

6.730

“Real” Semiconductor Project

GaAs

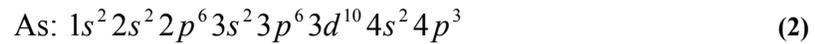
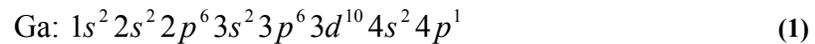
Part 3

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1. For our LCAO model we construct our trial wave function typically using only the outermost orbitals. In other words, in a system with  $b$  atoms in the basis and  $n$  outermost orbitals per atom, the total number of orbitals in the LCAO wave function is  $nb$ . How many atomic orbitals will you have for your material? Why?

Our material is gallium arsenide (GaAs). The electronic structures of atomic Ga (31 electrons) and As (33 electrons) are given as:



The valence, or outermost, electrons of Ga and As are the ones with principal quantum number  $n=4$ . In GaAs, the wave functions for these valence electrons are well described by the  $4s$  and  $4p$  wave functions of each atom, i.e., by the  $4s$ ,  $4p_x$ ,  $4p_y$ , and  $4p_z$  orbitals of Ga and As.

The basis of the GaAs crystal has 2 atoms (one Ga and one As). If the valence electrons are shared equally between the two, there are 4 outermost orbitals per atom, so the total number of orbitals in the LCAO wave function is  $2 \times 4 = 8$ . Thus, the Hamiltonian will be an  $8 \times 8$  matrix. Here, a linear combination of atomic orbitals has been assumed. We know from elsewhere that the tetrahedral structure of GaAs leads to  $sp^3$  hybridization. The  $sp^3$  hybrid orbitals can however be expressed as linear combinations of the atomic  $s$  and  $p$  orbitals. Therefore, the LCAO approximation used here is fairly good.

2. Conceivably, one could also construct the LCAO wave function out of core orbitals as well as valence orbitals. If you did so, how many atomic wave 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 bands? What if we used higher orbitals, too? How many orbitals per atom would we have to use to get an “exact” band structure? Why?

The atomic electronic structures of Ga and As were listed above in Eq. (1) and (2). From these equations, it is seen that Ga and As both have 14 core atomic orbitals. There are one  $1s$ ,  $2s$ , and  $3s$  orbitals each; there are three  $2p$  and  $3p$  orbitals each; and there are five  $3d$  orbitals for each atom. Combining the 28 total core orbitals with the 8 total valence orbitals gives 36 orbitals. Thus, 36 orbitals will be needed if both core and valence orbitals are included in the LCAO model for GaAs. The Hamiltonian matrix will correspondingly be  $36 \times 36$ .

Originally, when only the valence orbitals were included, only 8 bands were found. If all the core orbitals were also taken into account, then 36 bands would be calculated. These extra bands would lie below the previously calculated bands. Consequently, we would now have estimates for energies of lower lying bands. The original 8 bands would be only slightly affected by using a much larger Hamiltonian matrix. Since more basis functions are being used, we would expect that the calculated structure for the original 8 valence and conduction bands would improve, albeit only slightly, over the band structure determined when only the valence orbitals were used in the LCAO.

We can also include totally unoccupied orbitals. Since there are an infinite number of energy levels up to the 0 (free) energy, we could use an infinite number of unoccupied levels. Of course, adding unoccupied orbitals will increase the size of the Hamiltonian matrix and therefore increase the number of bands calculated. The extra bands would lie above the conduction bands calculated with valence orbital LCAO. These bands are almost completely empty at any moderate temperature, so they would not have a strong influence on the valence and conduction bands. However, they should improve the valence and conduction band calculations marginally because as more orbitals are added, the finite basis expansion more closely approximates a complete basis. To get an exact answer, we would have to have a complete basis, which requires that all the orbitals, an infinite number, be used (core, valence and unoccupied).

1. 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 atomic configurations of Ga and As as given in Eq. (1) and (2) are repeated below.

$$\text{Ga: } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$$

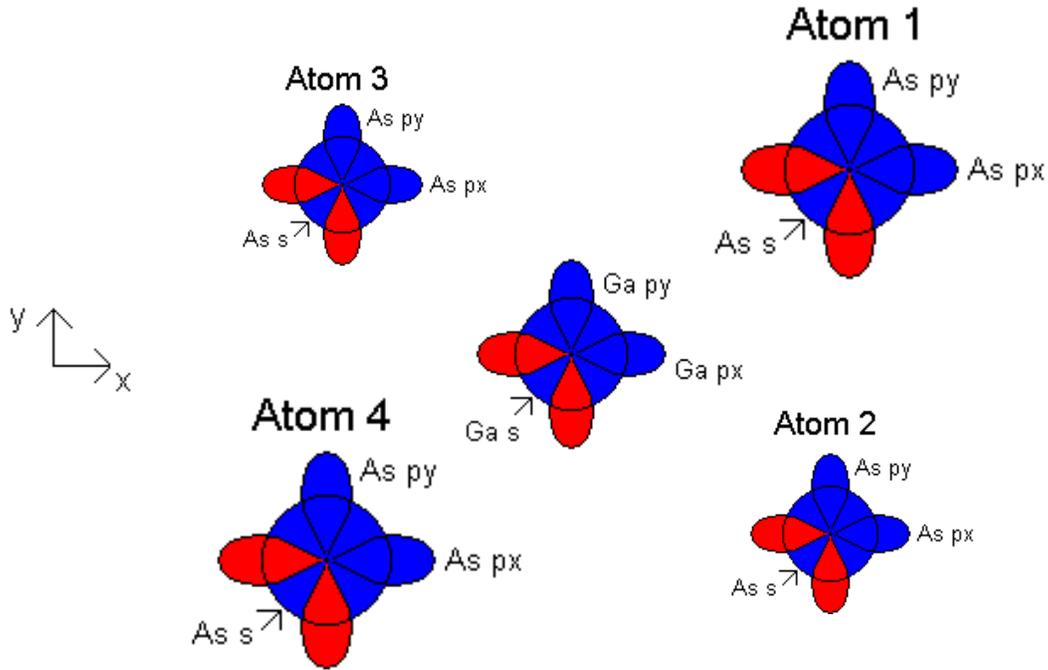
$$\text{As: } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$$

The orbitals that play a significant role in bonding are the outermost or valence orbitals. These are  $4s$ ,  $4p_x$ ,  $4p_y$ , and  $4p_z$  from both atoms in the basis (Ga and As).

2. 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). For example, the  $s$  orbital on the cation at lattice vector  $\mathbf{R}$ , basis vector  $\boldsymbol{\tau}$  would be labeled  $|\phi_{sc}(\mathbf{R} + \boldsymbol{\tau})\rangle$ .

The Ga atoms are anions and the As atoms are cations. The Ga atoms are arbitrarily chosen to be at the origin of the basis. Therefore, the basis Ga atoms are at basis vector  $(0,0,0)$  and cell vector  $\vec{R}$  and have orbitals  $|\phi_{s,Ga}(\vec{R})\rangle$ ,  $|\phi_{px,Ga}(\vec{R})\rangle$ ,  $|\phi_{py,Ga}(\vec{R})\rangle$ ,  $|\phi_{pz,Ga}(\vec{R})\rangle$ . The nearest neighbors of these Ga atoms are 4 As atoms. The Ga atom and its 4 neighboring atoms are shown in Fig. 1. Atom 1 is an As atom at  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ , with cell vector  $\vec{R}$ , and with orbitals  $|\phi_{s,As}(\vec{R})\rangle$ ,  $|\phi_{px,As}(\vec{R})\rangle$ ,  $|\phi_{py,As}(\vec{R})\rangle$ ,  $|\phi_{pz,As}(\vec{R})\rangle$ . Atom 2 is an As atom at  $\left(\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}\right)$ , with cell vector  $\vec{R} + \vec{R}_1$  (where  $\vec{R}_1 = -\frac{a}{2}(\hat{i}_y + \hat{i}_z)$ ), and with orbitals  $|\phi_{s,As}(\vec{R} + \vec{R}_1)\rangle$ ,  $|\phi_{px,As}(\vec{R} + \vec{R}_1)\rangle$ ,  $|\phi_{py,As}(\vec{R} + \vec{R}_1)\rangle$ ,  $|\phi_{pz,As}(\vec{R} + \vec{R}_1)\rangle$ . Atom 3 is an

As atom at  $\left(-\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}\right)$ , with cell vector  $\vec{R} + \vec{R}_2$  (where  $\vec{R}_2 = -\frac{a}{2}(\hat{i}_x + \hat{i}_z)$ ), and with orbitals  $|\phi_{s,As}(\vec{R} + \vec{R}_2)\rangle$ ,  $|\phi_{px,As}(\vec{R} + \vec{R}_2)\rangle$ ,  $|\phi_{py,As}(\vec{R} + \vec{R}_2)\rangle$ ,  $|\phi_{pz,As}(\vec{R} + \vec{R}_2)\rangle$ . Atom 4 is an As atom at  $\left(-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}\right)$ , with cell vector  $\vec{R} + \vec{R}_3$  (where  $\vec{R}_3 = -\frac{a}{2}(\hat{i}_x + \hat{i}_y)$ ), and with orbitals  $|\phi_{s,As}(\vec{R} + \vec{R}_3)\rangle$ ,  $|\phi_{px,As}(\vec{R} + \vec{R}_3)\rangle$ ,  $|\phi_{py,As}(\vec{R} + \vec{R}_3)\rangle$ ,  $|\phi_{pz,As}(\vec{R} + \vec{R}_3)\rangle$ .

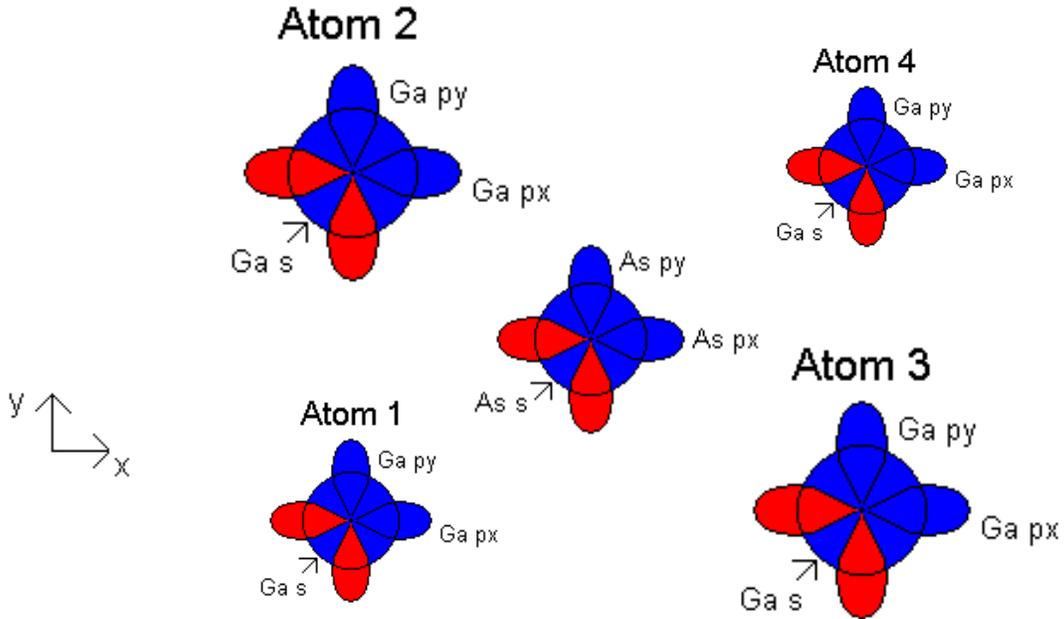


**Figure 1:** Basis Ga atom and four As nearest neighbors. Blue regions have a positive sign. Red regions have a negative sign.

To prevent Fig.1 from becoming too cluttered, the  $p_z$  orbitals are not shown. Displacements in the  $x$  and  $y$  directions are shown as a shift of the center and displacements in the  $z$  direction are shown as an increase (positive displacement) or decrease (negative displacement) in size. The origin is at the center of the Ga atom. The  $p_x$  and  $p_y$  orbitals have their positive lobes along the  $+x$  and  $+y$  directions.

The basis As atoms are then at basis vector  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  and cell vector  $\vec{R}$ , and have orbitals  $|\phi_{s,As}(\vec{R})\rangle$ ,  $|\phi_{px,As}(\vec{R})\rangle$ ,  $|\phi_{py,As}(\vec{R})\rangle$ ,  $|\phi_{pz,As}(\vec{R})\rangle$ . The nearest neighbors of these As atoms are 4 Ga atoms in a tetrahedral structure just as was the case with the Ga

atoms. The configuration is shown in Fig. 2. Atom 1 is at  $(0,0,0)$ , with cell vector  $\vec{R}$ , and with orbitals written above. Atom 2 is a Ga atom at  $\left(0, \frac{1}{2}, \frac{1}{2}\right)$ , with cell vector  $\vec{R} + \vec{R}_4$  (where  $\vec{R}_4 = \frac{a}{2}(\hat{i}_y + \hat{i}_z)$ ), and with orbitals  $|\phi_{s,Ga}(\vec{R} + \vec{R}_4)\rangle$ ,  $|\phi_{px,Ga}(\vec{R} + \vec{R}_4)\rangle$ ,  $|\phi_{py,Ga}(\vec{R} + \vec{R}_4)\rangle$ ,  $|\phi_{pz,Ga}(\vec{R} + \vec{R}_4)\rangle$ . Atom 3 is a Ga atom at  $\left(\frac{1}{2}, 0, \frac{1}{2}\right)$ , with cell vector  $\vec{R} + \vec{R}_5$  (where  $\vec{R}_5 = \frac{a}{2}(\hat{i}_x + \hat{i}_z)$ ), and with orbitals  $|\phi_{s,Ga}(\vec{R} + \vec{R}_5)\rangle$ ,  $|\phi_{px,Ga}(\vec{R} + \vec{R}_5)\rangle$ ,  $|\phi_{py,Ga}(\vec{R} + \vec{R}_5)\rangle$ ,  $|\phi_{pz,Ga}(\vec{R} + \vec{R}_5)\rangle$ . Atom 4 is a Ga atom at  $\left(\frac{1}{2}, \frac{1}{2}, 0\right)$ , with cell vector  $\vec{R} + \vec{R}_6$  (where  $\vec{R}_6 = \frac{a}{2}(\hat{i}_x + \hat{i}_y)$ ), and with orbitals  $|\phi_{s,Ga}(\vec{R} + \vec{R}_6)\rangle$ ,  $|\phi_{px,Ga}(\vec{R} + \vec{R}_6)\rangle$ ,  $|\phi_{py,Ga}(\vec{R} + \vec{R}_6)\rangle$ ,  $|\phi_{pz,Ga}(\vec{R} + \vec{R}_6)\rangle$ .



**Figure 2:** Basis As atom and four Ga nearest neighbors. Blue regions have a positive sign. Red regions have a negative sign.

Fig. 2 looks almost identical to Fig. 1, which is to be expected because the crystal is geometrically invariant with respect to switching Ga and As atoms. The center of the As atom is at  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ .

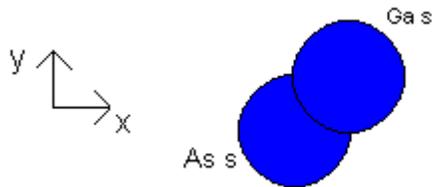
### 3. Show that one can approximate all the nearest neighbor interactions with one of the following...

There are three general types of interactions between the Ga and As atoms:

- A) interactions between 4s and 4s orbitals
- B) interactions between 4s and 4p orbitals, and
- C) interactions between 4p and 4p orbitals.

#### A) Interaction between 4s and 4s orbitals of different atoms

This interaction takes place between Ga at (0,0,0) and its 4 As nearest-neighbors, and between atom As at  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  and its 4 GA nearest neighbors. The distance between any nearest-neighbors is the same,  $\frac{\sqrt{3}}{4}a$ , and in each case, an s orbital of Ga interacts with an s orbital of As. The overlap with the Hamiltonian of the s states does not depend on the direction from As to Ga because the s states and the Hamiltonian are radially symmetric. The overlap of two s states is shown in Fig. 3



**Figure 3:** Overlap of Ga and As s states

In the following sections, the notations W and T are used for the 2 types of atoms, Ga and As. The notation W is used for Ga atoms (anions), and T for As atoms (cations).

$$E_{ss} = V_{ss\sigma} = \left\langle \phi_{s,W}(0,0,0) \left| \hat{H} \right| \phi_{s,T}\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right) \right\rangle = \left\langle \phi_{s,W}(\vec{R}) \left| \hat{H} \right| \phi_{s,T}(\vec{R}) \right\rangle \quad (3a)$$

$$= \left\langle \phi_{s,W}(\vec{R}) \left| \hat{H} \right| \phi_{s,T}(\vec{R} + \vec{R}_1) \right\rangle \quad (3b)$$

$$= \left\langle \phi_{s,W}(\vec{R}) \left| \hat{H} \right| \phi_{s,T}(\vec{R} + \vec{R}_2) \right\rangle \quad (3c)$$

$$= \left\langle \phi_{s,W}(\vec{R}) \left| \hat{H} \right| \phi_{s,T}(\vec{R} + \vec{R}_3) \right\rangle \quad (3d)$$

$$= \left\langle \phi_{s,T}(\vec{R}) \left| \hat{H} \right| \phi_{s,W}(\vec{R}) \right\rangle \quad (3e)$$

$$= \left\langle \phi_{s,T}(\vec{R}) \left| \hat{H} \right| \phi_{s,W}(\vec{R} + \vec{R}_5) \right\rangle \quad (3f)$$

$$= \left\langle \phi_{s,T}(\vec{R}) \left| \hat{H} \right| \phi_{s,W}(\vec{R} + \vec{R}_6) \right\rangle \quad (3g)$$

The phase factors are given as

$$g_0 = 1 + e^{-i\vec{k}\cdot\vec{R}_1} + e^{-i\vec{k}\cdot\vec{R}_2} + e^{-i\vec{k}\cdot\vec{R}_3} \quad (4)$$

and

$$1 + e^{-i\vec{k}\cdot\vec{R}_4} + e^{-i\vec{k}\cdot\vec{R}_5} + e^{-i\vec{k}\cdot\vec{R}_6} = g_0^* \quad (5)$$

because  $\vec{R}_4 = -\vec{R}_1$ ,  $\vec{R}_5 = -\vec{R}_2$ ,  $\vec{R}_6 = -\vec{R}_3$ .

Therefore, the terms in the Hamiltonian matrix will be

$E_{ss} g_0$  and  $E_{ss} g_0^*$ .

### B) Interaction between 4s and $4p_{x,y,z}$ orbitals of different atoms

This interaction, again, takes place between Ga at  $(0,0,0)$  and its 4 As nearest-neighbors,

and between As at  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  and its 4 Ga nearest neighbors. We analyze this interaction

in all the possible cases:

**Case B1:** Ga at  $(0,0,0)$  and its 4 As nearest-neighbors atoms at

$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right), \left(\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}\right), \left(-\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}\right), \left(-\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}\right)$ .  $\hat{d}$  vectors are from Ga to the As

atoms.

This is the situation shown in Fig. 1.

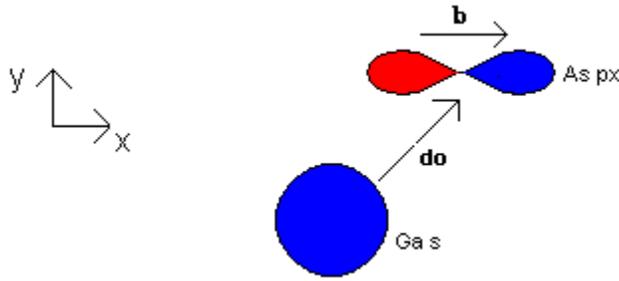
$$\hat{d}_0 = \left( \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right) \quad (6)$$

$$\hat{d}_1 = \left( \frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}} \right) \quad (7)$$

$$\hat{d}_2 = \left( -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}} \right) \quad (8)$$

$$\hat{d}_3 = \left( -\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right) \quad (9)$$

The relevant geometry for  $d_0$  is shown in Fig. 4



**Figure 4:** Interaction between Ga 4s and As 4p<sub>x</sub>

In the figure,  $\hat{b} = (1,0,0)$ . Calculating the individual inner products gives,

$$\frac{1}{\sqrt{3}} = \hat{d}_0 \cdot \hat{b} = \hat{d}_1 \cdot \hat{b} = -\hat{d}_2 \cdot \hat{b} = -\hat{d}_3 \cdot \hat{b} \quad (10)$$

$$\left\langle \phi_{s,W}(0) \left| \hat{H} \right| \phi_{px,T} \left( \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right) \right\rangle = \left\langle \phi_{s,W}(\vec{R}) \left| \hat{H} \right| \phi_{px,T}(\vec{R}) \right\rangle = \hat{d}_0 \cdot \hat{b} V_{sp\sigma} = \frac{1}{\sqrt{3}} V_{sp\sigma} = E_{sp} \quad (11)$$

with phase factor 1,

$$\left\langle \phi_{s,W}(\vec{R}) \left| \hat{H} \right| \phi_{px,T}(\vec{R} + \vec{R}_1) \right\rangle = \hat{d}_1 \cdot \hat{b} V_{sp\sigma} = \frac{1}{\sqrt{3}} V_{sp\sigma} = E_{sp} \quad (12)$$

with phase factor  $e^{-i\vec{k} \cdot \vec{R}_1}$ ,

$$\left\langle \phi_{s,W}(\vec{R}) \left| \hat{H} \right| \phi_{px,T}(\vec{R} + \vec{R}_2) \right\rangle = \hat{d}_2 \cdot \hat{b} V_{sp\sigma} = -\frac{1}{\sqrt{3}} V_{sp\sigma} = -E_{sp} \quad (13)$$

with phase factor  $e^{-i\vec{k} \cdot \vec{R}_2}$ , and

$$\langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{px,T}(\vec{R} + \vec{R}_3) \rangle = \hat{d}_3 \cdot \hat{b} V_{sp\sigma} = -\frac{1}{\sqrt{3}} V_{sp\sigma} = -E_{sp} \quad (14)$$

with phase factor  $e^{-i\vec{k} \cdot \vec{R}_3}$ .

Putting the above results together, the term in the Hamiltonian overlap matrix is:

$$E_{sp} (1 + e^{-i\vec{k} \cdot \vec{R}_1} - e^{-i\vec{k} \cdot \vec{R}_2} - e^{-i\vec{k} \cdot \vec{R}_3}) = E_{sp} g_1 \quad (15)$$

In calculating  $\langle \phi_{s,W} | \hat{H} | \phi_{py,T} \rangle$ , we must use  $\hat{b} = (0,1,0)$ . Then,

$$\frac{1}{\sqrt{3}} = \hat{d}_0 \cdot \hat{b} = -\hat{d}_1 \cdot \hat{b} = \hat{d}_2 \cdot \hat{b} = -\hat{d}_3 \cdot \hat{b} \quad (16)$$

and

$$\langle \phi_{s,W}(0) | \hat{H} | \phi_{py,T}(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \rangle = \langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{py,T}(\vec{R}) \rangle = \hat{d}_0 \cdot \hat{b} V_{sp\sigma} = \frac{1}{\sqrt{3}} V_{sp\sigma} = E_{sp} \quad (17)$$

$$\langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{py,T}(\vec{R} + \vec{R}_1) \rangle = \hat{d}_1 \cdot \hat{b} V_{sp\sigma} = -\frac{1}{\sqrt{3}} V_{sp\sigma} = -E_{sp} \quad (18)$$

$$\langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{py,T}(\vec{R} + \vec{R}_2) \rangle = \hat{d}_2 \cdot \hat{b} V_{sp\sigma} = \frac{1}{\sqrt{3}} V_{sp\sigma} = E_{sp} \quad (19)$$

$$\langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{py,T}(\vec{R} + \vec{R}_3) \rangle = \hat{d}_3 \cdot \hat{b} V_{sp\sigma} = -\frac{1}{\sqrt{3}} V_{sp\sigma} = -E_{sp} \quad (20)$$

Putting the above results together, the term in the overlap Hamiltonian matrix is:

$$E_{sp} (1 - e^{-i\vec{k} \cdot \vec{R}_1} + e^{-i\vec{k} \cdot \vec{R}_2} - e^{-i\vec{k} \cdot \vec{R}_3}) = E_{sp} g_2 \quad (21)$$

The calculation of the other matrix element,  $\langle \phi_{s,W} | \hat{H} | \phi_{pz,T} \rangle$ , proceeds in a similar fashion.

$\hat{b} = (0,0,1)$ ,  $\frac{1}{\sqrt{3}} = \hat{d}_0 \cdot \hat{b} = -\hat{d}_1 \cdot \hat{b} = -\hat{d}_2 \cdot \hat{b} = \hat{d}_3 \cdot \hat{b}$ , and

$$\langle \phi_{s,W}(0) | \hat{H} | \phi_{pz,T}(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \rangle = \langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{pz,T}(\vec{R}) \rangle = \hat{d}_0 \cdot \hat{b} V_{sp\sigma} = \frac{1}{\sqrt{3}} V_{sp\sigma} = E_{sp} \quad (22)$$

$$\langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{pz,T}(\vec{R} + \vec{R}_1) \rangle = \hat{d}_1 \cdot \hat{b} V_{sp\sigma} = -\frac{1}{\sqrt{3}} V_{sp\sigma} = -E_{sp} \quad (23)$$

$$\langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{pz,T}(\vec{R} + \vec{R}_2) \rangle = \hat{d}_2 \cdot \hat{b} V_{sp\sigma} = -\frac{1}{\sqrt{3}} V_{sp\sigma} = -E_{sp} \quad (24)$$

$$\langle \phi_{s,W}(\vec{R}) | \hat{H} | \phi_{pz,T}(\vec{R} + \vec{R}_3) \rangle = \hat{d}_3 \cdot \hat{b} V_{sp\sigma} = \frac{1}{\sqrt{3}} V_{sp\sigma} = E_{sp} \quad (25)$$

and the Hamiltonian overlap matrix term is

$$E_{sp} (1 - e^{-i\vec{k} \cdot \vec{R}_1} - e^{-i\vec{k} \cdot \vec{R}_2} + e^{-i\vec{k} \cdot \vec{R}_3}) = E_{sp} \mathbf{g}_3 \quad (26)$$

For  $\langle \phi_{px,y,z,W} | \hat{H} | \phi_{s,T} \rangle$ , the terms are equal to  $-\langle \phi_{s,W} | \hat{H} | \phi_{px,y,z,T} \rangle$  from above, and the Hamiltonian overlap matrix elements are  $-E_{sp} \mathbf{g}_1$ ,  $-E_{sp} \mathbf{g}_2$ , and  $-E_{sp} \mathbf{g}_3$  for  $p_x$ ,  $p_y$ ,  $p_z$ , respectively.

**Case B2:** As atom at  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  and its 4 nearest-neighbor Ga atoms at  $(0,0,0), \left(0, \frac{1}{2}, \frac{1}{2}\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(\frac{1}{2}, \frac{1}{2}, 0\right)$ .  $\hat{d}$  vectors are from As to the Ga atoms. This is the situation shown in Fig. 2.

$$\hat{d}_0' = \left(-\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}\right) = -\hat{d}_0 \quad (27)$$

$$\hat{d}_4 = \left(-\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right) = -\hat{d}_1 \quad (28)$$

$$\hat{d}_5 = \left(\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right) = -\hat{d}_2 \quad (29)$$

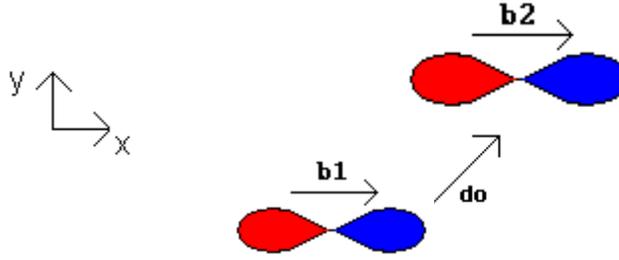
$$\hat{d}_6 = \left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}\right) = -\hat{d}_3 \quad (30)$$

Because  $\hat{d}_0' = -\hat{d}_0$ ,  $\hat{d}_4' = -\hat{d}_1$ ,  $\hat{d}_5' = -\hat{d}_2$ ,  $\hat{d}_6' = -\hat{d}_3$ , the values of all the  $s$ - $p_{x,y,z}$  combinations will be opposite in sign to their corresponding ones calculated above in Case B1. Also, because  $\vec{R}_4 = -\vec{R}_1$ ,  $\vec{R}_5 = -\vec{R}_2$ ,  $\vec{R}_6 = -\vec{R}_3$ , the terms  $\mathbf{g}_i$ 's will become  $\mathbf{g}_i^*$ . So, the terms in the Hamiltonian will be  $-E_{sp} \mathbf{g}_1^*$ ,  $-E_{sp} \mathbf{g}_2^*$ ,  $-E_{sp} \mathbf{g}_3^*$ ,  $E_{sp} \mathbf{g}_1^*$ ,  $E_{sp} \mathbf{g}_2^*$ ,  $E_{sp} \mathbf{g}_3^*$ .

### C) Interaction between $4p_{x,y,z}$ orbitals of different atoms.

**Case C1:** Interaction between a  $4p_x$  orbital of one atom and a  $4p_x$  orbital of its nearest neighbor.

For example, the case when there is a Ga atom at  $(0,0,0)$  and an As atom at  $\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  is shown in Fig. 5



**Figure 5:** Interaction of Ga  $p_x$  and As  $p_x$  orbitals

$\hat{d} = \left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)$ , and  $\hat{b}_1 = \hat{b}_2 = (1,0,0)$ . Thus,

$$\begin{aligned}
 \langle \phi_{px,W}(\vec{R}) | \hat{H} | \phi_{px,T}(\vec{R}) \rangle &= (\hat{d} \cdot \hat{b}_1)(\hat{d} \cdot \hat{b}_2)V_{pp\sigma} + [\hat{b}_1 - \hat{d}(\hat{b}_1 \cdot \hat{d})][\hat{b}_2 - \hat{d}(\hat{b}_2 \cdot \hat{d})]V_{pp\pi} = \\
 &= \frac{1}{\sqrt{3}} \cdot \frac{1}{\sqrt{3}}V_{pp\sigma} + [(1,0,0) - \frac{1}{\sqrt{3}}\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)] \cdot [(1,0,0) - \frac{1}{\sqrt{3}}\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)]V_{pp\pi} = \\
 &= \frac{1}{3}V_{pp\sigma} + [(1,0,0) - \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)] \cdot [(1,0,0) - \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)]V_{pp\pi} = \tag{31} \\
 &= \frac{1}{3}V_{pp\sigma} + \left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3}\right)\left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3}\right)V_{pp\pi} = \frac{1}{3}V_{pp\sigma} + \left(\frac{4}{9} + \frac{1}{9} + \frac{1}{9}\right)V_{pp\pi} = \frac{1}{3}V_{pp\sigma} + \frac{6}{9}V_{pp\pi} = \\
 &= \frac{1}{3}V_{pp\sigma} + \frac{2}{3}V_{pp\pi} = E_{xx}
 \end{aligned}$$

The value will be the same for different atoms  $p_x$ - $p_x$ ,  $p_y$ - $p_y$  and  $p_z$ - $p_z$  interactions, because

the distance between any nearest-neighbors is the same,  $\frac{\sqrt{3}}{4}a$ , and the orbitals considered

in the interaction are parallel to each other, so basically all pairs of nearest-neighbors are

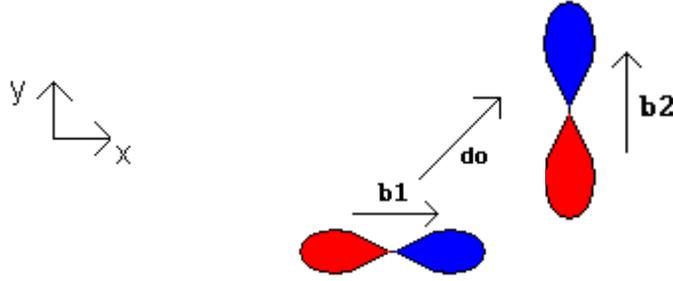
equivalent with respect to this type of interaction. The terms in the Hamiltonian will be

$$E_{xx}g_0 \text{ and } E_{xx}g_0^*.$$

**Case C2:**  $p$ - $p$  interactions not covered in Case C1.

For example, the case of a  $p_x$  orbital of Ga atom at  $(0,0,0)$  and  $p_y$  orbital of As at

$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$  is shown in Fig. 6.



**Figure 6:** Interaction of Ga  $p_x$  and As  $p_y$

$\hat{d} = \left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)$ , and  $\hat{b}_1 = (1,0,0)$  and  $\hat{b}_2 = (0,1,0)$ . Then

$$\begin{aligned} \langle \phi_{px,W}(\vec{R}) | \hat{H} | \phi_{py,T}(\vec{R}) \rangle &= (\hat{d} \cdot \hat{b}_1)(\hat{d} \cdot \hat{b}_2)V_{pp\sigma} + [\hat{b}_1 - \hat{d}(\hat{b}_1 \cdot \hat{d})][\hat{b}_2 - \hat{d}(\hat{b}_2 \cdot \hat{d})]V_{pp\pi} = \\ &= \frac{1}{\sqrt{3}} \cdot \frac{1}{\sqrt{3}}V_{pp\sigma} + [(1,0,0) - \frac{1}{\sqrt{3}}\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)] \cdot [(0,1,0) - \frac{1}{\sqrt{3}}\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)]V_{pp\pi} = \\ &= \frac{1}{3}V_{pp\sigma} + [(1,0,0) - \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)] \cdot [(0,1,0) - \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)]V_{pp\pi} = \\ &= \frac{1}{3}V_{pp\sigma} + \left(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3}\right) \cdot \left(-\frac{1}{3}, \frac{2}{3}, -\frac{1}{3}\right)V_{pp\pi} = \frac{1}{3}V_{pp\sigma} + \left(-\frac{2}{9} - \frac{2}{9} + \frac{1}{9}\right)V_{pp\pi} = \frac{1}{3}V_{pp\sigma} - \frac{3}{9}V_{pp\pi} = \\ &= \frac{1}{3}V_{pp\sigma} - \frac{1}{3}V_{pp\pi} = E_{xy} \end{aligned}$$

(32)

The value will be the same for different pairs because all pairs of nearest-neighbors are equivalent with respect to this type of interaction (the distance between any nearest-neighbors is the same, the perpendicular orbitals are along  $(1,0,0)$ ,  $(0,1,0)$  or  $(0,0,1)$ )

directions and the distance vector is always along or opposite the bisector of the solid angle generated by (1,0,0), (0,1,0) or (0,0,1), that is, of the form  $(\pm M, \pm M, \pm M)$ .

Various minus signs will appear when  $\langle \phi_{px,W}(\vec{R}) | \hat{H} | \phi_{py,z,T}(\vec{R} + \vec{R}_i) \rangle$  are considered

because  $\hat{d}_i = (\pm \frac{1}{\sqrt{3}}, \pm \frac{1}{\sqrt{3}}, \pm \frac{1}{\sqrt{3}})$ . In the end, it turns out that the Hamiltonian terms are

of the form  $E_{xy}g_1, E_{xy}g_2, E_{xy}g_3$  or  $E_{xy}g_1^*, E_{xy}g_2^*, E_{xy}g_3^*$ .

Thus, the values  $E_{ss}, E_{sp}, E_{xx}, E_{xy}$  describe all the nearest-neighbor interactions with the Hamiltonian.

**Comment on the validity of  $\langle \phi_{sc}(0) | \hat{H} | \phi_{pxa}(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}) \rangle = \langle \phi_{sa}(0) | \hat{H} | \phi_{pxc}(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}) \rangle$**

This equality is true because interchanging the origin of the lattice from a Ga atom to an As atom does not affect the calculations. Symmetry dictates that the interaction of an  $s$ -As orbital with a  $p_x$ -Ga orbital has the same value as the interaction of a  $p_x$ -As orbital with a  $s$ -Ga orbital.

**Can we write  $\langle \phi_{sc}(0) | \hat{H} | \phi_{sc}(0) \rangle = \langle \phi_{sa}(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}) | \hat{H} | \phi_{sa}(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}) \rangle$ ?**

No, this is not true, because the interaction of the  $s$  orbital in As with itself is different from the interaction of the  $s$ -Ga orbital with itself, because the Ga and As atoms are different (they have different number of protons).

#### 4. Write your trial wave function as a linear combination of atomic orbitals. Be explicit about your choice of phase factors.

Trial wave function

$$\begin{aligned} \psi(\vec{R}) = & a_1 \phi_{s,1}(\vec{R}) + b_1 \phi_{px,1}(\vec{R}) + c_1 \phi_{py,1}(\vec{R}) + d_1 \phi_{pz,1}(\vec{R}) + \\ & + a_2 \phi_{s,2}(\vec{R}) + b_2 \phi_{px,2}(\vec{R}) + c_2 \phi_{py,2}(\vec{R}) + d_2 \phi_{pz,2}(\vec{R}) + \end{aligned}$$

$$\begin{aligned}
& + a_{11}\phi_{s,2}(\vec{R} + \vec{R}_1) + b_{11}\phi_{px,2}(\vec{R} + \vec{R}_1) + c_{11}\phi_{py,2}(\vec{R} + \vec{R}_1) + d_{11}\phi_{pz,2}(\vec{R} + \vec{R}_1) + \\
& + a_{12}\phi_{s,2}(\vec{R} + \vec{R}_2) + b_{12}\phi_{px,2}(\vec{R} + \vec{R}_2) + c_{12}\phi_{py,2}(\vec{R} + \vec{R}_2) + d_{12}\phi_{pz,2}(\vec{R} + \vec{R}_2) + \\
& + a_{13}\phi_{s,2}(\vec{R} + \vec{R}_3) + b_{13}\phi_{px,2}(\vec{R} + \vec{R}_3) + c_{13}\phi_{py,2}(\vec{R} + \vec{R}_3) + d_{13}\phi_{pz,2}(\vec{R} + \vec{R}_3) + \\
& + a_{14}\phi_{s,1}(\vec{R} + \vec{R}_4) + b_{14}\phi_{px,1}(\vec{R} + \vec{R}_4) + c_{14}\phi_{py,1}(\vec{R} + \vec{R}_4) + d_{14}\phi_{pz,1}(\vec{R} + \vec{R}_4) + \quad (33) \\
& + a_{15}\phi_{s,1}(\vec{R} + \vec{R}_5) + b_{15}\phi_{px,1}(\vec{R} + \vec{R}_5) + c_{15}\phi_{py,1}(\vec{R} + \vec{R}_5) + d_{15}\phi_{pz,1}(\vec{R} + \vec{R}_5) + \\
& + a_{16}\phi_{s,1}(\vec{R} + \vec{R}_6) + b_{16}\phi_{px,1}(\vec{R} + \vec{R}_6) + c_{16}\phi_{py,1}(\vec{R} + \vec{R}_6) + d_{16}\phi_{pz,1}(\vec{R} + \vec{R}_6) .
\end{aligned}$$

5. Find the Hamiltonian matrix for the nearest neighbor approximation. Your answer should contain only  $E_{ss}$ ,  $E_{sp}$ ,  $E_{xx}$ ,  $E_{xy}$ , the s and p energies of the anion and cation and phase factors.

The elements in the Hamiltonian overlap matrix have already been calculated in part B.3 for each case of orbital interaction. Putting those results together, the Hamiltonian overlap matrix is:

	$ \phi_{s1}\rangle$	$ \phi_{px1}\rangle$	$ \phi_{py1}\rangle$	$ \phi_{pz1}\rangle$	$ \phi_{s2}\rangle$	$ \phi_{px2}\rangle$	$ \phi_{py2}\rangle$	$ \phi_{pz2}\rangle$
$ \phi_{s1}\rangle$	$E_{s1}$	0	0	0	$E_{ss}\mathcal{G}_0$	$E_{sp}\mathcal{G}_1$	$E_{sp}\mathcal{G}_2$	$E_{sp}\mathcal{G}_3$
$ \phi_{px1}\rangle$	0	$E_{p1}$	0	0	$-E_{sp}\mathcal{G}_1$	$E_{xx}\mathcal{G}_0$	$E_{xy}\mathcal{G}_3$	$E_{xy}\mathcal{G}_2$
$ \phi_{py1}\rangle$	0	0	$E_{p1}$	0	$-E_{sp}\mathcal{G}_2$	$E_{xy}\mathcal{G}_3$	$E_{xx}\mathcal{G}_0$	$E_{xy}\mathcal{G}_1$
$ \phi_{pz1}\rangle$	0	0	0	$E_{p1}$	$-E_{sp}\mathcal{G}_3$	$E_{xy}\mathcal{G}_2$	$E_{xy}\mathcal{G}_1$	$E_{xx}\mathcal{G}_0$
$ \phi_{s2}\rangle$	$E_{ss}\mathcal{G}_0^*$	$-E_{sp}\mathcal{G}_1^*$	$-E_{sp}\mathcal{G}_2^*$	$-E_{sp}\mathcal{G}_3^*$	$E_{s2}$	0	0	0
$ \phi_{px2}\rangle$	$E_{sp}\mathcal{G}_1^*$	$E_{xx}\mathcal{G}_0^*$	$E_{xy}\mathcal{G}_3^*$	$E_{xy}\mathcal{G}_2^*$	0	$E_{p2}$	0	0
$ \phi_{py2}\rangle$	$E_{sp}\mathcal{G}_2^*$	$E_{xy}\mathcal{G}_3^*$	$E_{xx}\mathcal{G}_0^*$	$E_{xy}\mathcal{G}_1^*$	0	0	$E_{p2}$	0
$ \phi_{pz2}\rangle$	$E_{sp}\mathcal{G}_3^*$	$E_{xy}\mathcal{G}_2^*$	$E_{xy}\mathcal{G}_1^*$	$E_{xx}\mathcal{G}_0^*$	0	0	0	$E_{p2}$

(34)

where  $E_{s1} = \langle \phi_{s,1}(\vec{R}) | \hat{H} | \phi_{s,1}(\vec{R}) \rangle$ ,  $E_{s2} = \langle \phi_{s,2}(\vec{R}) | \hat{H} | \phi_{s,2}(\vec{R}) \rangle$ ,

$$E_{p1} = \langle \phi_{px,1}(\vec{R}) | \hat{H} | \phi_{px,1}(\vec{R}) \rangle = \langle \phi_{py,1}(\vec{R}) | \hat{H} | \phi_{py,1}(\vec{R}) \rangle = \langle \phi_{pz,1}(\vec{R}) | \hat{H} | \phi_{pz,1}(\vec{R}) \rangle$$

and  $E_{p2} = \langle \phi_{px,2}(\vec{R}) | \hat{H} | \phi_{px,2}(\vec{R}) \rangle = \langle \phi_{py,2}(\vec{R}) | \hat{H} | \phi_{py,2}(\vec{R}) \rangle = \langle \phi_{pz,2}(\vec{R}) | \hat{H} | \phi_{pz,2}(\vec{R}) \rangle$ .

## 1. Look up a “real” energy band diagram for your material

The experimentally determined band diagram for GaAs is shown in: Blakemore, J.S. Semiconducting and other major properties of gallium arsenide. J. Appl. Phys. 53(10), Oct. 1982.

- ## 2. Write a Matlab program to plot the free-electron band structure for your material 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?

A substantial amount of information can be obtained about the Bloch electron assuming the electron experiences zero potential energy. In the free-electron model, we solve the Schrodinger’s Equation by setting the potential  $V(r)$  to be zero. The solution consists of plane waves with a continuous wave vector  $\mathbf{k}$  and energies given by Eq. (35). The relationship between  $E$  and  $\mathbf{k}$  is parabolic.

$$E(\vec{k}) = \frac{\hbar^2}{2m} \vec{k}^2 \quad (35)$$

The free-electron energy bands can be represented in the reduced zone scheme. The wave vector  $\mathbf{k}$  is reduced to the first Brillouin zone by a suitable choice of reciprocal lattice vector  $\mathbf{G}$ :

$$\vec{k} = \vec{k}' + \vec{G} \quad (36)$$

where  $G$  is defined by the linear superposition of primitive reciprocal lattice vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$  and  $\mathbf{b}_3$ :

$$\vec{G} = h\vec{b}_1 + q\vec{b}_2 + l\vec{b}_3 \quad (37)$$

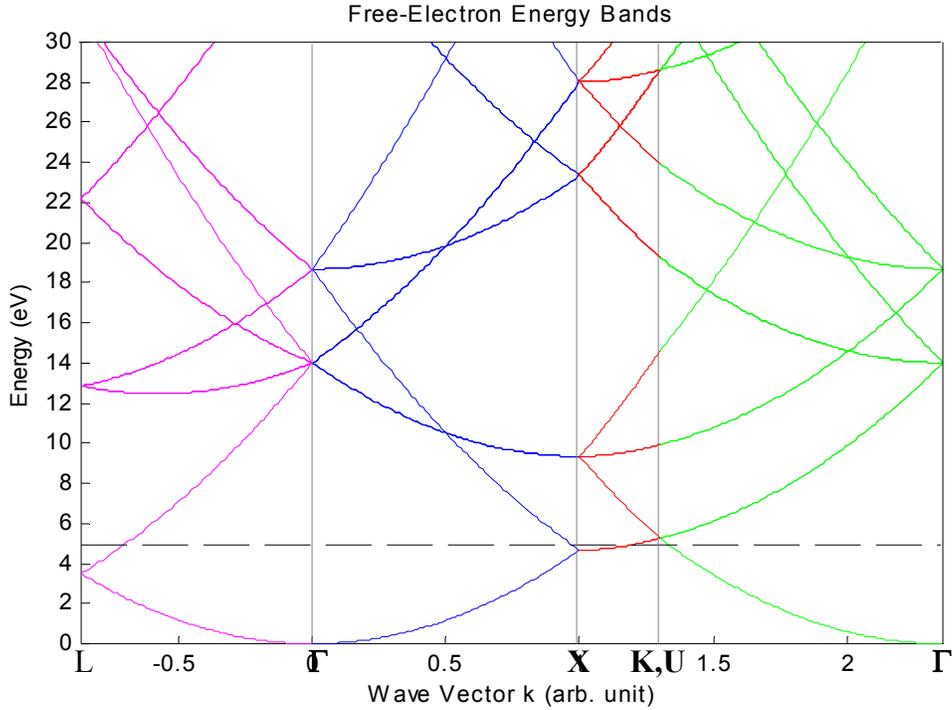
For a face-centered cubic lattice, it is much more convenient to rewrite  $\mathbf{G}$  in terms of the orthogonal unit vectors:

$$\vec{G} = \frac{2\pi}{a}[(-h + q + l)\hat{x} + (h - q + l)\hat{y} + (h + k - l)\hat{z}] \quad (38)$$

where  $a$  is the conventional lattice constant and is 5.65325Å for GaAs. We can now rewrite the energies in the reduced zone scheme notation:

$$E(\vec{k}) = \frac{\hbar^2}{2m}(\vec{k}' + \vec{G})^2 \quad (39)$$

where  $\mathbf{k}'$  is restricted within the first Brillouin zone. The corresponding energy band diagram for a face-centered cubic is shown in Fig. 8. The bands from L to  $\Gamma$  were plotted in pink,  $\Gamma$  to X in blue, X to (K ,U) in red, and K to  $\Gamma$  in green. Consider the  $\Gamma$  point with  $\mathbf{k}' = [0 \ 0 \ 0]$ . The lowest energy band is given by setting  $\mathbf{G}$  in Eq. (38) to zero ( $h=q=l=0$ ). The minimum of the point is  $E = 0$  which increases parabolically until it reaches the zone boundaries at the X-point on the right ( $E = \frac{\hbar^2}{2m}(\frac{2\pi}{a})^2$ ) and L-point on the left ( $E = \frac{\hbar^2}{2m}(\frac{\sqrt{3}\pi}{a})^2$ ). The next energy value at the  $\Gamma$ -point occurs by setting either one of  $h, q$  or  $l$  to be  $\pm 1$ . With the same idea, the complete energy bands were computed by increasing the indices  $h, q$  and  $l$  and evaluating  $E$  at the different symmetry points.



**Figure 8:** Free-electron band structures along symmetry directions for GaAs. (applied to any face-centered cubic structure) The dotted line shows the approximate Fermi energy level at  $T=0$ .

The accepted free-electron band structure is shown in: Kittel, C., Introduction to Solid State Physics, 1986. The computed results agree extremely well with literature. An interesting point to note is that we computed the bands from X to U  $[1 \ 1/4 \ -1/4]$  instead of X to K  $[3/4 \ 3/4 \ 0]$  in order to match the results from the literature.

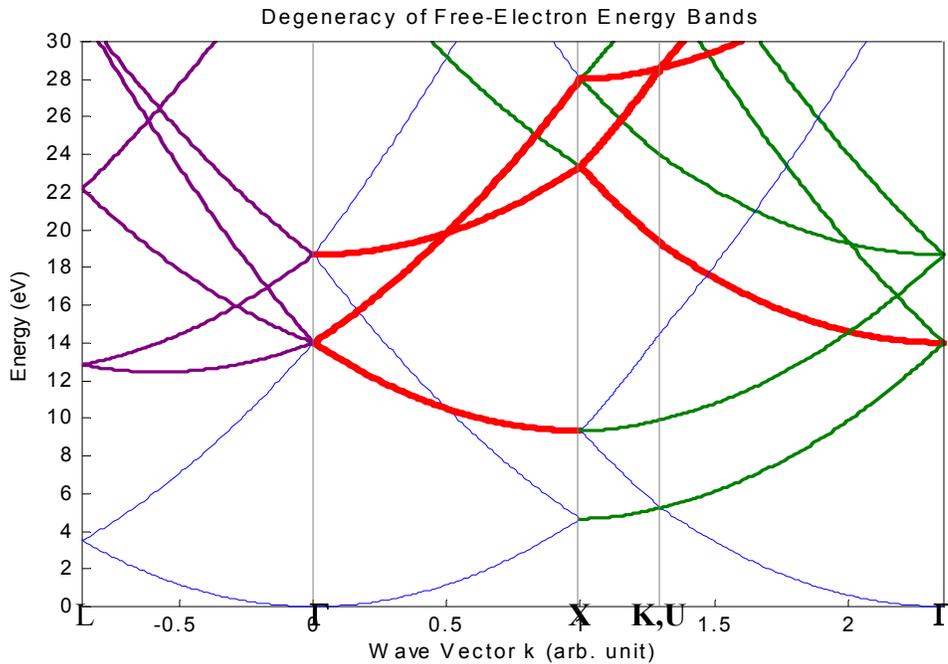
At zero temperature the Fermi energy for free electrons is given by:

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad (40)$$

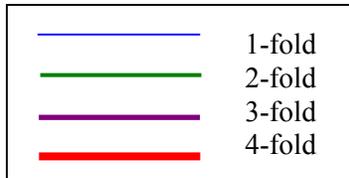
where  $n$  is the electron number density. For GaAs,  $n \sim 5 \times 10^{22}/\text{cm}^3$ , and thus  $E_F \sim 4.9\text{eV}$ . The Fermi level is shown in Fig. 8.

The energies are degenerate if different combinations of  $(h,q,l)$  give the same energy values. Referring to the  $\Gamma$  point example mentioned before, the next energy value at the  $\Gamma$ -point will be 6-fold degenerate since either one of  $h, q$  or  $l$  being  $\pm 1$  will give the same

energy. Figure 10 shows the band structure again but with the degeneracy emphasized. It should be noted that the free electron structures are highly degenerate.



Legend:



**Figure 10:** Degeneracy of the free-electron band structure for GaAs. (face-centered cubic)

It is reasonable to compare the free-electron band structure with the real band structure (Fig. 7). The first observation is that although the free-electron band structure gives a fairly good approximation to the shape of the bands, it shows no evidence of energy gaps. In addition, a lot of the degeneracy is removed in the real band structure.

3. Algebraically diagonalize the Hamiltonian matrix at the G point. What are the different energies and eigenvectors, and what do they correspond to physically? Using Harrison's Solid State

Table find numerical values for  $E_{sa}$ ,  $E_{sc}$ ,  $E_{pa}$ ,  $E_{pc}$ ,  $E_{ss}$ ,  $E_{sp}$ ,  $E_{xx}$ , and  $E_{xy}$ .

The Hamiltonian matrix was given in Eq. (34). It is reproduced here for the case when  $\mathbf{k}=(0,0,0)$ , i.e. at the  $\Gamma$  point.

$$\mathbf{H} = \begin{bmatrix} E_{s1} & 0 & 0 & 0 & 4E_{ss} & 0 & 0 & 0 \\ 0 & E_{p1} & 0 & 0 & 0 & 4E_{xx} & 0 & 0 \\ 0 & 0 & E_{p1} & 0 & 0 & 0 & 4E_{xx} & 0 \\ 0 & 0 & 0 & E_{p1} & 0 & 0 & 0 & 4E_{xx} \\ 4E_{ss} & 0 & 0 & 0 & E_{s2} & 0 & 0 & 0 \\ 0 & 4E_{xx} & 0 & 0 & 0 & E_{p2} & 0 & 0 \\ 0 & 0 & 4E_{xx} & 0 & 0 & 0 & E_{p2} & 0 \\ 0 & 0 & 0 & 4E_{xx} & 0 & 0 & 0 & E_{p2} \end{bmatrix} \quad (41)$$

It is clear that this is a block diagonal matrix and therefore calculations can be done easily by hand. To diagonalize a symmetric matrix like this, you use the eigenvalue equation

$$\mathbf{H}\mathbf{V}=\mathbf{V}\mathbf{E} \quad (42)$$

Where  $\mathbf{V}$  is a matrix of eigenvectors, and  $\mathbf{E}$  is a diagonal matrix of eigenvalues, which happen to be the energies. Pre-multiplying both sides of the equation gives

$$\mathbf{V}^{-1}\mathbf{H}\mathbf{V}=\mathbf{E} \quad (43)$$

Thus, diagonalizing the  $\mathbf{H}$  matrix gives the energies along the diagonal. The eigenvectors and eigenvalues for this system can be found from inspection. As an example, to find two of the eigenvalues, we solve the pair of simultaneous equations

$$E_{s1}\epsilon_1 + 4E_{ss}\epsilon_5 = E \epsilon_1 \quad (44)$$

$$4E_{ss}\epsilon_1 + E_{s2}\epsilon_5 = E \epsilon_5 \quad (45)$$

This set of equations can be solved analytically for  $E$  as

$$E = \frac{(E_{s1} + E_{s2}) \pm \sqrt{(E_{s1} + E_{s2})^2 - 4(E_{s1}E_{s2} - 16E_{ss}^2)}}{2} \quad (46)$$

Thus, Eq. (45) gives us two values for the energy. Once we have the energy, we can calculate the corresponding eigenvectors. We simply substitute the two values of  $E$

obtained from Eq. (46) into Eq. (44) and (45) and get two eigenvectors. The results of this process are given in Tables 1 and 2 below. Table 1 shows the calculated eigenvalues or energies for this matrix along with a comparison with literature values [1]. The calculated energy values have been scaled so that zero corresponds to the top of the valence band.

**Table 1:** Calculated vs Experimental Values for Energy at G point [1]

Calculated Energy (eV)	Measured Energy (eV)
-12.64	-12.6
0	-0.5
0	0
0	0
3.12	1.4
3.12	4.7
3.12	4.7
6.42	4.7

The table shows that the calculated and experimental values for the energy levels at the  $\Gamma$  point are reasonably close. Table 2 shows the eigenvectors for the energy modes.

**Table 2:** Calculated eigenvectors for Hamiltonian matrix at G

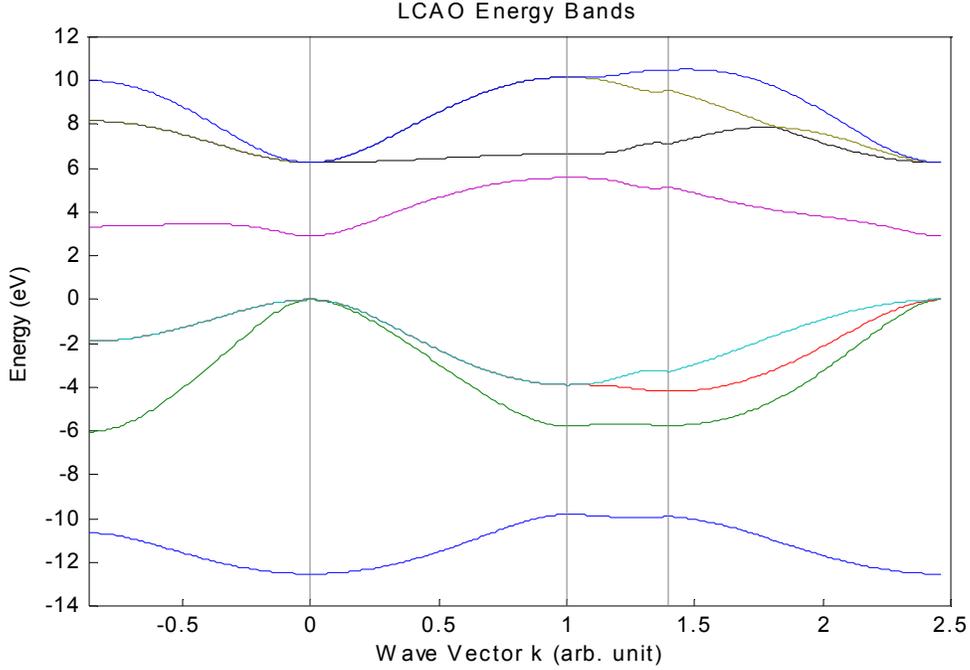
$\phi_{s1}$	0	0	-0.80	0.60	0	0	0	0
$\phi_{px1}$	0	0	0	0	-0.82	0.57	0	0
$\phi_{py1}$	-0.82	-0.57	0	0	0	0	0	0
$\phi_{pz1}$	0	0	0	0	0	0	-0.82	0.57
$\phi_{s2}$	0	0	0.60	0.80	0	0	0	0
$\phi_{px2}$	0	0	0	0	-0.57	-0.82	0	0
$\phi_{py2}$	-0.57	0.82	0	0	0	0	0	0
$\phi_{pz2}$	0	0	0	0	0	0	-0.57	-0.82

The eigenvectors represent the coefficients by which each of the bases in the finite state basis expansion are weighted. It is seen that all of the eigenvectors have only two non-zero components. We already knew this from before when we demonstrated the calculation of energies and eigenvalues analytically. With these eigenvectors, the energy can actually be estimated as well because if the eigenvector is mainly weighting one of the atomic orbital functions, then the corresponding energy for that eigenvector will approximately be equal to the energy of the atomic orbital.

4. Write a Matlab program to plot the LCAO energy bands along the same directions as above, along with the approximate location of the Fermi level. How do your results compare qualitatively with the band structure you found in the literature? Optimize the matrix elements for your material if you wish.
5. Where are the valence band maximum and conduction band minimum located? What is the energy gap? Is your material direct or indirect?

The Hamiltonian matrix obtained in part B was used to find the energy bands. Recall that we chose the trial wave function to be a linear combination of  $4s$ ,  $4p_x$ ,  $4p_y$ ,  $4p_z$  orbitals from each Ga and As atoms. The resulting  $8 \times 8$  Hamiltonian matrix should give 8 eigenenergies for each  $[k_x \ k_y \ k_z]$ , thus we expect to get 8 energy bands. The values for the physical parameters used in the computation were from the Solid State table [3] and are summarized in Table 3. The LCAO band diagram along the same symmetry points is shown in Fig. 11. The zero energy point was taken to be the maximum of the valence

band.



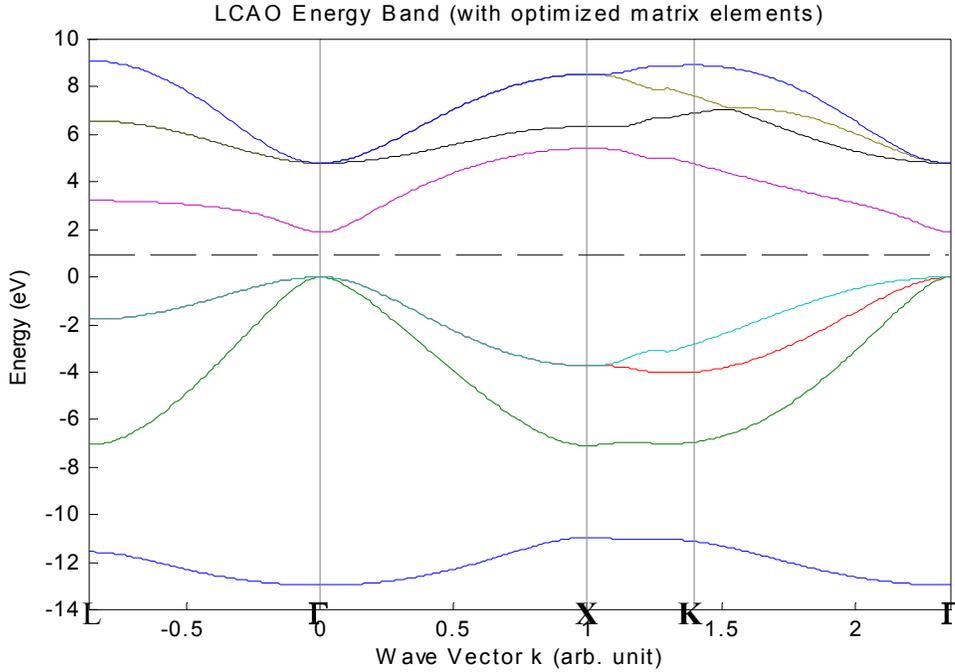
**Figure 11:** LCAO energy bands for GaAs. The zero energy point is chosen to be the maximum of the valence band (at the  $\Gamma$  point).

The 8 energy bands are best evidenced along the K- $\Gamma$  direction. The 3<sup>rd</sup> and 4<sup>th</sup> bands and the 7<sup>th</sup> and 8<sup>th</sup> bands are degenerate for X- $\Gamma$  and L- $\Gamma$ . Although there is a band gap between the first two bands, it is not of main interest since they are all filled up and doesn't contribute to the semiconducting properties. The actual semiconductor gap is located between the 4<sup>th</sup> (valence band) and the 5<sup>th</sup> (conduction band). The energy gap is the difference between the maximum of the valence band ( $E_V = 0\text{eV}$ ) and the minimum of the conduction band ( $E_C = 2.91\text{eV}$ ). The resulting band gap of 2.91 eV is much higher than the accepted value of 1.43eV for GaAs. This discrepancy naturally posed a need to optimize the matrix elements. We fudged the four overlap parameters  $V_{ss\sigma}$ ,  $V_{sp\sigma}$ ,  $V_{pp\sigma}$  and  $V_{pp\pi}$  since they are the most crucial matrix elements. The optimized values are summarized in Table 3.

**Table 3:** The numerical values of the physical parameters used in the computation. The first set was obtained from the solid state table [3] and the second set was the optimized values. The band gaps computed with each set of values are also shown. The values in parenthesis indicate the discrepancy with the accepted value (1.43eV) for GaAs.

Matrix Elements		Solid State Table (eV)	Optimized (eV)
Ga	$E_s$	-11.37	---
	$E_p$	-4.9	---
As	$E_s$	-17.44	---
	$E_p$	-7.91	---
$V_{ss\sigma}$		-1.78	-1.70
$V_{sp\sigma}$		2.34	2.60
$V_{pp\sigma}$		4.12	3.44
$V_{pp\pi}$		-1.03	-1.02
Band Gap		2.91 (103%)	1.88 (31%)

Taking into account that it is difficult to judge whether the values are optimized merely by comparing the band structures qualitatively, the final values we used were based on the suggestions from ref. [3]. The improved LCAO band structure is shown in Figure 12. It can be seen that the shapes of the band structures agree more with the literature (Fig. 7) and the corresponding band gap is 1.88eV. The discrepancy is reduced from 103% to 31%. It should be noted that the optimization process did not only take into account the energy gap but also the shape of the bands as well.



**Figure 12:** Improved LCAO energy bands with optimized matrix elements for GaAs. The locations of the valence band minimum and conduction band maximum both occur at the  $\Gamma$  point, indicating that GaAs has a direct band gap. The Fermi energy level at  $T = 0$  is mid-way between the band gap (dotted line).

The Fermi energy level as a function of temperature is given by

$$E_F = \frac{E_c + E_v}{2} + kT \ln\left(\frac{N_v}{N_c}\right) \quad (47)$$

where  $k$  is Boltzmann constant,  $N_v$  and  $N_c$  are the degeneracy at  $E_v$  and  $E_c$  respectively. At zero temperature, it is mid-way between the energy gap and is approximately  $E_{F0} \sim 0.94\text{eV}$  with  $E_v$  being the zero energy point. At higher temperature, it will be slightly shifted towards the valence band.

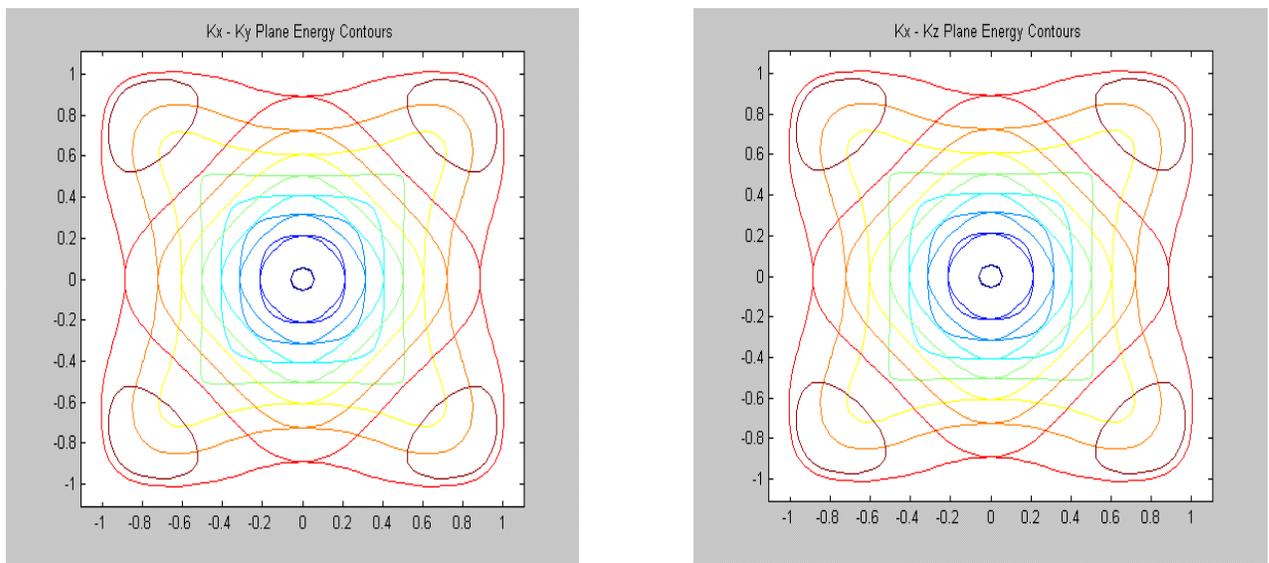
The energy bands obtained using the LCAO method compares well with the real energy bands. The LCAO approach is particularly useful in providing information about the presence and location of the energy gaps, and the general trend of the bands. However its limitation lies in the inability to predict some band features including the dips and also the fine separation of some of the nearly degenerate bands.

Nevertheless, the LCAO band diagram accurately predicts the locations of the valence band minimum and the conduction band maximum; they both occur at the  $\Gamma$  point. Therefore GaAs is a direct band gap material, with a band gap computed to be  $1.88\text{eV}$  (31% discrepancy).

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1. Plot constant energy contours near the valence and conduction band edges for “appropriate” planes. Fig13, Eq48

The constant energy contours along selected planes are shown below. Since the maximum energy in the conduction band and the minimum energy in the valence band occur at  $\Gamma = (0,0,0)$  for our direct material, a plot of the energy contours along the  $k_x$ - $k_y$  plane ( $k_z=0$ ) and along the  $k_x$ - $k_z$  plane ( $k_y=0$ ) will be a suitable choice to capture the energy content about the band gap of our material.



**Figure 13:** Constant energy contours along selected planes

2. Solve for the energy at a number of  $k$  points near the valence and conduction band edges. Fit these points using a quadratic polynomial. 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?

In general, a quadratic fit near the conduction band minimum is in the general form

$$E = E_c + \frac{\hbar^2}{2} \left( \frac{(k_x - k_{x0})^2}{m_x^*} + \frac{(k_y - k_{y0})^2}{m_y^*} + \frac{(k_z - k_{z0})^2}{m_z^*} \right) \quad (48)$$

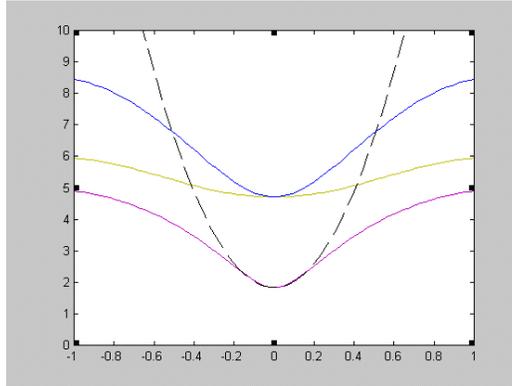
For GaAs, simplifications may be made by taking the cubic symmetry into account ( $m_x^* = m_y^* = m_z^* = m_c^*$ ) and by noting that the conduction band minimum occurs at  $(k_{x0}, k_{y0}, k_{z0}) = (0, 0, 0)$ . This results in Eq. (49)

$$E = E_c + \frac{\hbar^2}{2} \left( \frac{(k_x)^2}{m_c^*} + \frac{(k_y)^2}{m_c^*} + \frac{(k_z)^2}{m_c^*} \right) \quad (49)$$

For simplicity, the effective mass is calculated by fitting the energy dispersion relation along the  $\Gamma$ -X direction, which results in the following simplified equation

$$E = E_c + \frac{\hbar^2}{2} \left( \frac{(k_x)^2}{m_c^*} \right) \quad (50)$$

Choosing an appropriate value for the effective mass results in a quadratic polynomial fit as is shown below for the conduction band



**Figure 14:** Conduction band effective mass

where  $m_c$  is found to be

$$m_c^* = .2m_0 \quad (51)$$

Similarly, the quadratic polynomial fit for the valence bands is written in general

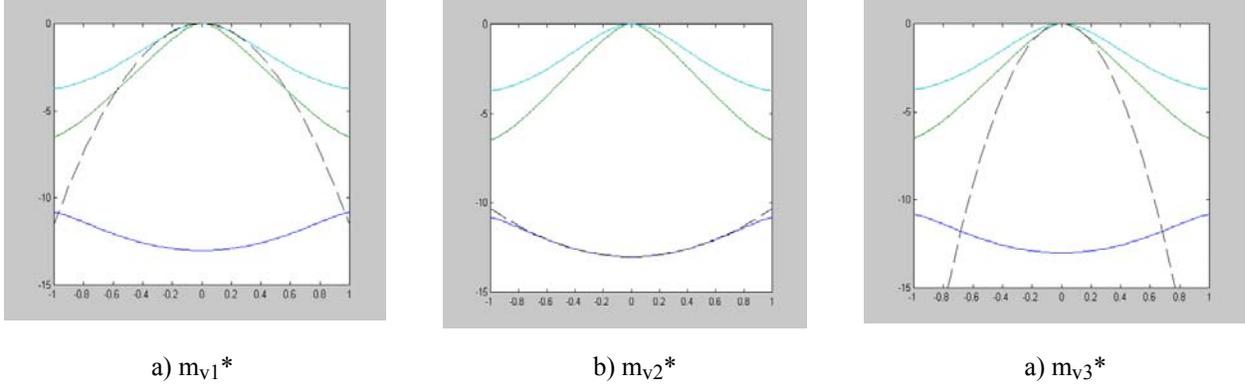
$$E = E_v - \frac{\hbar^2}{2} \left( \frac{(k_x - k_{x0})^2}{m_x^*} + \frac{(k_y - k_{y0})^2}{m_y^*} + \frac{(k_z - k_{z0})^2}{m_z^*} \right) \quad (52)$$

Using the same simplifications as in the conduction band,

$$E = E_v - \frac{\hbar^2}{2} \left( \frac{(k_x)^2}{m_v^*} \right) \quad (53)$$

The effective mass constants fitted for the valence band maximums are found to be

$$\begin{aligned}
 m_v^* &= .33m_0 \\
 m_{v2}^* &= .15m_0 \\
 m_{v3}^* &= 1.41m_0
 \end{aligned}
 \tag{54}$$



**Figure 15:** Valence band effective mass

In comparing the calculated values with the literature, one finds that the effective masses obtained by using the LCAO method does not closely match the experimental results. A table from Harrison, W. A., Electronic Structure and Properties of Solids, Freeman, (1980) shows typical experimental and theoretical values.

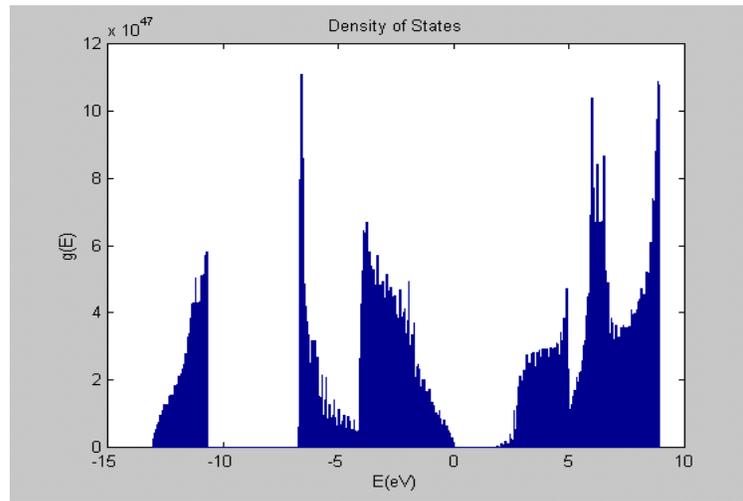
In providing an explanation for the discrepancy, we will suggest that the nearest neighbors LCAO method could be improved by allowing for more trial wavefunctions by choosing next nearest neighbors. This would allow for more curvature in the energy band dispersion relationship, and therefore improve the estimation for the effective mass calculations.

**Table 5:** Valence band effective mass

Effective Mass	Literature Values [1]	Calculated Values
Conduction Band	$m_{c0} = 0.067m_0$	$m_c = .2 m_0$
Light Hole Band	$m_l = .082 m_0$	$m_l = .33m_0$
Split Off Band	$m_{s0} = 0.154 m_0$	$m_{s0} = 0.15 m_0$
Heavy Hole Band	$m_h = 0.51m_0$	$m_h = 1.41m_0$

3. Plot the total density of states 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.?

Figure 16 shows the calculated density of states using the histogram method.



**Figure 16:** Density of States

An approximation for the total density of states could be made by using the calculated values for the effective mass in the conduction and valence band and the equations shown below

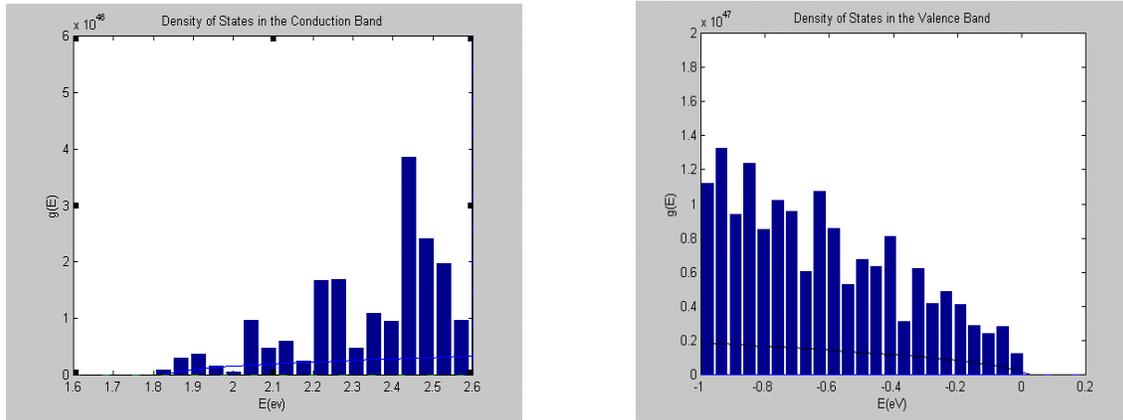
$$g_c(E) = \frac{m_c^* \sqrt{2m_c^* (E - E_c)}}{\pi^2 \hbar^2} \quad (54)$$

$$m_{veff}^* = [2(m_{v1}^*)^{3/2} + (m_{v2}^*)^{3/2}]^{2/3} \quad (55)$$

$$g_v(E) = \frac{m_{veff}^* \sqrt{2m_{veff}^* (E_v - E)}}{\pi^2 \hbar^2} \quad (56)$$

The 2 in front of the first term results from the fact that the first band is doubly degenerate [5]

Using our calculated values for  $m_{\text{veff}}^* = .576$  and  $m_c^* = .2 m_0$ , we obtain the plots shown in the figure below where the solid lines represent the analytical expression using the calculated effective masses.



**Figure 16:** Density of states near the conduction and valence band edges and effective mass approximation

- 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.

In calculating the specific heat of GaAs, a numerical integration technique is utilized in order to use the numerical density of states. First, the expected value of the energy is found from

$$\left\langle \frac{E}{V} \right\rangle = \int E g(E) f(E) dE \quad (57)$$

Noting that the Fermi distribution function has an explicit temperature dependence, as well as an additional implicit temperature dependence in the Fermi energy level itself

$$f(E) = \frac{1}{1 + e^{\frac{E-E_f}{k_b T}}} \quad (58)$$

where the Fermi energy is approximately given by

$$E_f = \frac{E_c + E_v}{2} + kT \ln\left(\frac{N_v}{N_c}\right) \quad (59)$$

and

$$N_v = 2\left(\frac{2\pi m_v^* kT}{h^2}\right)^{\frac{3}{2}} \quad (60)$$

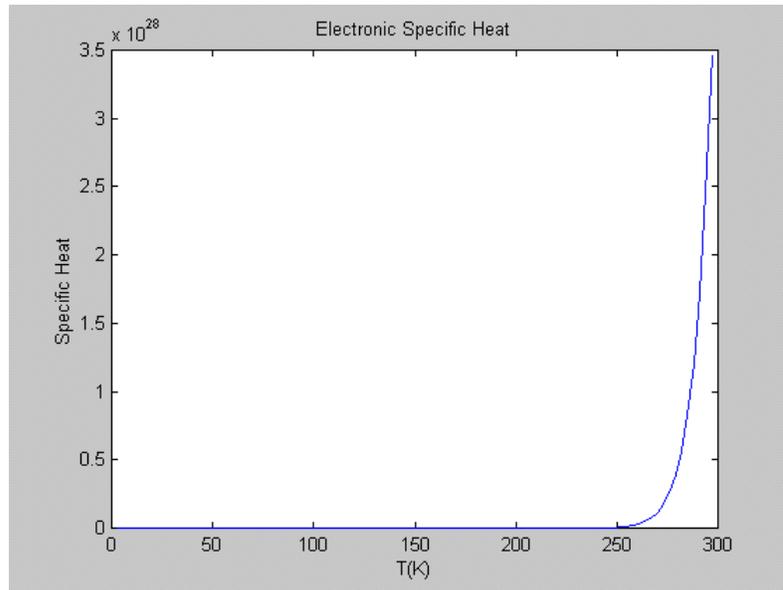
$$N_c = 2\left(\frac{2\pi m_c^* kT}{h^2}\right)^{\frac{3}{2}} \quad (61)$$

The electronic specific heat is shown in Figs. 17 and 18 over different temperature ranges. It is still unclear to us what the relevant temperature range should be and how the exact specific heat calculation should be done. Initially, we tried to calculate the energy density using the valence and conduction bands. However, this appeared to give us a specific heat of zero due to some type of cancellation. Then, upon the (perhaps nebulous) advice of a former student, we tried calculating the specific heat using only the conduction bands. This idea seemed to make sense because the valence band is pretty much full, so there is not much room for the valence electrons to increase in energy while still staying in the valence bands. The conduction band electrons, however, have access to a seemingly infinite number of free states to which they can be excited by thermal energy. Therefore, the specific heat was calculated using only the conduction band density of states. Perhaps this approximation becomes less valid as the temperature increases and there are a greater fraction of available states in the valence bands, implying that the specific heat due to valence band electrons cannot be ignored.

We expect the semiconductor to behave as an insulator at low temperatures and a conductor at high temperatures. In an insulator, there are no available energy levels to which electrons can transition (that are of the same order of magnitude as the thermal energy). Therefore, the electronic specific heat should be zero for the insulator. In a

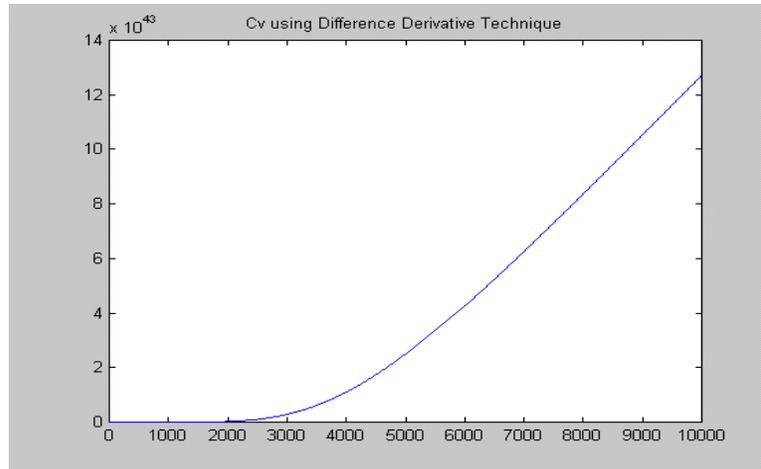
metal, the electronic specific heat has a linear variation with temperature. We therefore expect that the electronic specific heat will start at zero and become linear at some point.

Initially, we plotted Fig. 17 shown below.



**Figure 17:** Electronic specific heat up to 300K

From this plot, it seemed like the “knee” for the transition between nonzero specific heat and linear specific heat occurred around 275K. In order to compare the electronic specific heat to the phonon specific heat, we decided to plot over a much larger temperature range. This plot is shown as Fig. 18. Figure 18 seems to indicate that the “knee” is around 2500K. Upon some consideration, this latter temperature seemed more reasonable because  $2500\text{K} \sim 0.2 \text{ eV}$  and the bandgap is on the order of an electron-Volt.



**Figure 18:** Electronic specific heat up to 1000K

We already know that the phonon specific heat dominates over the electronic specific heat for high temperatures. We also know that the total specific heat saturates at high temperatures. Obviously then, the electronic specific heat cannot continue to grow indefinitely. In a metal, the phonons freeze out below some temperature and only electrons contribute to total specific heat. Here, however, it seems that the electrons also “freeze out” because they are virtually all in the valence band and do not have enough energy to jump into the conduction band. So, it is not necessarily true that electrons are dominant for very small temperature either, even though the phonon specific heat displays a  $T^3$  dependence around  $T=0$ . However, these are issues that the authors have not fully understood at this point.

5. 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?

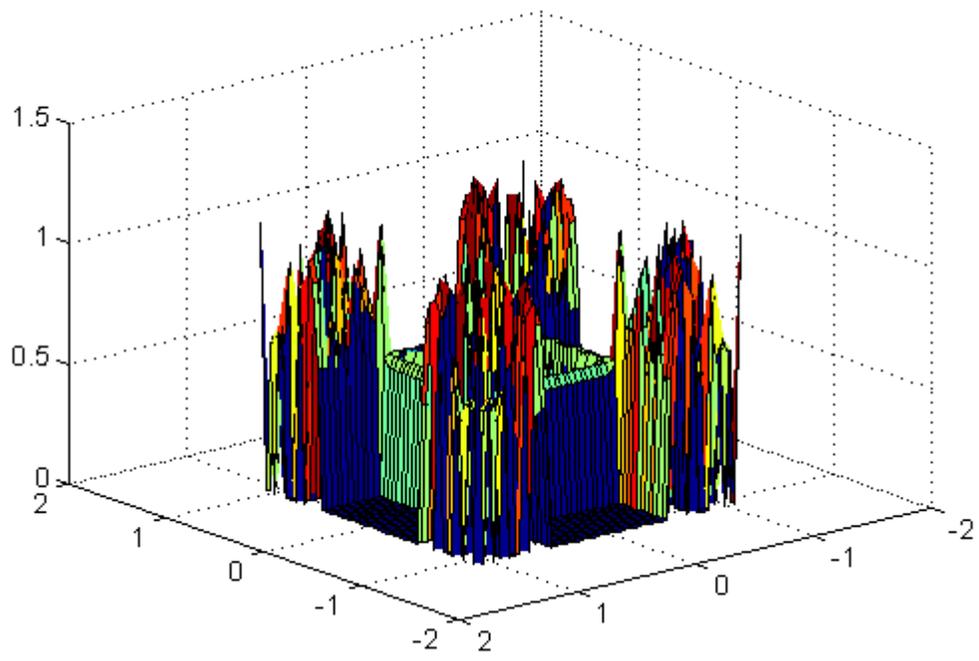
There are two main characteristics of the GaAs band structure which can be exploited for electronic and/or optical applications. They are the fact that GaAs has a direct bandgap at  $\Gamma$  and that the effective mass of the electron is far less than it is for silicon ( $0.067m$  compared to  $0.19m$  for light electrons in Si). In addition, the light holes in GaAs are  $0.074m$  compared to  $0.16m$  for Si.

A direct bandgap occurs when the minimum of the conduction band occurs at the same point in k-space as the maximum of the valence band. In semiconductors with a direct bandgap, an electron can make a transition from the valence band to the conduction band with simply a change in energy. In indirect bandgap semiconductors, the electron must also change its momentum when it transitions. In indirect bandgap semiconductors, a third particle is required for momentum conservation. Silicon has an indirect bandgap. Because only an energy change is required for direct bandgaps, an electron can make transitions between the conduction and valence bands by emitting or absorbing a single photon. No other particles are needed. For this reason, GaAs is a very useful material for making light-emitting or light-detecting devices. Thus, GaAs is often used for LEDs as a light source and CCDs as a light detector.

The effective mass of electrons and holes in GaAs can also be exploited for commercial purposes. Since the charge carriers are “lighter” than they are in silicon, one would suppose that they could be accelerated faster and perhaps to higher velocities (although the latter does not necessarily hold). However, it does turn out that GaAs has a higher electron mobility than silicon by a factor of six and a half. The increased mobility allows for faster electronics because electrons move through transistor channels and junctions much quicker. In practical terms, this corresponds to faster switching speeds for digital electronics and higher operational frequency for both analog and digital components. Indeed GaAs is very commonly used for applications that place such demands.

## 6. Plot the 3D constant energy surfaces near the top of the valence band and bottom of the conduction band.

The figure below shows constant energy surfaces near the bottom of the conduction band.



## References

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