Gallium Arsenide: Calculation of Band Structure

PHY 626

A report by

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1   Introduction

The electronic structure of gallium arsenide has been considered, using the tight-binding approach in which only the nearest neighbor interactions are included. The energies of the Bloch functions have been calculated along the paths Λ and Δ in terms of the wave vector $\mathbf{k}$. This is used to generate the band structure and determine the band gap of the binary semi-conductor GaAs.

The zincblende structure and the use of hybrid orbitals (instead of atomic orbitals) is discussed in Section 2. Then, in Section 3 the construction of tight-binding hamiltonian is done for GaAs taking analogy from that of Si. The Section 4 elaborates the programming implemented for the required calculations and finally the results are discussed in Section 5.

2   The zincblende structure and the equivalent orbitals approach

The diamond cubic structure can be seen as fcc with two atoms at each lattice point. It can also be described as two inter-penetrating fcc lattices with one of them shifted in the direction of body diagonal by a distance of a/4, where $\mathbf{a}$ is the size of a single cube in the diamond structure. A cube of such structure is depicted in Fig. 1a and the unit cell is indicated by the dotted lines. There are two atoms in the basis in each unit cell; when these 2 atoms are different, the resulting arrangement is the zincblende crystal. In the present case, Ga (group III) and As (group V) are the 2 atoms.

Since there are four states associated with each atom, we have eight states in the unit cell. These are the set of s, p_x, p_y and p_z orbitals centred on each of the 2 atoms. This implies that the hamiltonian would be 8×8 sized. We can use these orbital states as our basis sets but it is more convenient to use equivalent or hybrid orbitals directed along the bond directions. The parameters appearing in this approach (referred to later in the next section also), are related to s-p interaction parameters of hamiltonian (H) matrix as shown below. As a result, each of the 8 states can be represented by the sp^3 hybridized orbitals directed along that particular bond.

$$
\begin{aligned}
V_1 &= \left\langle n \left| \hat{H} \right| m \right\rangle = \frac{E_s^0 - E_p^0}{4} \\
V_2 &= \left\langle n \left| \hat{H} \right| m \right\rangle = \frac{V_{ss\sigma} - 2\sqrt{3}V_{sp\sigma} - 3V_{pp\sigma}}{4}
\end{aligned}
\tag{1}
$$

In case of V_1, n and m are the hybrids on same atom; whereas for V_2, n and m are the nearest neighbor hybrids on different atom. It should also be noted that since all the discussed energy parameters are interaction energies, they are negative. V_1 and

V_2 are metallic and covalent energies for diamond structure and their significance has been established more clearly in the next section, and other terms have usual meanings.
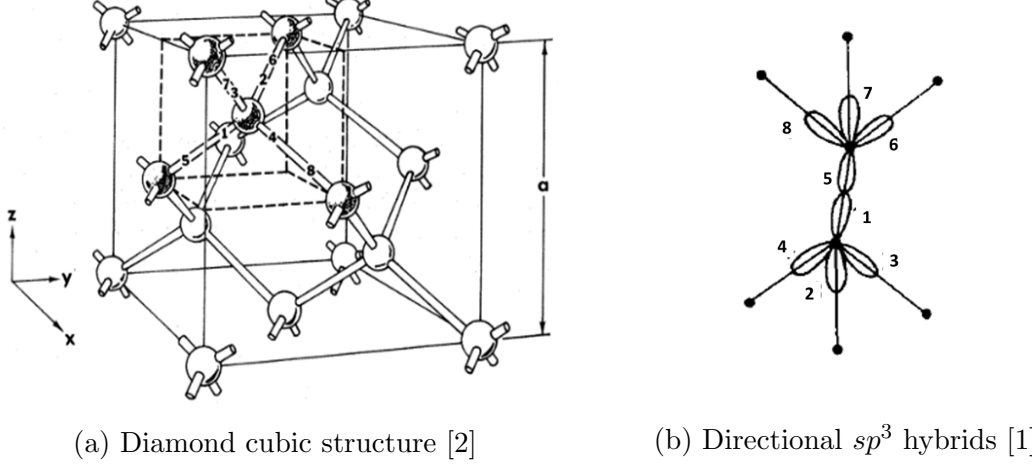

(a) Diamond cubic structure [2] (b) Directional sp^3 hybrids [1]

Figure 1: (a)A single cube of the diamond cubic structure and its unit cell shown by dotted lines and (b)Directed sp^3 hybrid orbitals between adjacent atoms

3 The Tight-Binding Hamiltonian

We take the similar formulation of hamiltonian as in case of Si (diamond structure)[2]. All the atoms are tetrahedrally coordinated, so we can consider sp^3 hybridized orbitals (LCAO of the s and p orbitals of Si atoms) for each atom of the structure. The difference from Si is that the two basis atoms are different - Ga and As. First, we look at simple Si type hamiltonian and then taking analogy from here, we will build the hamiltonian for GaAs.

The following calculations are for Si lattice [2]. The orthonormal hybrid orbitals are labelled by site index i and j for different basis atoms in unit cell as shown in Fig. 1a. It is important to note that throughout these calculations we use the nearest neighbor tight-binding model. Let ϕ_{ij} be the localized sp^3 hybridized orbitals, V_1 is interaction energy between hybrid orbitals of same atom(the **metallic energy**) and V_2 is interaction energy between hybrid orbitals of different atoms in the same unit cell, called the **covalent energy**. The interaction of a hybrid orbital with itself, on-site energy is taken as zero. Then the hamiltonian can be written as:

$$H = \sum_{i,j\neq j'} V_1 \left|\phi_{ij}\right\rangle \left\langle\phi_{ij'}\right| + \sum_{i\neq i',j} V_2 \left|\phi_{ij}\right\rangle \left\langle\phi_{i'j}\right| \tag{2}$$

If we take all atoms identical in Fig.2, then using Bloch theorem, due to translational symmetry, the basis states can be expressed as:

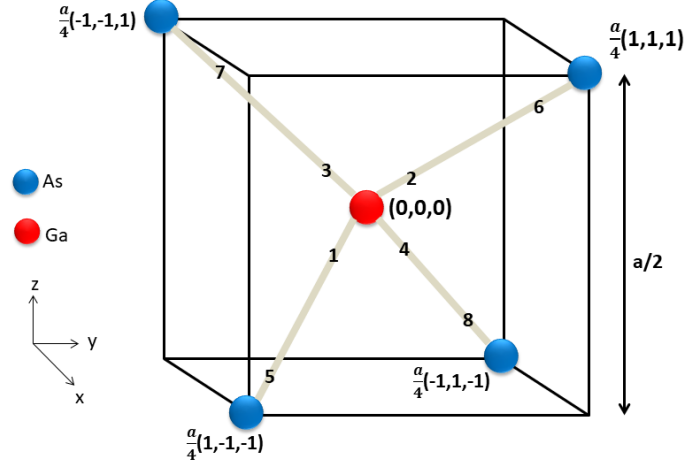$$|n\rangle_{\vec{k}} = \sqrt{\frac{2}{N}} \sum_{\vec{r_i}} e^{i\vec{k}.\vec{r_i}} |n\rangle \tag{3}$$

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Figure 2: Unit cell for GaAs with the notations used in generating the tight- binding hamiltonian.

where n goes from 0 to 8; $\vec{k}$ is the reciprocal lattice vector. The hamiltonian of eqn. 2, for Si, can be written as:

$$H_{\vec{k}} = \begin{pmatrix} 0 & V_1 & V_1 & V_1 & V_2 & 0 & 0 & 0 \\ V_1 & 0 & V_1 & V_1 & 0 & V_2 & 0 & 0 \\ V_1 & V_1 & 0 & V_1 & 0 & 0 & V_2 & 0 \\ V_1 & V_1 & V_1 & 0 & 0 & 0 & 0 & V_2 \\ V_2 & 0 & 0 & 0 & 0 & V_1\gamma_y\gamma_z & V_1\gamma_x^*\gamma_z & V_1\gamma_x^*\gamma_y \\ 0 & V_2 & 0 & 0 & V_1\gamma_y^*\gamma_z^* & 0 & V_1\gamma_x^*\gamma_y^* & V_1\gamma_x^*\gamma_z^* \\ 0 & 0 & V_2 & 0 & V_1\gamma_x\gamma_z^* & V_1\gamma_x\gamma_y & 0 & V_1\gamma_y\gamma_z^* \\ 0 & 0 & 0 & V_2 & V_1\gamma_x\gamma_y^* & V_1\gamma_x\gamma_z & V_1\gamma_y^*\gamma_z & 0 \end{pmatrix} \tag{4}$$

In calculating above hamiltonian we have used:

$$H_{ij} = V_1 e^{i\vec{k}.\vec{r_{ij}}} \tag{5}$$

where $\vec{r_{ij}} = \vec{r_j} - \vec{r_i}$, ; applicable when the interacting orbitals are present in the next unit cell (for 5≤i,j≤8). The $\vec{r_i}$s are as shown in fig. 2 for ith orbital. Also,

$$\gamma_x = exp(ik_x a/2), \ \gamma_y = exp(ik_y a/2), \ \gamma_z = exp(ik_z a/2)$$

Now, we shift to GaAs hamiltonian. The fig. 2 has been taken as the reference. The Ga atom is taken at the origin (1, 2, 3, 4) and As atoms as indicated coordinates in the figure (5, 6, 7, 8). Here, instead of V_1 we have different metallic energies for Ga and As atoms, which are V_{1+} and V_{1-} respectively. These have been replaced accordingly in eqn. 7. The covalent energy V_2 remains same in representation (not value). The **polar energy** V_3 defined by:

$$V_3 = \frac{E_{h+} - E_{h-}}{2} \tag{6}$$

where, E_{h+} and E_{h-} are on-site energies for cation (Ga) and anion (As) respectively.

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We have taken E_{h-} as 0, so $E_{h+} = 2V_3$. Again the required changes are made in eqn 7.

$$
H_{\vec{k}} = \begin{pmatrix}
2V_3 & V_{1+} & V_{1+} & V_{1+} & V_2 & 0 & 0 & 0 \\
V_{1+} & 2V_3 & V_{1+} & V_{1+} & 0 & V_2 & 0 & 0 \\
V_{1+} & V_{1+} & 2V_3 & V_{1+} & 0 & 0 & V_2 & 0 \\
V_{1+} & V_{1+} & V_{1+} & 2V_3 & 0 & 0 & 0 & V_2 \\
V_2 & 0 & 0 & 0 & 0 & V_{1-}\gamma_y\gamma_z & V_{1-}\gamma_x^*\gamma_z & V_{1-}\gamma_x^*\gamma_y \\
0 & V_2 & 0 & 0 & V_{1-}\gamma_y^*\gamma_z^* & 0 & V_{1-}\gamma_x^*\gamma_y^* & V_{1-}\gamma_x^*\gamma_z^* \\
0 & 0 & V_2 & 0 & V_{1-}\gamma_x\gamma_z^* & V_{1-}\gamma_x\gamma_y & 0 & V_{1-}\gamma_y\gamma_z^* \\
0 & 0 & 0 & V_2 & V_{1-}\gamma_x\gamma_y^* & V_{1-}\gamma_x\gamma_z & V_{1-}\gamma_y^*\gamma_z & 0
\end{pmatrix}
\tag{7}
$$

The eigen values at $\vec{k}$ have been calculated using Python3 along given paths, i.e, $L \xrightarrow{\Delta} \Gamma \xrightarrow{\Delta} X$. Here, L = $(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$; Γ = (0 , 0 , 0); X = $(\frac{2\pi}{a}, 0, 0)$. Also, since we have been given the value of distance between Ga and As atoms, d_{Ga-As}, so we need to convert it to a using $d_{Ga-As} = \frac{\sqrt{3}a}{4}$.

4   Programming

This section discusses the code developed(in Python3) for generation of GaAs band-structure in LCAO basis along with the density of states (DOS) and also serves as a manual for using this code. The code has been designed to evaluate the band-structure of any crystal with similar structure. The following steps were involved:

1. Take the coordinates of atoms in the unit cell.

2. Input the parameters (lattice parameter,covalent energy, polar energy, metallic energy) for the atoms (ions).

3. Define the k-point paths along which the band structure is to be calculated.

4. Define the tight-binding hamiltonian matrix for the system.

5. Find the eigenvalues of the hamiltonian matrix for each point along the k-point path and from this calculate the DOS.

4.1   Functions defined in the code

1. **kpath** : Takes in two coordinates (**ini** and **fin**) and generates a straight line joining the coordinates with **n** intermediate points.

2. **dot** : Takes as input, two vectors, and returns thier dot product.

3. **elements** : Takes as input, two numbers (**i** and **j**) and a vector (**k**) along the k-point path. Returns the H_{ij} element of the hamiltonian matrix **H**.

4. **Ham** : Takes in a vector(**k**) along the k-point path and returns an 8×8 Hamiltonian matrix by using the **elements** function.

5. **Neigen** : Takes in a list of eigenvalues(**l**), and two numbers (**a** and **b**). Returns the number of eigenvalues lying between **a** and **b**. This function is used for the calculation of DOS.

4.2   How to use the code...

The whole code is divided into 6 different files, each of which can be adjusted according to the requirement of the problem of concern.

1. **GaAs_parameter.py** : The parameters (lattice parameter, covalent energy, polar energy and metallic energy) for the crystal are to be set here.

2. **GaAs_dot.py and GaAs_kpath.py** : The definition for dot product and generation of k-paths are in these files.

3. **GaAs_Hamiltonian.py** : The hamiltonian for the system is generated using the **elements** and **ham** functions described above.

4. **GaAs_eigen_2.py** and **GaAs_DOS.py** : This includes solving the hamiltonian, plotting of the band structure and generate the DOS from the calculated band structure.

5   Results and Discussion

The following results were obtained from the hamiltonian described in eqn. 6.

1. **Band-gap** : We calculated the band structure using $a = 5.658\mathring{A}$, $V_{1+} = -1.47eV$, $V_{1-} = -2.48eV$, $V_2 = -4.09eV$ and $V_3 = -2.16eV$. From fig. 3a the band structure is calculated to be **1.12eV** with a direct band gap between bands 4(or 3, red band) and 5(violet band) at the Γ point.

2. **Degenerate flat bands** : From our calculations we obtained two flat bands (i.e. bands with very low dispersion) which are doubly degenerate . Now the the dispersion of bands occurs due to the interactions between the orbitals. Stronger interaction implies stronger dispersion and no dispersion implies no interaction at all. This can be clearly observed from our hamiltonian described in Eqn. 7 in which some of the elements are 0 i.e. we have neglected some weak interactions (like 1-6,3-6,4-6 etc interactions in fig. 2). Now as these interactions are assumed to be 0, there will not be any dispersion of the bands arising from them and thus we will get the flat bands.
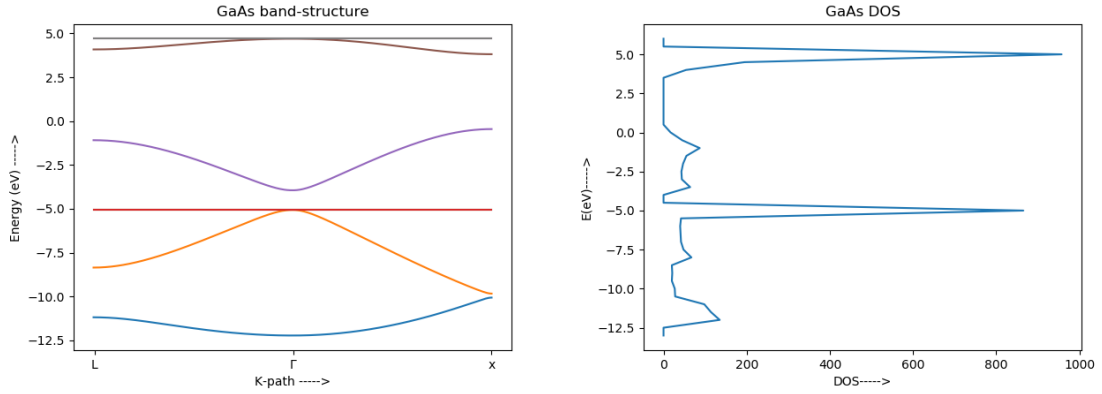
(a) GaAs band-structure along L-Γ-X

(b) DOS of GaAs based on the left figure

Figure 3: Band structure calculation for GaAs with the only interactions being $V_{1\pm}$, V_2 and V_3

References

[1] D. J. Chadi and M. L. Cohen. "Tight-Binding Calcultions of the Valence Bands of Diamond and Zincblende Crystals". In: *Phys. stat. sol. (b)* 68 (1975), pp. 405–419.

[2] D. Weaire and M. F. Thorpe. "Electronic Properties of an Amorphous Solid. I. A Simple Tight Binding Theory". In: *Phys. Rev. B,* 4 (1971), pp. 2508–2520.