Weekly Report

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August 20, 2020 - September 18, 2020

1 How band structure forms

Here I use two materials to study how band structure forms.

1.1 GaP

The following figures are GaP's bandstructure and DOS when Ga and P gradually get closer with each other.

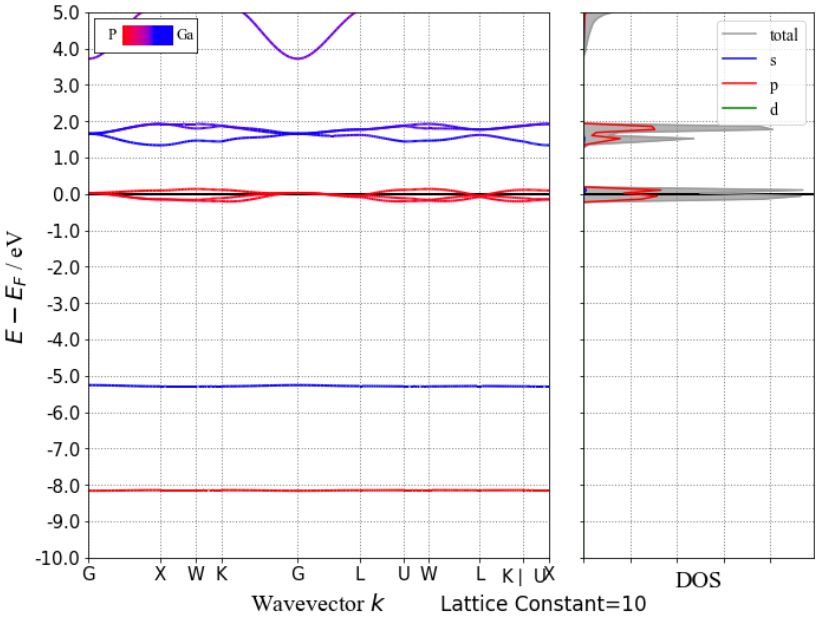

Figure 1: Lattice constant = 10Å

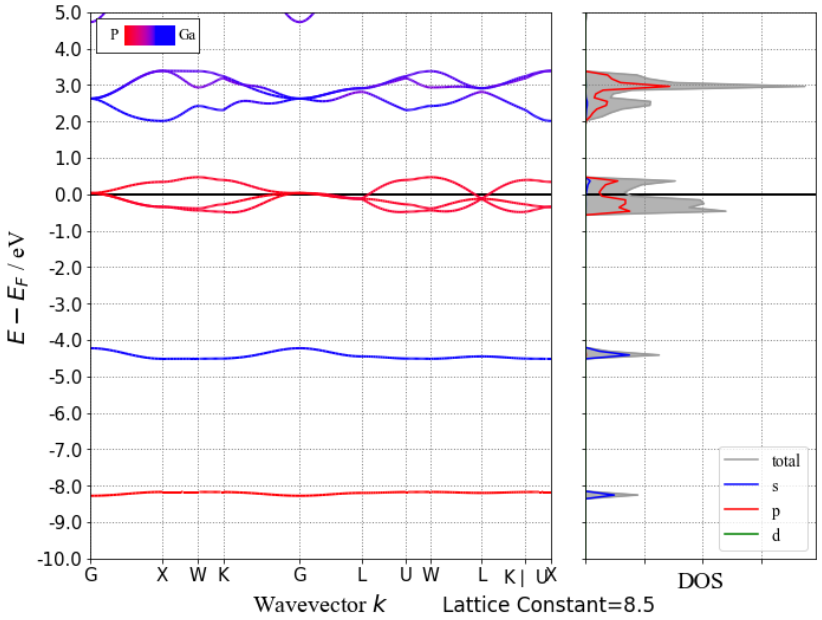

Figure 2: Lattice constant = 8.5Å

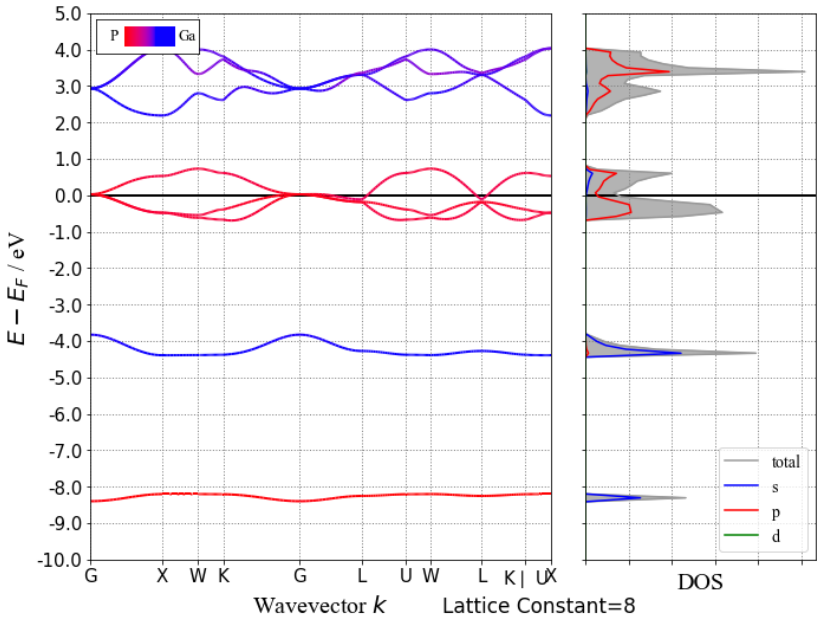

Figure 3: Lattice constant = 8Å

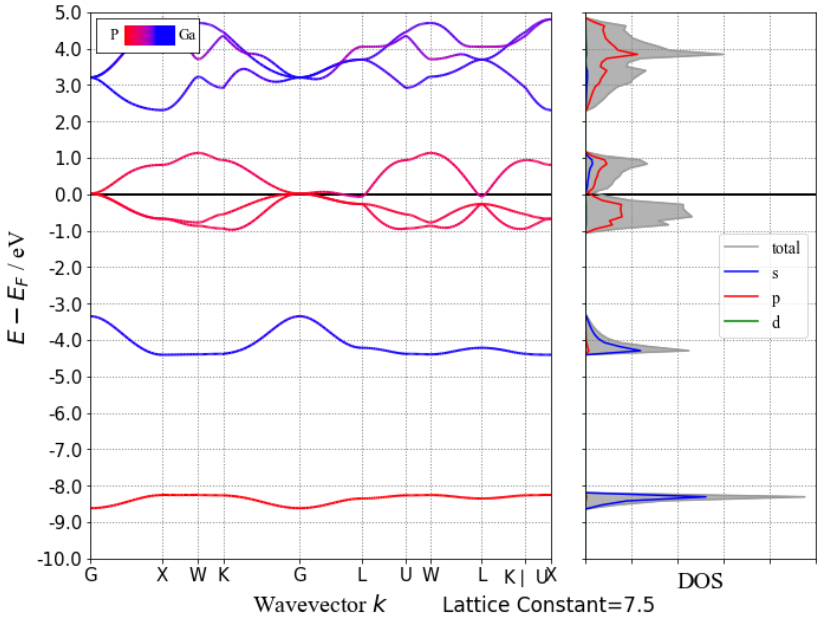

Figure 4: Lattice constant = 7.5Å

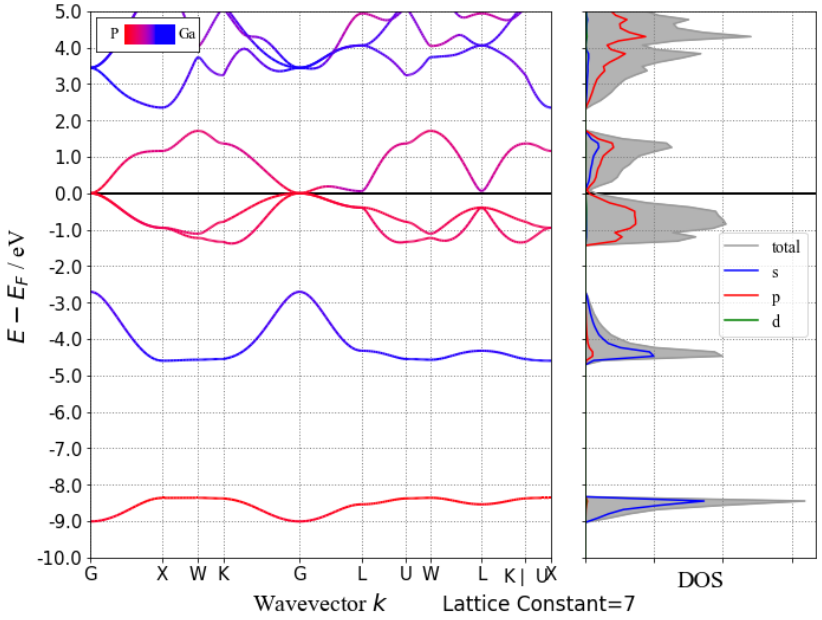

Figure 5: Lattice constant = 7Å

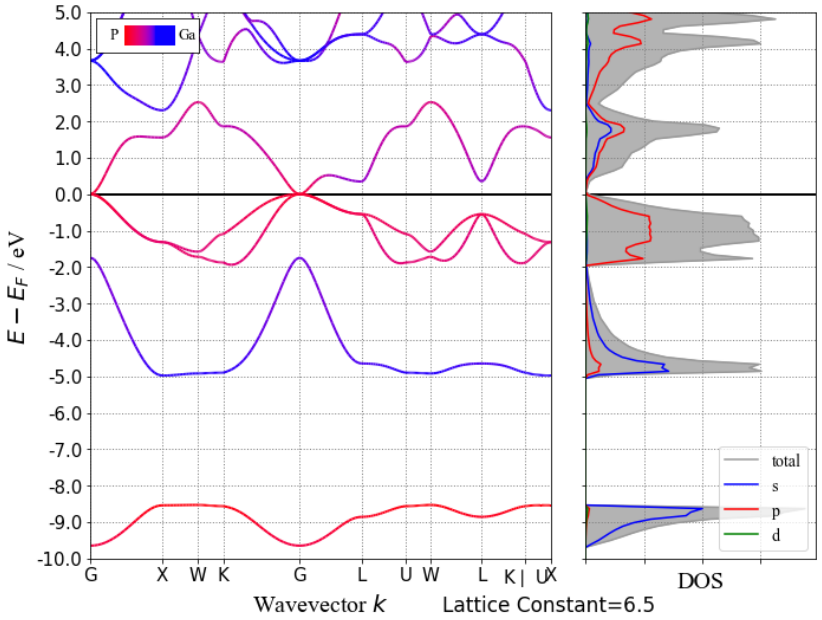

Figure 6: Lattice constant = 6.5Å

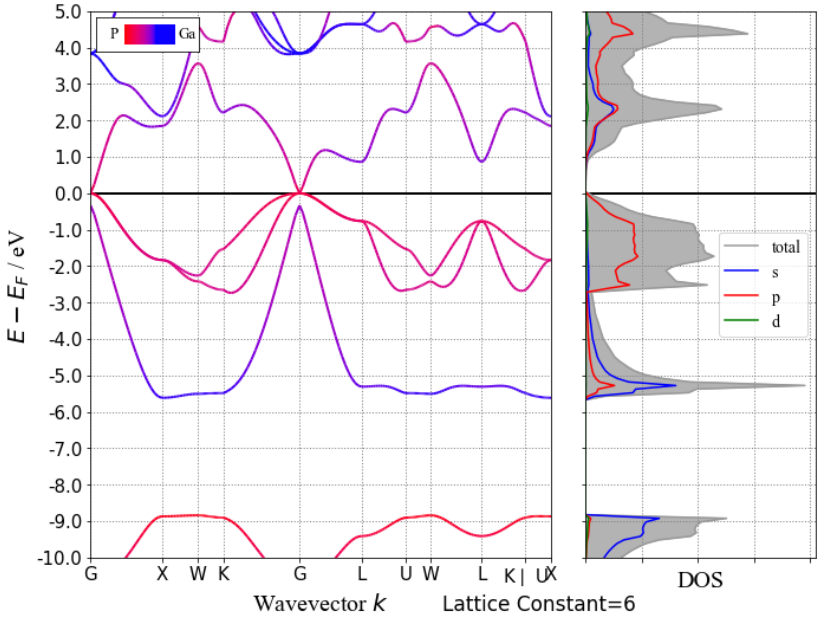

Figure 7: Lattice constant = 6Å

At long distance(10Å) Ga 4s orbital occupies around -5eV and P 3s occupies around -8eV. Around Fermi level are P 3p orbitals. At this very beginning, P orbitals already start to couple as they are outer orbitals. So the main question is where and how does s-p coupling happen. I'd like to analyze valence band and conduction band respectively.

For valence band, the interesting thing happens at about 8.5Å. From DOS we can find that tiny s orbital ingredients appears near fermi surface and Ga 4s orbital begin to 'rise' at Γ points in bandstructure plot. I assume that's the signal of s-p coupling. As we keep decreasing the distance, the process of sp coupling is like P 3p orbitals draging Ga 4s orbitals up. As for P 3s and Ga 4p orbitals, they don't couple until the atom distance is below 6.5Å.

When it comes to conduction band, things get a little bit complex. p-p orbital coupling exists all the time. P 3s orbital undergoes an interesting journel during the process. By virtue of bandstructure contribution plot(Figure 8,9,10),we can find that at about 7.5Å, P 3s orbital starts to couple with Ga 4s orbital and its influence goes up in energy plot as distance decrease. At about 6Åit reaches conduction band and starts to couple with Ga 4p orbitals. In real GaP crystal, P 3s play an important role in the lowest conduction band.

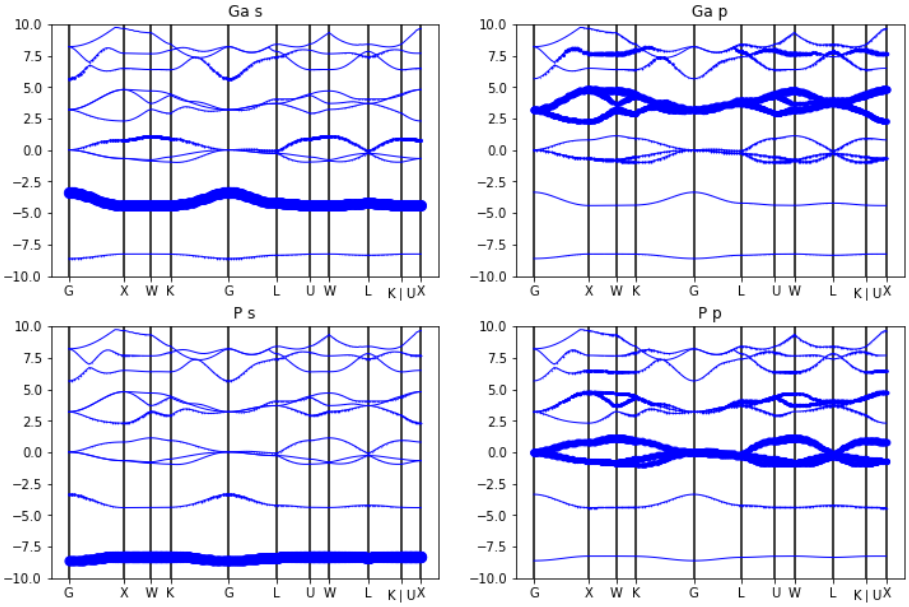

Figure 8: Band structure contribution when lattice constant = 7.5Å

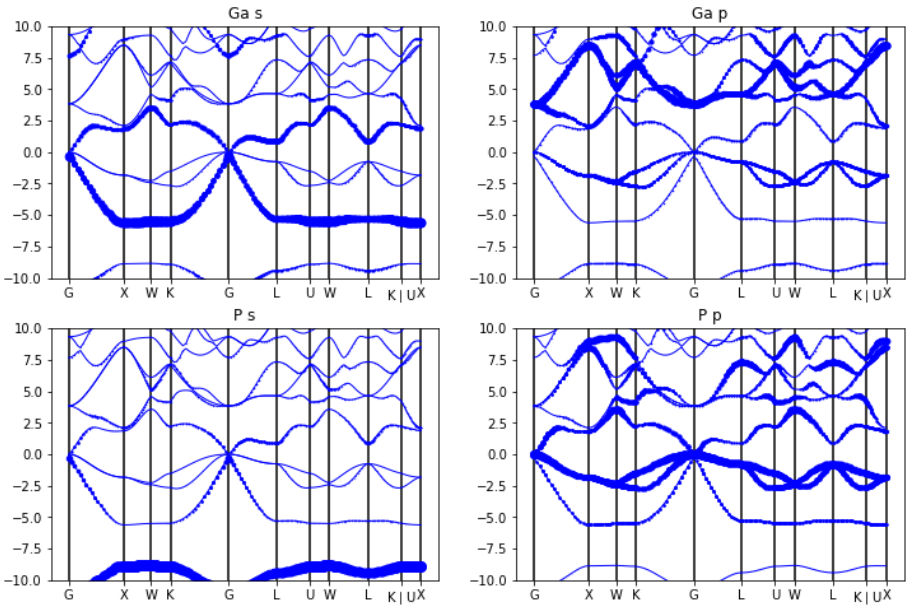

Figure 9: Band structure contribution when lattice constant = 6Å

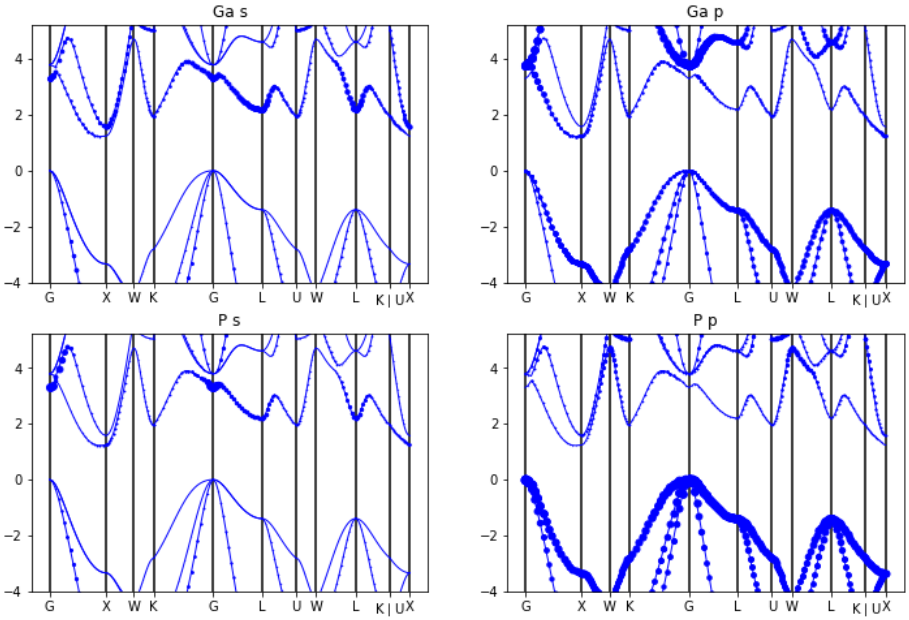

Figure 10: Band structure contribution in real GaP crystal

Another exciting thing is about Ga 3d orbitals. Its impact appears when lattice constant is under 6Åand dominate DOS plot.

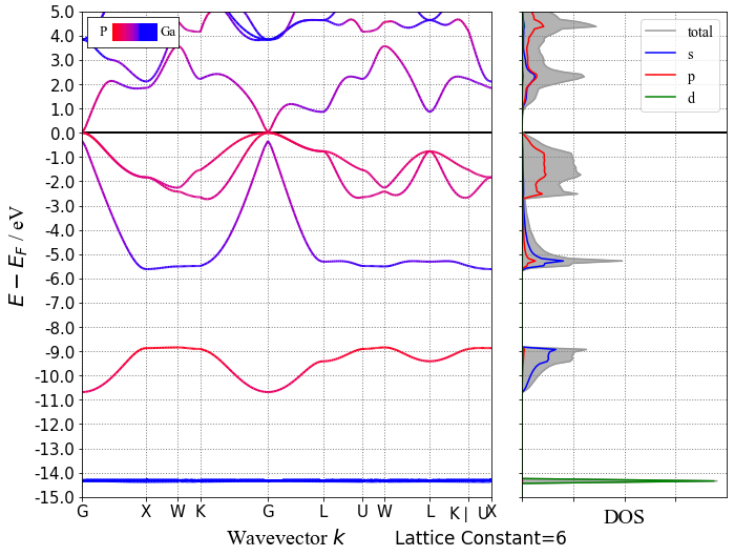

Figure 11: Lattice constant = 6Å

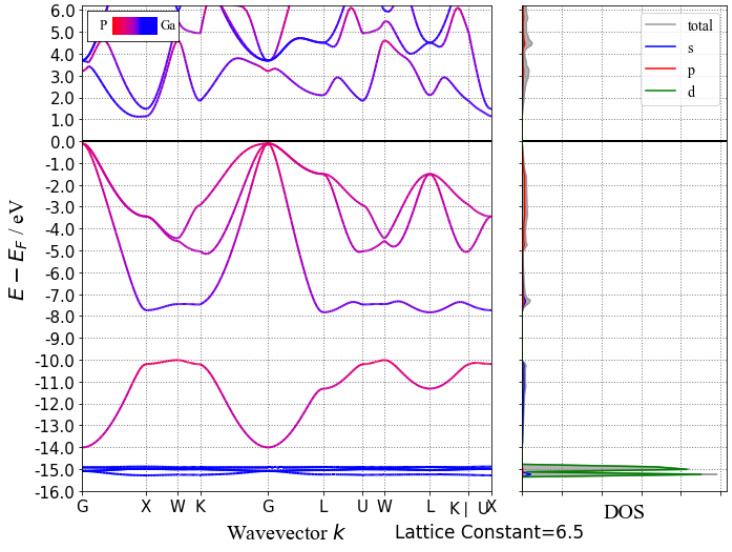

Figure 12: Lattice constant = 5.15Å

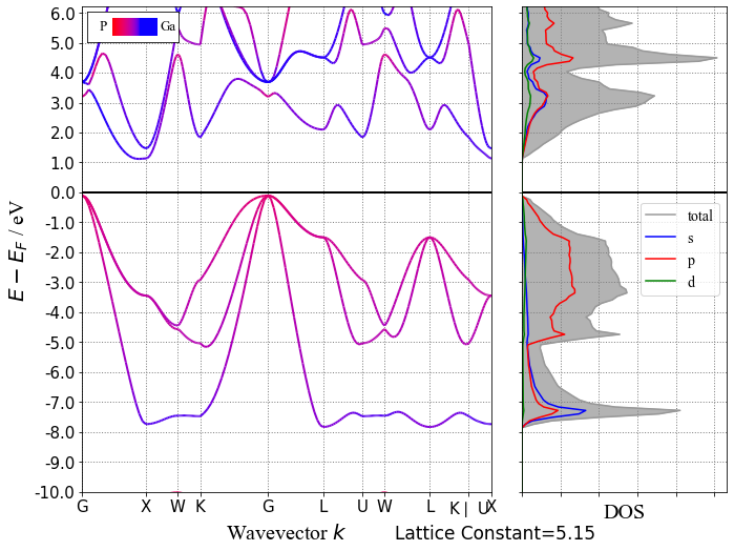

Figure 13: Lattice constant = 5.15Å

From bandstructure contribution(Figure 14) we can see that in real crystal d orbital mainly affect around X,K and L points, which push the conduction band energy levels at the X and L valley up, but leave the Γ-valley conduction state unchanged.(It would better to put a bandstructure without Ga d orbitals by comparsion).

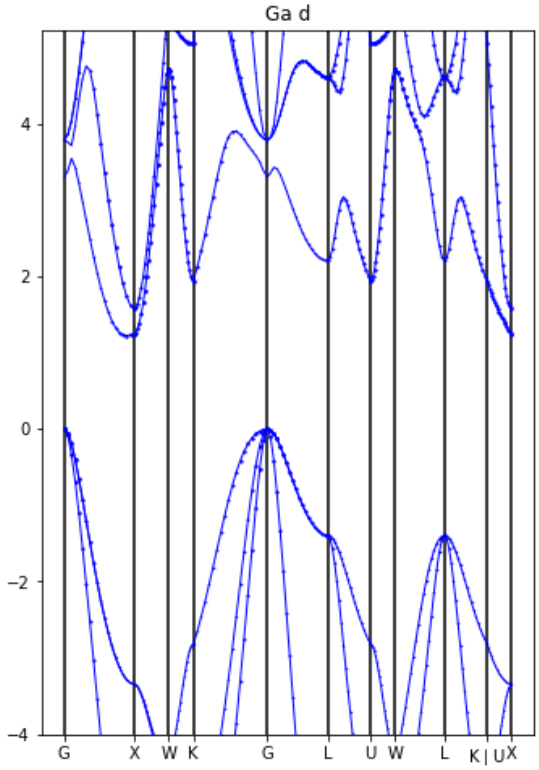

Figure 14: d orbital contribution in real GaP crystal

In summary, the following table could clearly show my observation. To study how the specific curve forms, I suppose these plots are not enough. Perhaps we should return to tight binding model.

Coupling orbitals	**Action scope(Å)**	**Main occupation**
Ga 4p - P 3p	from >10	conduction band
Ga 4s - P 3p	<8.5	valence band
Ga 4s - P 3s	<7.5,weaken when 4s-3p coupling happens	valence band
Ga 4p - P 3s	<6	conduction band
Ga 3d - P 3s 3p	<6	conduction band

1.2 AlAs

In GaP, 3d orbitals are in group 3 elements. What if 3d orbitals are in the group 5 elements? By comparsion I repeat the above analysis in AlAs. The

trend is similar to GaP so I will amalgamate them into an animation which is attached in the mail.

What needs special care is that even when lattice constant is down to 5Å(Figure 15) 3d orbitals still almost take part in no couplings which differs from GaP. I suppose it's becasue Group 5 elemnts have relatively higher electronegativity which makes it hard for d band electrons coupling with other orbitals. Combining this result with the fact that Al-Group 5 compounds are all indirect band gap semiconductors, we can naturally realize the importance of d orbitals on determining the band type of Group 3-5 compounds.

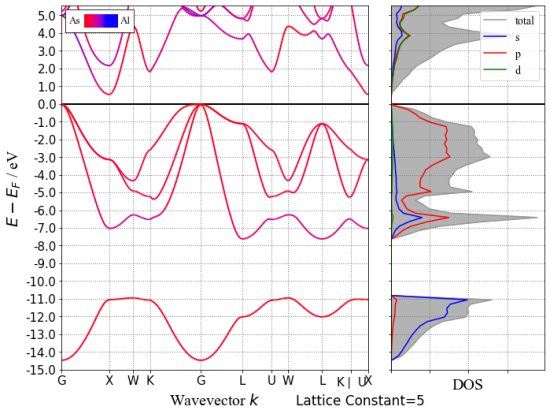

Figure 15: AlAs bandstructure and DOS when lattice constant = 5Å

2 Machine learning

On the other, I also try to use CGCNN model to classify band type. CGCNN is a numerical model so here I set direct band gap to be 1 and indirect band to be 0. Then I add a decision tree to post-process the results of the test set under some numerical standard(I'm not sure if this process is proper). Under 19445 data acquired from MP, the accuracy rate can be around 70% to 80% which basically accords with our estimation that it is relative but not precise enough. After we find some suitable features maybe we can combine them with CGCNN to improve the accuracy. The relatve files has been attached in the last email.