

Weekly Report

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1 Introduction

In this report I mainly want to discuss two aspects: group theory and Wannier functions. First I will give a brief review of group theory in electronic structure. Then, I'd like to show some interesting breakthrough about wannier functions and tight binding model. Beside, I also solved some questions remained in the last meeting.

2 Progress

2.1 A Pedestrian's Guide to Group Theory

2.1.1 Symmetry Operations and Group

Figure 1 shows the structures of the diamond and zinc-blende crystals. Under some operations like rotations in special angle, the structure would be invariant. To describe these properties, physicists name these operations symmetry operations and the ensemble of them forms a set, which are called group.

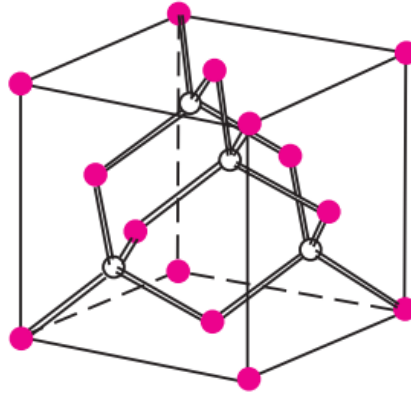


Figure 1: The crystal structure of zinc-blende

Zinc-blende structure has 24 symmetry operations, which are showed in Figure 2. They can be divide into five subgroups. Here the notation $[kln]$ is the Miller indices.

E :	identity
eight C_3 operations:	clockwise and counterclockwise rotations of 120° about the $[111]$, $[\bar{1}11]$, $[1\bar{1}1]$, and $[11\bar{1}]$ axes, respectively;
three C_2 operations:	rotations of 180° about the $[100]$, $[010]$, and $[001]$ axes, respectively;
six S_4 operations:	clockwise and counterclockwise improper rotations of 90° about the $[100]$, $[010]$, and $[001]$ axes, respectively;
six σ operations:	reflections with respect to the (110) , $(\bar{1}\bar{1}0)$, (101) , $(10\bar{1})$, (011) , and $(01\bar{1})$ planes, respectively.

Figure 2: Symmetry operations of zinc-blende

2.1.2 Symmetry in Bandstructure

Here I will use the s,p orbitals of simple cubic to examplify how group theory works on band sturcture. First, recalling solid state physic, we have:

$$E_n(k) = E_n(\alpha k) \quad (2.1)$$

Here α stands for a symmetry operation. The wave functions can be expressed as Bloch waves:

$$\varphi_{nk}(r) = e^{ik \cdot r} \mu_{nk}(r) \quad (2.2)$$

When imposing a symmetry operation $T(\beta)$, The wave functions would change in this way:

$$T(\beta) [e^{ik \cdot r} \mu_{nk}(r)] = e^{ik \cdot \beta^{-1} r} \mu_{nk}(\beta^{-1} r) = e^{ik \cdot r} \mu_{nk}(\beta^{-1} r) \quad (2.3)$$

The functions before and after aren't necessarily identical, which means at a K point in brillioun zone a symmetry operation would not affect the energy but perhaps change the wave functions. In order words, different wave functions may appear the same energy which we usually call it degeneracy. Based on above functions, We can find that the whole characters in bandsturcture are well defined by group operation $T(\beta)$ and wave function $\mu_{nk}(r)$.

In Γ point of BCC, the group is O_h . Let's consider the transformation of s,p orbitals in tight binding model under symmetry operations of O_h group.

S band:

$$\psi_\Gamma^s(r) = \sum_m \varphi_s(r - R_m) \quad (2.4)$$

Imposing symmetry operation $T(\beta)$:

$$T(\beta)\psi_\Gamma^s(r) = \sum_m \varphi_s[\beta^{-1}(r - R_m)] \quad (2.5)$$

S band has spherical symmetry which is invariant under any rotation or inversion, so:

$$T(\beta)\psi_{\Gamma}^S(r) = \psi_{\Gamma}^S(r) \quad (2.6)$$

That is to say, under symmetry operations of O_h group $\psi_{\Gamma}^S(r)$ stay invariant. This regualtion is expressed as Γ_1 . Strictly speaking, Γ_1 *irreducible representation*.

P bands:

$$\begin{aligned} \psi_{\Gamma}^{p_x} &= \sum_m \varphi_{p_x}(r - R_m) \\ \psi_{\Gamma}^{p_y} &= \sum_m \varphi_{p_y}(r - R_m) \\ \psi_{\Gamma}^{p_z} &= \sum_m \varphi_{p_z}(r - R_m) \end{aligned} \quad (2.7)$$

Imposing symmetry operation $T(\beta)$:

$$\begin{aligned} T(\beta)\psi_{\Gamma}^{p_x} &= \sum_m \varphi_{p_x}[\beta^{-1}(r - R_m)] \\ T(\beta)\psi_{\Gamma}^{p_y} &= \sum_m \varphi_{p_y}[\beta^{-1}(r - R_m)] \\ T(\beta)\psi_{\Gamma}^{p_z} &= \sum_m \varphi_{p_z}[\beta^{-1}(r - R_m)] \end{aligned} \quad (2.8)$$

That is to say, transition among $\{\psi_{\Gamma}^{p_x}, \psi_{\Gamma}^{p_y}, \psi_{\Gamma}^{p_z}\}$ is the same as $\{\varphi_{\Gamma}^{p_x}, \varphi_{\Gamma}^{p_y}, \varphi_{\Gamma}^{p_z}\}$, which is the same as $\{x, y, z\}$ (thinking of the specific forms of p orbitals). $\{x, y, z\}$ are called *basic functions* which means the character of p bands under symmetry operations is just $\{x, y, z\}$. For example, a rotation matrix that will convert x to y would convert p_x to p_y . This regualtion is called Γ_{15} irreducible representation. By the way, imposing different symmetry operations at the same Γ point we could get three different wave functions which mean p bands is threefold degeneracy in Γ point.

2.1.3 Group theory related to our research

Now our research mainly focus on Zinc-blende structure. To study band-structure, we should study the group in reciprocal space(Figure 3). It is O_h group which has ten irreducible representations. I assume irreducible representations could be simply understood as the small groups in a big group. Figure 4 shows *the character table* of O_h group at Γ point.

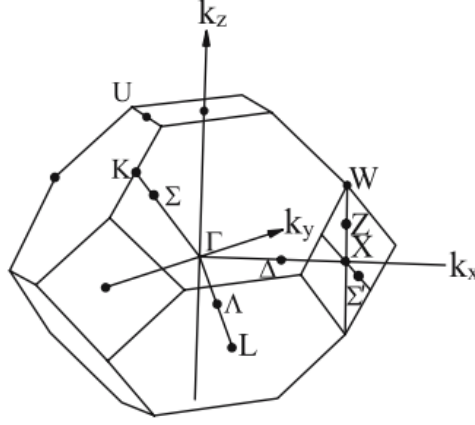


Figure 3: Reciprocal space of zinc-blende(also the first Brillouin zone)

repr.	basis functions	E	$3C_4^2$	$6C_4$	$6C_2'$	$8C_3$	i	$3iC_4^2$	$6iC_4$	$6iC_2'$	$8iC_3$
$\Gamma_1 (\Gamma_1^+)$	1	1	1	1	1	1	1	1	1	1	1
$\Gamma_2 (\Gamma_2^+)$	$\begin{cases} x^4(y^2 - z^2) + \\ y^4(z^2 - x^2) + \\ z^4(x^2 - y^2) \end{cases}$	1	1	-1	-1	1	1	1	-1	-1	1
$\Gamma_{12} (\Gamma_{12}^+)$	$\begin{cases} x^2 - y^2 \\ 2z^2 - x^2 - y^2 \end{cases}$	2	2	0	0	-1	2	2	0	0	-1
$\Gamma_{15} (\Gamma_{15}^-)$	x, y, z	3	-1	1	-1	0	-3	1	-1	1	0
$\Gamma_{25} (\Gamma_{25}^-)$	$z(x^2 - y^2) \dots$	3	-1	-1	1	0	-3	1	1	-1	0
$\Gamma_1' (\Gamma_1^-)$	$\begin{cases} xyz[x^4(y^2 - z^2) + \\ y^4(z^2 - x^2) + \\ z^4(x^2 - y^2)] \end{cases}$	1	1	1	1	1	-1	-1	-1	-1	-1
$\Gamma_2' (\Gamma_2^-)$	xyz	1	1	-1	-1	1	-1	-1	1	1	-1
$\Gamma_{12}' (\Gamma_{12}^-)$	$xyz(x^2 - y^2) \dots$	2	2	0	0	-1	-2	-2	0	0	1
$\Gamma_{15}' (\Gamma_{15}^+)$	$xy(x^2 - y^2) \dots$	3	-1	1	-1	0	3	-1	1	-1	0
$\Gamma_{25}' (\Gamma_{25}^+)$	xy, yz, zx	3	-1	-1	1	0	3	-1	-1	1	0

† The basis functions for Γ_{25}^- are $z(x^2 - y^2)$, $x(y^2 - z^2)$, $y(z^2 - x^2)$, for Γ_{12}^- are $xyz(x^2 - y^2)$, $xyz(3z^2 - x^2 - y^2)$ and for Γ_{15}^+ are $xy(x^2 - y^2)$, $yz(y^2 - z^2)$, $zx(z^2 - x^2)$

Figure 4: Character table for group O_h corresponding to the group of the wave vector at $k = 0$

The form of the basis functions is helpful in identifying $s(\Gamma_1)$, $p(\Gamma_{15})$ and $d(\Gamma_{15}, \Gamma'_{25})$.

In other high symmetry point like X and L, we can also get a character table and its according irreducible representations.

Another important thing is *Selection Rule*. In our stage it can be understood as only when the irreducible representations of two bands are compatible (identical or one contain the other) could they couple with each other. Detail proof need *orthogonality relations* which you can check the reference book I list in the end.

For example, at Γ point in zinc-blende, $d(\Gamma_{15}, \Gamma'_{25})$ orbitals are compatible with $p(\Gamma_{15})$ orbitals, so the coupling between p and d orbitals at the Γ point could be quite significant. However, the $s-d$ coupling is forbidden because the atomic d orbitals have no common irreducible representations with the $s(\Gamma_1)$ CB Γ -valley state. Similarly, other high symmetry points (X, L, etc) would be analyzed in this way.

In our research of the emergence of bandgap (Figure 5 and 6), we can see that before and after the bandgap appears these states are both dominated by p bands (check DOS plot), which are threefold degeneracy based on above analysis, so we can safely draw the conclusion that threefold degeneracy must exist during the splitting of bands.

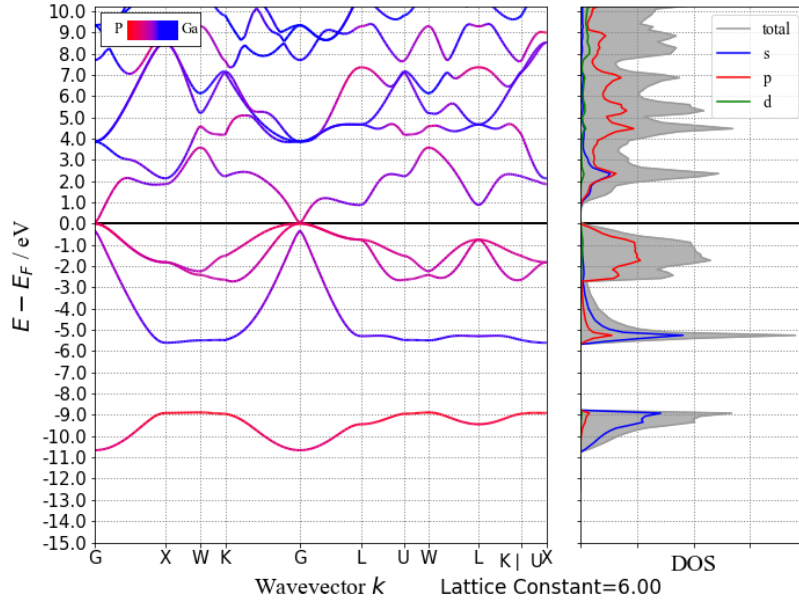


Figure 5: Bandstructure of GaP when lattice constant = 6.00 Å

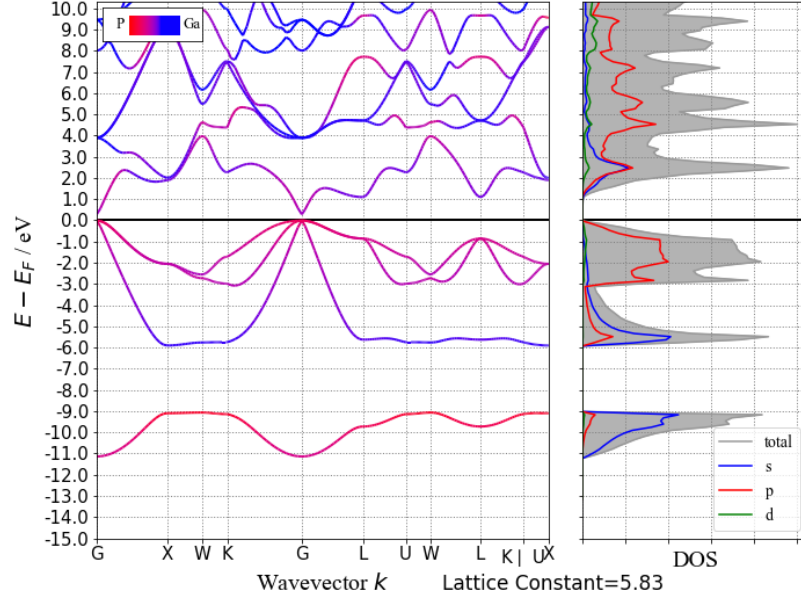


Figure 6: Bandstructure of GaP when lattice constant = 5.83 Å

2.2 Wannier functions and Tight binding model

These weeks I have basically handled Wannier90 and utilized PythTB to post processing the result of Wannier90 to acquire tight binding model.

The most important output file for tight binding model is *seedname_hr.dat*, which contains the whole hopping parameter of TB model. First, I tried GaP (5.50Å) with projection functions to be 8 s and p bands of Ga and P. Figure 7 shows the result of the 8 band TB model results.

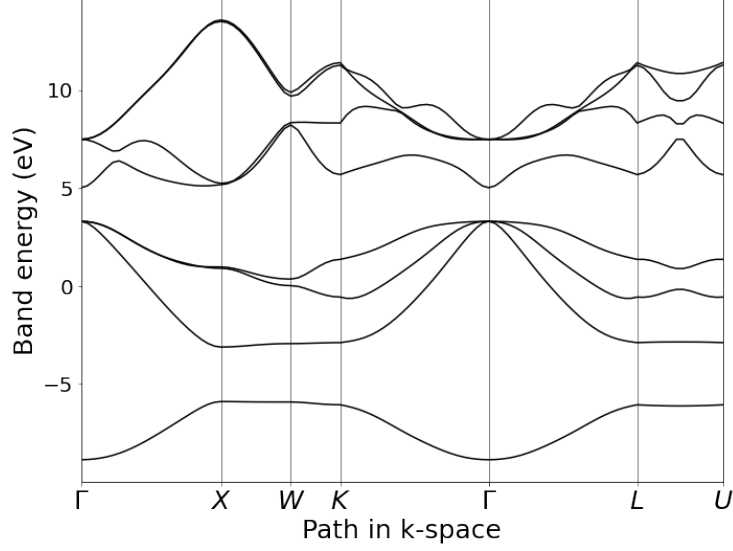


Figure 7: 8 band TB model bandstructure of GaP (5.5Å)

Checking *seedname_hr.dat* file, 1431432 hopping parameters are calculated to reach such accuracy, which considers bands in five conventional cells away. Figure 8 visualizes those parameters. X values means distances between Wannier function centers (i and $j+R$) in Angstroms. I take the logarithm of primitive values of hopping intensity to classify the hoppings, so the upper in the picture the greater in the intensity. Besides, the nearest other atom bands should be at between 2.5Å and 5Å. So many parameters are definitely improper for us to extract crucial features. Therefore I gradually drop some of the hoppings that are lower than certain value and make an animation which I will attach in accessory. From the videos we can find that it's similar to the trend when we gradually decrease the lattice constant, which corresponds to our assertion that couplings gradually appear as atoms get closer to each other. In this respect I assume that for next step we can generate a continuous TB model during the decline of lattice constant and figure out the numerical features of those hoppings, such as using functions like inverse square relation to fit some hopping parameters during the procedure.

A even more interesting thing is that this model only get indirect band gap. Is it because I didn't take d band into account? With this thought I tested different basic projection functions that include Ga d bands. However, the results are disappointing. It turned out that whether I used Ga: s,p,d and P: s,p bands (Figure 9) or even consider 40 bands (Figure 10) the band type is still direct.

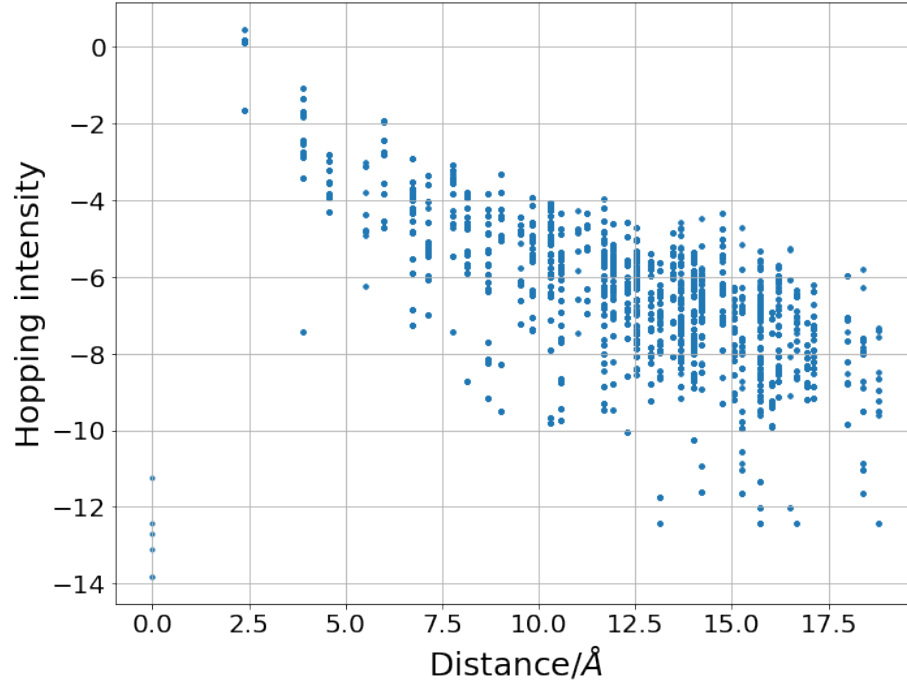


Figure 8: Hopping intensity VS hopping distances in GaP 8 band TB model

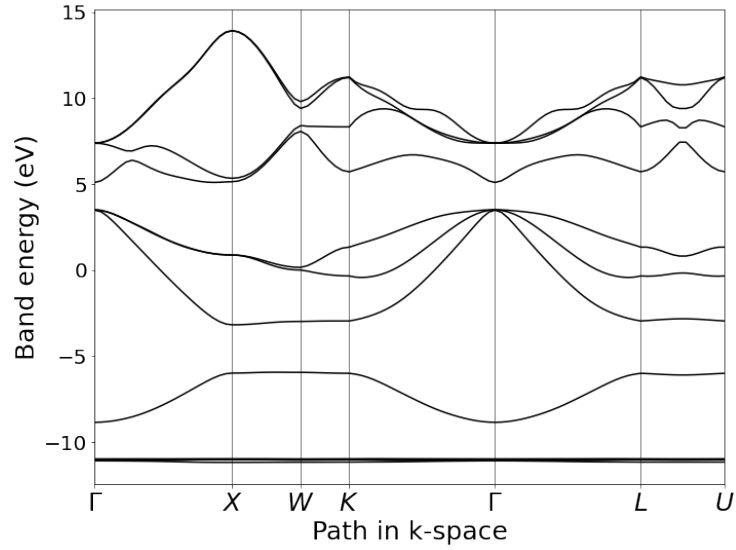


Figure 9: 13 band TB model bandstructure of GaP (5.5Å)

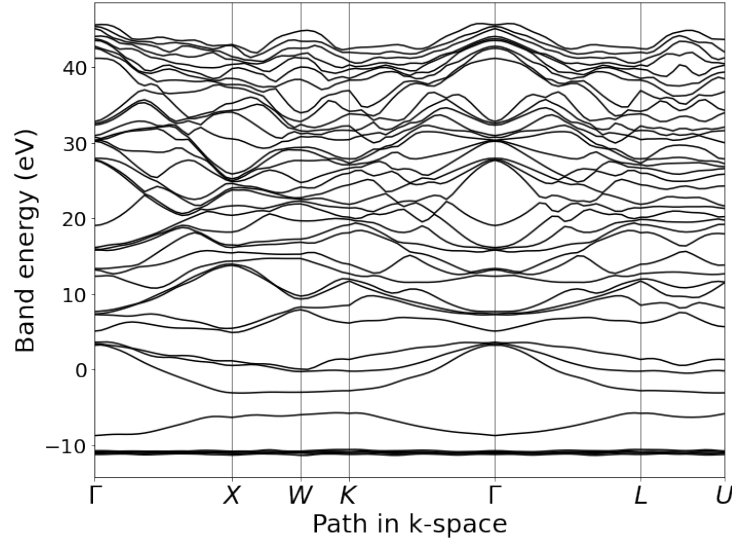


Figure 10: 40 band TB model bandstructure of GaP (5.5Å)

The input files acquired from VASP is correct (A further non self-consistent calculation would give right indirect band gap). So there must be something wrong with Wannier90 since d band influence is very weak in Figure 9 or I set some parameters incorrectly. This is the main questions for me in these weeks.

2.3 Formation energy VS Lattice Constant

Figure 11 shows the formation energy VS lattice constant of GaP. Obviously the stablest structure corresponds to the lowest formation energy. It can be simply explained by the Lenard-Jones inter-atom pair potential and it's just like the normal self-consistent calculations we do for determining the lattice constant.

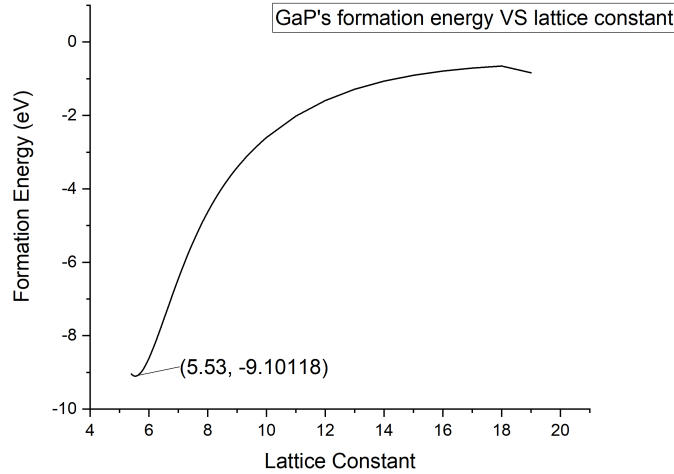


Figure 11: Formation energy VS Lattice Constan

2.4 Integral of COHP

I suppose if we calculate the integral of COHP, we should first understand the physical meaning of it. After looking some COHP papers, I don't find anywhere using the integral of COHP to explain something. It seems that COHP are more applicable in analyzing the bonding information in complex systems such as a molecule consisted of tens of types of atoms. Based on my own understanding, I think the integral of COHP under fermi surface would be just like the integral of DOS which is identical to the total number of valence band electrons. Besides, I don't think the result of lobster is accurate enough to perform delicate numerical analysis. Maybe we can further discuss it in the meeting.

2.5 Others

In addition, I also draw the core level bandstructure videos of GaP which I will attach in the mail. Further analysis is needed.

3 Reference

1. M.S. Dresselhaus, G. Dresselhaus, A. Jorio, *Group Theory Application to the Physics of Condensed Matter*
2. Peter Y. Yu Manuel Cardona, *Fundamentals of Semiconductors*

3. Kun Huang, *Solid State Physics*