

Weekly Report

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1 Introduction

In the past two weeks, I've been focusing on raising some hypothesis about the derivation of indirect band gap. Besides, I also try to understand some complex tight binding models and topology to explore how to get real electronic bandstructure by PythTB.

2 Progress

2.1 Hypothesis

Up to now I come up with two hypothesis that have to do with indirect band gap:

2.1.1 Hypothesis I

When it comes to the structure or layer induced indirect-to-direct bandgap difference, different structures would contain different coupling between orbitals, which means introducing new terms like $V_{sd\sigma}$ (s-d couplings) in tight binding model. This additional term also varies along the high symmetry line and maybe appear different trends compared with previous ones. For instance, the additional term would be zero in Γ point but add a big minus value to X point in conduction band which changes the CBM from Γ to X . I think this effect would play a role more or less in the AlSb band type change due to structural difference. Besides, it's obvious in layer induced direct-to-indirect bandgap change. I will try to give a specific example to verify this assumption. As we can see in Figure 1, the MoS2 bandstructure suffer a direct-to-indirect change from monolayer to bilayer. The sharp shoulder in the DOS of the monolayer at the top of the valence band is quickly smoothed out as the number of layers is increased. I think it can be explained by orbital couplings between different layers. S would form new covalent bonds like $V_{pp\sigma}$ between the first and second layer. Perhaps Mo would also couple with S in the different layer and form $V_{pd\sigma}$ or $V_{sd\sigma}$ bonds. The details are remained to be explored in the next few weeks.

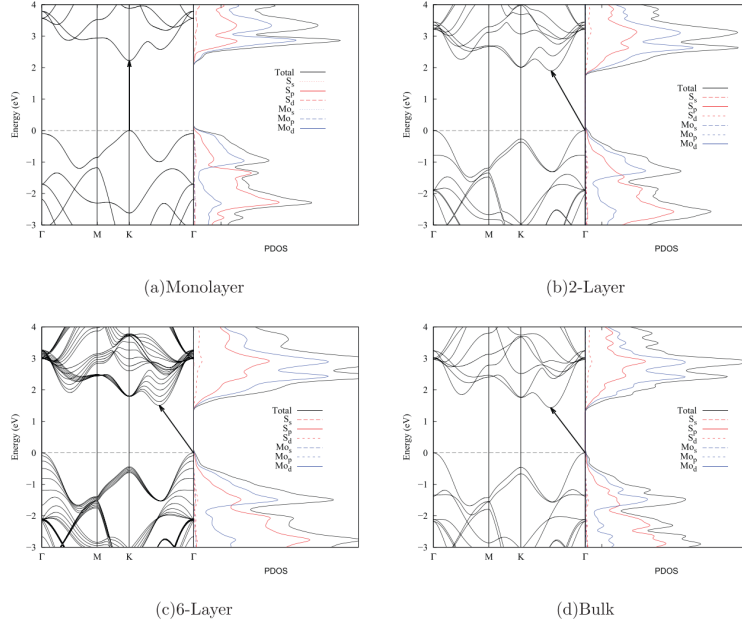


FIG. 2. (Color online) Band Structure for layered MoS_2 . The zero of the energy scale has been set to the top of the valence band, indicated with a horizontal dashed line. There is a strong shift in the valence band from the monolayer to the bilayer and the conduction band minimum along the $\mathbf{K} \rightarrow \Gamma$ line is increasingly shifted down with the addition of more layers.

Figure 1: MoS_2 bandstructure trends(via ref 1)

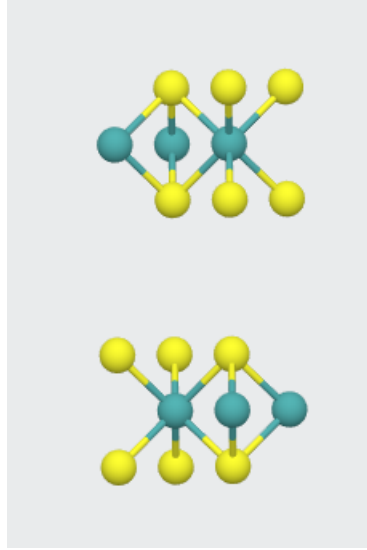


Figure 2: Layered MoS_2

2.1.2 Hypothesis II

The moderation of structure would destroy symmetry, which results in the split of high degeneracy state. I think we can explore it by first analyzing the topology of the bands in direct or indirect bands. So now I'm learning some topology insulators to see if I can find something interesting.

2.2 PythTB

I have tried to reproduce the practice in PythTB official document in the past weeks, but it is still far from real bandstructure. After some meaningless experiments, I think I'd better return to tight bindings model to get a better understanding about 'hopping' in PythTB. Hopping is a second quantization form to express orbital couplings in a concise way. First we should get bond integrals between two orbitals, such as $V_{pd\sigma}$ or $V_{sd\sigma}$. Then interatomic matrix elements can be calculated as Figure 3 shows. And Hamiltonian can be expressed as a matrix of those elements. For each k in k -space the eigenvalues is exactly the eigenvalues of the matrix. Theoretically, if we take all the atomic orbitals into account and calculate the matrix elements, we can get the indirect bandgap. Take *AlSb* for example. First we should check the bond integral for Al and Sb. Then we analyze which interatomic matrix elements should be included. Maybe we should try different couplings to fit the bandstructure, so it will be a really time-consuming work. What's more, I'm afraid that this work would easily turn to a curve fitting problem, so it's a challenge to always keep the physical explanations in mind. I'd like to discuss this point in detail at meeting.

3 Summary

These two weeks I mainly think about how to raise meaningful hypothesis and learn tight binding models. In fact up to now I don't think I can reach the state which Prof. Sun mentioned in the meeting. At first I just stared at the *AlSb* bandstructure and think of nothing. Only when reading some papers or books can I get some inspirations. There is still a long way to go.

4 Reference

1. Jason K. Ellis, Melissa J. Lucero,¹ and Gustavo E. Scuseria, Appl. Phys. Lett. 99, 261908 (2011); <https://doi.org/10.1063/1.3672219>

$$\begin{aligned}
E_{s,s} &= V_{ss\sigma} \\
E_{s,x} &= lV_{sp\sigma} \\
E_{x,x} &= l^2V_{pp\sigma} + (1-l^2)V_{pp\pi} \\
E_{x,y} &= lmV_{pp\sigma} - lmV_{pp\pi} \\
E_{x,z} &= lnV_{pp\sigma} - lnV_{pp\pi} \\
E_{s,xy} &= \sqrt{3}lmV_{sd\sigma} \\
E_{s,x^2-y^2} &= \frac{\sqrt{3}}{2}(l^2-m^2)V_{sd\sigma} \\
E_{s,3z^2-r^2} &= [n^2-(l^2+m^2)/2]V_{sd\sigma} \\
E_{x,xy} &= \sqrt{3}l^2mV_{pd\sigma} + m(1-2l^2)V_{pd\pi} \\
E_{x,yz} &= \sqrt{3}lmnV_{pd\sigma} - 2lmnV_{pd\pi} \\
E_{x,zx} &= \sqrt{3}l^2nV_{pd\sigma} + n(1-2l^2)V_{pd\pi} \\
E_{x,x^2-y^2} &= \frac{\sqrt{3}}{2}l(l^2-m^2)V_{pd\sigma} + l(1-l^2+m^2)V_{pd\pi} \\
E_{y,x^2-y^2} &= \frac{\sqrt{3}}{2}m(l^2-m^2)V_{pd\sigma} - m(1+l^2-m^2)V_{pd\pi} \\
E_{z,x^2-y^2} &= \frac{\sqrt{3}}{2}n(l^2-m^2)V_{pd\sigma} - n(l^2-m^2)V_{pd\pi} \\
E_{x,3z^2-r^2} &= l[n^2-(l^2+m^2)/2]V_{pd\sigma} - \sqrt{3}ln^2V_{pd\pi} \\
E_{y,3z^2-r^2} &= m[n^2-(l^2+m^2)/2]V_{pd\sigma} - \sqrt{3}mn^2V_{pd\pi} \\
E_{z,3z^2-r^2} &= n[n^2-(l^2+m^2)/2]V_{pd\sigma} + \sqrt{3}n(l^2+m^2)V_{pd\pi} \\
E_{xy,xy} &= 3l^2m^2V_{dd\sigma} + (l^2+m^2-4l^2m^2)V_{dd\pi} + (n^2+l^2m^2)V_{dd\delta} \\
E_{xy,yz} &= 3lm^2nV_{dd\sigma} + ln(1-4m^2)V_{dd\pi} + ln(m^2-1)V_{dd\delta} \\
E_{xy,zx} &= 3l^2mnV_{dd\sigma} + mn(1-4l^2)V_{dd\pi} + mn(l^2-1)V_{dd\delta} \\
E_{xy,x^2-y^2} &= \frac{3}{2}lm(l^2-m^2)V_{dd\sigma} + 2lm(m^2-l^2)V_{dd\pi} + [lm(l^2-m^2)/2]V_{dd\delta} \\
E_{yz,x^2-y^2} &= \frac{3}{2}mn(l^2-m^2)V_{dd\sigma} - mn[1+2(l^2-m^2)]V_{dd\pi} + mn[1+(l^2-m^2)/2]V_{dd\delta} \\
E_{zx,x^2-y^2} &= \frac{3}{2}nl(l^2-m^2)V_{dd\sigma} + nl[1-2(l^2-m^2)]V_{dd\pi} - nl[1-(l^2-m^2)/2]V_{dd\delta} \\
E_{xy,3z^2-r^2} &= \sqrt{3} [lm(n^2-(l^2+m^2)/2)]V_{dd\sigma} - 2lmn^2V_{dd\pi} + [lm(1+n^2)/2]V_{dd\delta} \\
E_{yz,3z^2-r^2} &= \sqrt{3} [mn(n^2-(l^2+m^2)/2)]V_{dd\sigma} + mn(l^2+m^2-n^2)V_{dd\pi} - [mn(l^2+m^2)/2]V_{dd\delta} \\
E_{zx,3z^2-r^2} &= \sqrt{3} [ln(n^2-(l^2+m^2)/2)]V_{dd\sigma} + ln(l^2+m^2-n^2)V_{dd\pi} - [ln(l^2+m^2)/2]V_{dd\delta} \\
E_{x^2-y^2,x^2-y^2} &= \frac{3}{4}(l^2-m^2)^2V_{dd\sigma} + [l^2+m^2-(l^2-m^2)^2]V_{dd\pi} + [n^2+(l^2-m^2)^2/4]V_{dd\delta} \\
E_{x^2-y^2,3z^2-r^2} &= \sqrt{3} [(l^2-m^2)[n^2-(l^2+m^2)/2]V_{dd\sigma}/2 + n^2(m^2-l^2)V_{dd\pi} + [(1+n^2)(l^2-m^2)/4]V_{dd\delta}] \\
E_{3z^2-r^2,3z^2-r^2} &= [n^2-(l^2+m^2)/2]^2V_{dd\sigma} + 3n^2(l^2+m^2)V_{dd\pi} + \frac{3}{4}(l^2+m^2)^2V_{dd\delta}
\end{aligned}$$

Figure 3: Interatomic matrix elements(via Wikipedia)