \sigma} g_{2} & 0 \\ V_{s p \sigma} g_{1} & V_{p p \sigma} g_{3}+V_{p p \pi} g_{4} & \left(V_{p p \sigma}+V_{p p \pi}\right) g_{5} & 0 \\ V_{s p \sigma} g_{2} & \left(V_{p p \sigma}+V_{p p \pi}\right) g_{5} & V_{p p \sigma} g_{3}+V_{p p \pi} g_{4} & 0 \\ 0 & 0 & 0 & V_{p p \pi} g_{0}\end{array}\right]$.
The phase factors in $B_{2 \times 2}$ are
$g_{0}=1+e^{-i \mathbf{k} \cdot \mathbf{R}_{B}}+e^{-i \mathbf{k} \cdot \mathbf{C}} \quad g_{1}=1-\frac{1}{2} e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}-\frac{1}{2} e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}$
$g_{2}=\frac{\sqrt{3}}{2}\left(e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}-e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}\right) \quad g_{3}=1+\frac{1}{4} e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}+\frac{1}{4} e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}$
$g_{4}=\frac{3}{4}\left(e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}-e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}\right) \quad g_{5}=\frac{\sqrt{3}}{4}\left(e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}-e^{-i \mathbf{k} \cdot \mathbf{R}_{C}}\right)$.

Conduction in the plane is limited entirely to $\pi$ bonding, so the graphene band structure of graphene is limited to a subset of the matrix given in Equation 2

$$
H_{2 D}=\left[\begin{array}{cc}
E_{p} & V_{p p \pi} g_{0}  \tag{2.13}\\
V_{p p \pi} g_{0}^{*} & E_{p}
\end{array}\right] .
$$

## 3. BAND CALCULATIONS

Look up a real energy band diagram for your material. Include a copy in your report.

An accepted electronic band energy diagram is shown in Figure 3.

Write a matlab program to plot the freeelectron band structure for your material


FIG. 4: Free-electron band structure for graphene.
along the same directions as used in the energy band you found in the literature. Indicate the degeneracies of the different bands. Where is the Fermi level located? How does the free electron band structure compare to the real band structure?

Our calculated free-electron band structure for graphene is included in Figure 4. In this model, we assume that the electron experiences no potential energy, and therefore has energies described by

$$
\begin{equation*}
E(k)=\frac{\hbar^{2} \mathbf{k}^{2}}{2 m} \tag{3.0}
\end{equation*}
$$

This is applied in the reduced-zone scheme, where the evaluation to reciprocal lattice vectors $\mathbf{K}$ in the first Brillouin zone. Subsequently, the energies are evaluated at K for

$$
\begin{equation*}
E(k)=\frac{\hbar^{2}}{2 m}\left(\mathbf{k}^{\prime}+\mathbf{K}\right)^{2} \tag{3.0}
\end{equation*}
$$

where $\mathbf{k}^{\prime}$ is restricted to the symmetries of the first Brillouin zone.
For the free electron model of graphene using the six nearest neighbors in reciprocal space, there are six degeneracies at the $K$ point, two double degeneracies and one triple degeneracy at both the $\Gamma$ and $M$ points. We see two degenerate pairs along $K$ to Gamma, one along $\Gamma$ to $M$ and three along $M$ to $K$. For this model, the Fermi energy is found exactly where the conduction and valence bands touch at the $K$ point. It is clear when comparing this band structure to those found in the literature that the free electron model is not a good approximation for electron transport in graphene. We see several band degeneracies that do not match the actual band structure and the general shapes are very different.

Algebraically diagonalize the Hamiltonian matrix at the $\Gamma$ point. What are the different energies and eigenvectors, and what do


FIG. 5: Energy dispersion relations for graphene.
they correspond to physically? Using Harrisons Solid State Table (attached) find numerical values for $E_{s a}, E_{s c}, E_{p a}, E_{p c}, E_{s s}$, $E_{s p}, E_{x x}$, and $E_{x y}$. Compare your calculated energies at the $\Gamma$ point with values from the literature.

Our calculated total density of states for the conduction and valence bands is included in Figure 5. Denoting $t=E_{p p \pi}$ as the tight-binding energy from the valence orbitals, the band structure depicted in Figures 5 and 6 is given analytically by
$E_{2 D}^{ \pm}= \pm t \sqrt{1+4 \cos \left(\frac{\sqrt{3} k_{x} a}{2}\right) \cos \left(\frac{k_{y} a}{2}\right)+4 \cos ^{2}\left(\frac{k_{y} a}{2}\right)}$
after diagonalizing Equation 2. Dresselhaus cites $t=$ -3.033 eV , differing from optimized value of $t=-8.1 \mathrm{eV}$ (see Matlab code)[1].

Write a Matlab program to plot the LCAO energy bands along the same directions as above, along with the approximate location of


FIG. 6: Graphene energy dispersion from $\pi$-bonding.
the Fermi level. How do your results compare (qualitatively) with the band structure you found in the literature? If you wish, optimize the matrix elements for your material.

The LCAO energy dispersion is shown in Figure 6. Because this figure is based on a known analytic solution, the results compare almost exactly in qualitative features to the known literature [3].

Where are the valence band maximum and the conduction band minimum located? What is the energy gap? Is your material direct or indirect?

The valence band maximum and the conduction band minimum are degenerate at the $K$-point, yielding a zero energy band gap. Because the points are coincident in the plane, the material is direct. Notably, because the energy dispersion around the $K$ point is linear, corresponding to dispersion relation of a relativistic Dirac fermion [3].

## 4. EFFECTIVE MASSES, CONSTANT ENERGY SURFACES, AND DENSITY OF STATES

Plot constant energy contours near the valence and conduction band edges for appropriate planes. For example, if your minimum is at $k_{\text {min }}$ along $\Gamma-X$, you should probably plot an energy contour for the $k_{x}-k_{y}$ plane, and for the plane parallel to $k_{y}-k_{z}$ that contains $k_{\text {min }}$.

A close up of the conduction and valence band edges and a contour plot is shown in Figures 7 and 8, respectively.

Solve for the energy at a number of $k$ points near the valence and conduction band


FIG. 7: Valence and conduction band edges for graphene.


FIG. 8: Energy contours for graphene.
edges. Fit these points using a quadratic polynomial (be sure to think about your results from D1 when you do this). Use your results to find the effective masses for both the valence bands and the conduction band. How do your results compare with results from the literature? How would you improve your results?

The energy surface near the conduction band edges form cones that touch each other precisely at the K points as shown in Figure 6, making graphene effectively a zerobandgap material. This differs greatly from the form of cubic semiconductors, which have band edges that can be approximated by parabaloids. Since the band structure is resultant from a $2 \times 2$ Hamiltonian, its scale is completely determined by the energy offset (which we set to zero) and a scaling factor $\eta_{p p \pi}$. The results are as close as they possibly can be for our near-neighbor approximation, as we initially scaled our band structure along its high-symmetry points to that of the literature. Given the linear shape of the dispersion relation around the band edges, an electron in graphene for our approximation has


FIG. 9: Electronic density of states for graphene.
an effective mass of zero everywhere around the band edge except exactly where the bands meet, where it has an infinite effective mass.

Plot the total density of states (histogram method, include all bands) versus energy. Use your calculated effective masses to determine an approximate expression for the density of states near the valence and conduction band edges. How does this calculation compare with the total D.O.S.?

Our calculated total density of states for the conduction and valence bands is included in Figure 9. As shown, our generated density of states defies simple expression, as unlike a cubic system we cannot represent the density of states as a straightforward $\sqrt{E}$ relation. As shown in Figure 9, our calculated DOS matches the shape of experimental data for the conduction band well.

Using your total D.O.S., calculate the electronic specific heat of your material as a function of temperature. Compare this with your calculations for the phonons, and comment.

Our calculated total density of states for the conduction and valence bands is included in Figure 8. Our electronic specific heat of graphene is largely linear, matching well with the literature. However, the electronic specific is significantly smaller than its phonon counterpart. Accordingly, the specific heat is completely dominated by the phonon specific heat by two orders of magnitude [2].

Our calculated total density of states for the conduction and valence bands is included in Figure 10.


FIG. 10: Electronic heat capacity for graphene.

Use the band structure you found in the literature to discuss the characteristics of your material. What electronic/optical applications would your material be good/bad for? Why?

Because the expression of the $\pi$ band in graphene is exact, our band structure calculation is exactly similar to the those found in the literature. Figure 6 shows the upper $\pi^{*}$-energy anti-bonding and lower $\pi$-energy bonding bands that are degenerate at the $K$-point; the two electrons in the $\pi$ band are fully occupy the lower $\pi$ band. From the degeneracy at the $K$-point, the density of states at the Fermi level is zero, making graphene a zero band gap semiconductor [3]. The planar $\pi$-bonding bestows graphene with extremely high room temperature electron mobility, allowing a conductivity greater than silver. The linear shape of the energy dispersion formed the basis of frequency multiplier chip produced by MIT [3].
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# Part IV: Electronic Band Structure of Graphene Continued 

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## 1. A. OPTICAL PROPERTIES

Utilizing the (optimized) LCAO bandstructure from Part III, use the lowest energy direct bandgap (from valence band to conduction band) to estimate the momentum matrix element.

The band structure around graphene's bandedge (the $K$ point) is a pair of intersecting cones. As such, the double gradient of the band structure in that region is discontinuous, yielding an effective mass $m^{*}$ of zero at the $K$ point and infinity in the immediate vicinity. Looking at the momentum matrix element calculation outlined in Lecture 27:

$$
\begin{equation*}
\frac{1}{m^{*}}=\frac{1}{m}+\frac{2}{m^{2}} \frac{\left|p_{c v}\right|^{2}}{E_{g}} \tag{1.1}
\end{equation*}
$$

we see that $\frac{1}{m^{*}}=\frac{1}{E_{g}}=\infty$ at the $K$ point, which gives us intuition that something special is happening at that location. If we think about the band structure, we realize that the matrix element must be zero at the $K$ point, since the valence and conduction bands are degenerate there-there is no gap across which to absorb a photon. However, if we move away from the $K$ point and no longer have a linear dispersion relation, $E_{g}$ becomes nonzero as does $\left|p_{c v}\right|$, but the effective mass becomes zero. Clearly this equation, which was formulated for zinc-blende crystals cannot help us with determining the momentum matrix element aside from suggesting. Since 1.1 is not directly useful in analytically finding $\left|p_{c v}\right|$ for our conic bandstructure approximation, we instead turned to the literature.

Within the literature [1] [2], the momentum matrix elements are derived explicitly, by the dot product of a photon polarization vector $\mathbf{P}$ and the dipole vector $\mathbf{D}$ where

$$
\begin{equation*}
\mathbf{D} \equiv<\Psi_{f}|\nabla| \Psi_{i}> \tag{1.2}
\end{equation*}
$$

and

$$
\begin{equation*}
\left|p_{c v}\right|=\mathbf{P} \cdot \mathbf{D}=\mathbf{P} \cdot\left\langle\Psi_{f}\right| \nabla \mid \Psi_{i}> \tag{1.3}
\end{equation*}
$$

[^3]this formulation is then broken down into its Bloch constituents and further simplified. Orienting the sheet of graphene in the x-y plane, it is pointed out that for two lattice atoms $R_{j 1}$ and $R_{j 2}$
\[

$$
\begin{equation*}
<\phi\left(\mathbf{r}-\mathbf{R}_{\mathbf{j} \mathbf{1}}\right)\left|\frac{\partial}{\partial z}\right| \phi\left(\mathbf{r}-\mathbf{R}_{\mathbf{j} \mathbf{2}}\right)>=0 \tag{1.4}
\end{equation*}
$$

\]

since the integrand is an odd function of $z$. Thus we can restrict the atomic dipole vector to the $x-y$ plane, ie $\mathbf{D}=\left(d_{x}, d_{y}, 0\right)$. The matrix element $\mathbf{P} \cdot \mathbf{D}$ is further simplified using a Taylor expansion around the $K$ point ( $k_{x 0}, k_{y 0}$ ) until the arrival of the result

$$
\begin{equation*}
\left|p_{c v}\right|=\mathbf{P} \cdot \mathbf{D}=\frac{3 M}{2 k}\left(p_{y}\left(k_{x}-k_{x 0}\right)-p_{x}\left(k_{y}-k_{y 0}\right)\right) \tag{1.5}
\end{equation*}
$$

where M is the optical matrix element for two nearestneighbor atoms separated by $\mathbf{b}_{\mathbf{1}}$

$$
\begin{equation*}
M=<\phi\left(\mathbf{R}+\mathbf{b}_{\mathbf{1}}\right)\left|\frac{\partial}{\partial x}\right| \phi(\mathbf{R})> \tag{1.6}
\end{equation*}
$$

The above can be numerically evaluated for a tightbinding model including 2 s and 2 p orbitals, giving a value of $M=0.206 \quad[1]$

Utilize the optimized LCAO bandstructure and momentum matrix element from $A 1$ to estimate the optical absorption. Plot the absorption coefficient for your material from the direct bandedge to 5 kBT above the bandedge.

Using the absorption coefficient formula derived in Lecture 27, we arrive at

$$
\begin{equation*}
\alpha(\omega)=\left.\frac{\pi q^{2} c \mu_{0}}{m_{0}^{2} \omega n}\left|\frac{3 M}{2 k}\right|^{2}\left(p_{y} \Delta k_{x}-p_{x} \Delta k_{y}\right)\right|^{2} p_{r}\left(h \omega-E_{g}\right) \tag{1.7}
\end{equation*}
$$

where $p_{r}\left(h \omega-E_{g}\right)$ is the reduced density of states we calculated in Part II.

As shown in Figure 1, the absorption is zero directly at the $K$ points (as our intuition suggested) and grows as $k$ moves away in most directions. Notice the line of zero absorption, however, for $k$ directions associated with $\left(p_{y} \Delta k_{x}-p_{x} \Delta k_{y}\right)=0$.

Compare your estimate for the interband absorption coefficient with literature values. What are the major sources of discrepancy between your theory and experiment?


FIG. 1: Absorption spectrum for graphene for polarization P $=(0,1)$ [1]. Darker areas correspond to stronger absorption

Considering that our method of derivation was almost identical to that of the literature, it matches *very* well. In many of the articles we reviewed, we found that the optical absorption was solely shaped by a density of states, scaled by constants that appeared to be of approximately the same form as those in Equation 1.7

## 2. B. ELECTRON-PHONON SCATTERING

Utilize the LCAO bandstructure from Part III to estimate the deformation potential for electrons near the conduction bandedge and holes at the valence bandedge. Compare the estimated deformation potentials with the literature values for the longitudinal acoustic deformation potential.

We can calculate the deformation potential directly from the bandstructure since we have it in analytic form from Part III, as
$E_{2 D}^{ \pm}= \pm t \sqrt{1+4 \cos \left(\frac{\sqrt{3} k_{x} a}{2}\right) \cos \left(\frac{k_{y} a}{2}\right)+4 \cos ^{2}\left(\frac{k_{y} a}{2}\right)}$
where $t=8.1 \mathrm{eV}, a=1.42 \AA$, and $A=a^{2}$. At the bandedge point $K, k_{x}=\frac{2 \pi}{\sqrt{3} a}$ and $k_{y}=\frac{2 \pi}{3 a}$ To perform the calculation we took a small increment and divide it by the change in atomic areal lattice spacing.

$$
\begin{align*}
D_{A} & =\left.\frac{\partial E_{n}(K)}{\partial A}\right|_{e q} A=\left.\frac{\partial E_{n}(K)}{\partial a}\right|_{e q} \cdot \frac{a}{2}  \tag{2.2}\\
& \approx \frac{E(a+d a)-E(a)}{d a} \cdot \frac{a}{2}=\frac{1}{2} \frac{a}{d a} \Delta E  \tag{2.3}\\
& =14.15 \mathrm{eV} \tag{2.4}
\end{align*}
$$

the resulting calculation is in very good accordance with experimental values from graphene devices grown on $\mathrm{SiO} 2, D_{A}(e m p)=18 \pm 1 \mathrm{eV} \quad[3]$.

Utilize the phonon dispersion from Part II to estimate the phonon occupancy for all modes within the Brillouin zone. Assume a lattice temperature of 300 K .

Considering the lattice temperature is so high, we can approximate the phonon occupancy function in the Boltzmann limit, ie

$$
\begin{equation*}
N(w)=\frac{k_{B} T}{\hbar w} \tag{2.5}
\end{equation*}
$$

Using the LCAO density-of-states and the results from B1 and B2, estimate the longitudinal acoustic phonon scattering for your material. Compare your result with literature values.

Beginning with Eq (2.76) from Lundstrom, modified for 2D (after doing the integral present in Eq (2.75) the only difference is the removal of a factor of $\beta$ )

$$
\begin{equation*}
\frac{1}{\tau}=\frac{\Omega}{4 \pi^{2}} \int_{\beta_{\min }}^{\beta_{\max }}\left(N_{\beta}+\frac{1}{2} \mp \frac{1}{2}\right) C_{\beta} \beta d \beta \tag{2.6}
\end{equation*}
$$

and since we're calculating the acoustic deformation potential

$$
\begin{equation*}
C_{\beta}=\frac{\pi m^{*} D_{A}^{2}}{\hbar \rho v_{s}} p \Omega \tag{2.7}
\end{equation*}
$$

we're operating in the Boltzmann limit as well so

$$
\begin{gather*}
\frac{1}{\tau}=\frac{\Omega}{4 \pi^{2}} \int_{\beta_{\min }}^{\beta_{\max }} N_{\omega_{s}} C_{\beta} \beta d \beta  \tag{2.8}\\
N_{\omega_{s}}=\frac{k_{B} T_{L}}{\hbar \omega_{s}}=\frac{k_{B} T_{L}}{\hbar \beta v_{s}} \tag{2.9}
\end{gather*}
$$

we find that

$$
\begin{align*}
\frac{1}{\tau} & =\frac{m^{*} D_{A}^{2} k_{B} T_{L}}{4 \pi \hbar^{2} c_{l} p} \int_{\beta_{\min }}^{\beta_{\max }} d \beta  \tag{2.10}\\
& =\frac{m^{*} D_{A}^{2} k_{B} T_{L}}{4 \pi \hbar^{2} c_{l} p} \frac{2 p}{\hbar}  \tag{2.11}\\
& =\frac{D_{A}^{2} k_{B} T_{L}}{2 \hbar c_{l}} \frac{m^{*}}{\pi \hbar^{2}}  \tag{2.12}\\
& =\frac{D_{A}^{2} k_{B} T_{L}}{2 \hbar c_{l}} g_{2 D}(E) \tag{2.13}
\end{align*}
$$

We can calculate $c_{l}$ using $\rho=6.5 \cdot 10^{-7}$ and using the longitudinal sound velocity $v_{s}=13.12 \mathrm{~km} / \mathrm{s}$ from Part III of the project, and $T_{L}$ is 300 K . The first part of the


FIG. 2: Density of states histogram calculated in Part III
final equation form yields a constant factor to proportion $g_{2 D}(E)$, which is the density of states calculated via histogram method in Part III and shown in Figure 2.

$$
\begin{equation*}
c_{l}=v_{s}^{2} * \rho=8.51 \cdot 10^{-3} \mathrm{~kg} / \mathrm{s} \tag{2.14}
\end{equation*}
$$

Within the relaxation time approximation in the Boltzmann limit, estimate the heavyhole mobility. Compare your result with literature values. What are the major sources of discrepancy between your theory and experiment?

The verdict is still out on the methodology to determine the mobility of graphene. Measured values of graphene mobility show that it has extremely high mobilities, theoretically infinite at the Dirac points, but that these values are limited by acoustic phonon scattering [3]. Graphene has been experimentally shown to have hole mobilities commonly in the range of 3400-4400 $V / \mathrm{cm}^{2} s$ [4] and as high as $15,000 \mathrm{~V} / \mathrm{cm}^{2} s$ [5]. Current research suggests that graphene mobility is limited by the density of charged impurities within the lattice, and so the key to increasing mobility for use in higher-frequency electronics is to reduce the number of impurities when building graphene components. [6]
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