Weekly Report

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1 Introduction

This week I mainly focus on understanding how real space variation influences on hopping parameter and why PythTB cannot simulate real band structure. Some progress have been made and some questions come along the way.

2 Progress

2.1 real space variation and hopping parameters

First, I try to use PythTB to simulate band structure as real as possible. Considering the failure of simulating advanced tight binding model, I choose the simple tight binding model of zinc-blende structure group III-V compounds which is proposed in Reference 1. Figure 1 is the specific model.

By specifying the hopping we get the PythTB model. Here I use the parameters of GaAs. For comparison I list the results showed in Reference in the right. We can see that PythTB could reflect the basic features but fail to totally repeat the band structure. I think perhaps that's my fault when setting the inter lattice hopping but this should be enough for furthur study.

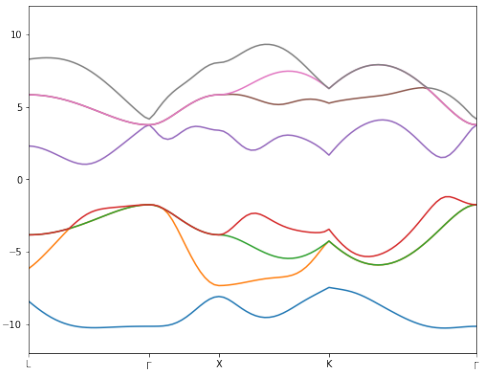


Figure 2: GaAs PythTB results

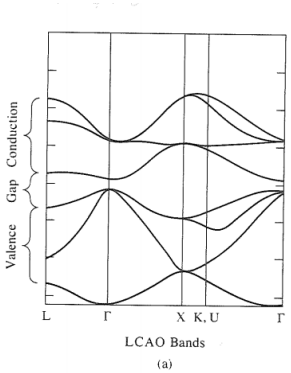
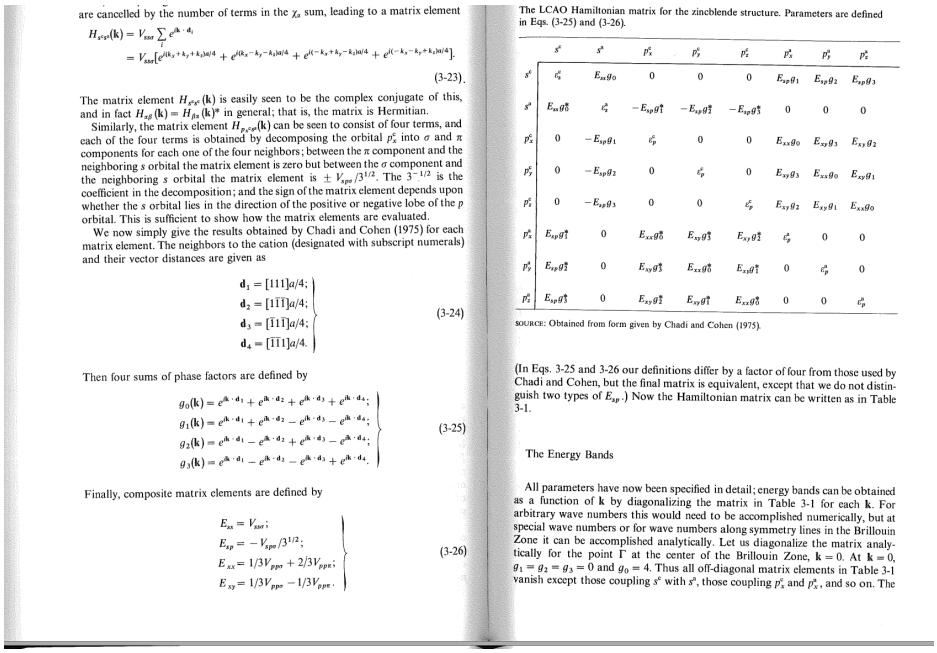


Figure 3: GaAs LCAO results



are cancelled by the number of terms in the χ_n sum, leading to a matrix element

$$H_{s^c s^a}(\mathbf{k}) = V_{sss} \sum_i e^{i\mathbf{k}\cdot\mathbf{d}_i}$$
$$= V_{sss}[e^{i(k_x+k_y+k_z)a/4} + e^{i(k_x-k_y-k_z)a/4} + e^{i(-k_x+k_y-k_z)a/4} + e^{i(-k_x-k_y+k_z)a/4}]. \quad (3\text{-}23)$$

The matrix element $H_{s^a s^c}(\mathbf{k})$ is easily seen to be the complex conjugate of this, and in fact $H_{s\beta}(\mathbf{k}) = H_{\beta s}(\mathbf{k})^*$ in general; that is, the matrix is Hermitian.

Similarly, the matrix element $H_{p_x s^a}(\mathbf{k})$ can be seen to consist of four terms, and each of the four terms is obtained by decomposing the orbital p_x^c into σ and π components for each one of the four neighbors; between the π component and the neighboring s orbital the matrix element is zero but between the σ component and the neighboring s orbital the matrix element is $\pm V_{sp\sigma}/3^{1/2}$. The $3^{-1/2}$ is the coefficient in the decomposition; and the sign of the matrix element depends upon whether the s orbital lies in the direction of the positive or negative lobe of the p orbital. This is sufficient to show how the matrix elements are evaluated.

We now simply give the results obtained by Chadi and Cohen (1975) for each matrix element. The neighbors to the cation (designated with subscript numerals) and their vector distances are given as

$$\left.\begin{aligned} \mathbf{d}_1 &= [111]a/4; \\ \mathbf{d}_2 &= [1\bar{1}\bar{1}]a/4; \\ \mathbf{d}_3 &= [\bar{1}1\bar{1}]a/4; \\ \mathbf{d}_4 &= [\bar{1}\bar{1}1]a/4. \end{aligned}\right\} \quad (3\text{-}24)$$

Then four sums of phase factors are defined by

$$\left.\begin{aligned} g_0(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{d}_1} + e^{i\mathbf{k}\cdot\mathbf{d}_2} + e^{i\mathbf{k}\cdot\mathbf{d}_3} + e^{i\mathbf{k}\cdot\mathbf{d}_4}; \\ g_1(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{d}_1} + e^{i\mathbf{k}\cdot\mathbf{d}_2} - e^{i\mathbf{k}\cdot\mathbf{d}_3} - e^{i\mathbf{k}\cdot\mathbf{d}_4}; \\ g_2(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{d}_1} - e^{i\mathbf{k}\cdot\mathbf{d}_2} + e^{i\mathbf{k}\cdot\mathbf{d}_3} - e^{i\mathbf{k}\cdot\mathbf{d}_4}; \\ g_3(\mathbf{k}) &= e^{i\mathbf{k}\cdot\mathbf{d}_1} - e^{i\mathbf{k}\cdot\mathbf{d}_2} - e^{i\mathbf{k}\cdot\mathbf{d}_3} + e^{i\mathbf{k}\cdot\mathbf{d}_4}. \end{aligned}\right\} \quad (3\text{-}25)$$

Finally, composite matrix elements are defined by

$$\left.\begin{aligned} E_{ss} &= V_{sss}; \\ E_{xp} &= -V_{sp\sigma}/3^{1/2}; \\ E_{xx} &= 1/3V_{pp\sigma} + 2/3V_{pp\pi}; \\ E_{xy} &= 1/3V_{pp\sigma} - 1/3V_{pp\pi}. \end{aligned}\right\} \quad (3\text{-}26)$$

The LCAO Hamiltonian matrix for the zincblende structure. Parameters are defined in Eqs. (3-25) and (3-26).

	s^c	s^a	p_x^c	p_y^c	p_z^c	p_x^a	p_y^a	p_z^a
s^c	ε_s^c	$E_{ss}g_0$	0	0	0	$E_{xp}g_1$	$E_{xp}g_2$	$E_{xp}g_3$
s^a	$E_{ss}g_0^*$	ε_s^a	$-E_{xp}g_1^*$	$-E_{xp}g_2^*$	$-E_{xp}g_3^*$	0	0	0
p_x^c	0	$-E_{xp}g_1$	ε_p^c	0	0	$E_{xx}g_0$	$E_{xy}g_3$	$E_{xy}g_2$
p_y^c	0	$-E_{xp}g_2$	0	ε_p^c	0	$E_{xy}g_3$	$E_{xx}g_0$	$E_{xy}g_1$
p_z^c	0	$-E_{xp}g_3$	0	0	ε_p^c	$E_{xy}g_2$	$E_{xy}g_1$	$E_{xx}g_0$
p_x^a	$E_{xp}g_1^*$	0	$E_{xx}g_0^*$	$E_{xy}g_3^*$	$E_{xy}g_2^*$	ε_p^a	0	0
p_y^a	$E_{xp}g_2^*$	0	$E_{xy}g_3^*$	$E_{xx}g_0^*$	$E_{xy}g_1^*$	0	ε_p^a	0
p_z^a	$E_{xp}g_3^*$	0	$E_{xy}g_2^*$	$E_{xy}g_1^*$	$E_{xx}g_0^*$	0	0	ε_p^a

SOURCE: Obtained from form given by Chadi and Cohen (1975).

(In Eqs. 3-25 and 3-26 our definitions differ by a factor of four from those used by Chadi and Cohen, but the final matrix is equivalent, except that we do not distinguish two types of E_{xp}.) Now the Hamiltonian matrix can be written as in Table 3-1.

The Energy Bands

All parameters have now been specified in detail; energy bands can be obtained as a function of $\mathbf{k}$ by diagonalizing the matrix in Table 3-1 for each $\mathbf{k}$. For arbitrary wave numbers this would need to be accomplished numerically, but at special wave numbers or for wave numbers along symmetry lines in the Brillouin Zone it can be accomplished analytically. Let us diagonalize the matrix analytically for the point Γ at the center of the Brillouin Zone, $\mathbf{k} = 0$. At $\mathbf{k} = 0$, $g_1 = g_2 = g_3 = 0$ and $g_0 = 4$. Thus all off-diagonal matrix elements in Table 3-1 vanish except those coupling s^c with s^a, those coupling p_x^c and p_x^a, and so on. The

Figure 1: Tight binding model of zinc-blende structure group III-V compounds(upper right), some parameters are illustrated in the left page

In the interactive picture, we can see the indirect to direct bandgap change by draging the button. In order to explain the phenomenon, I review the tight binding model theory. This time I find that the relationship between real space variation and hopping parameters is not that hard to be understood. First, there are some fixed parameters between orbital couplings such as $V_{sp\sigma}$, $V_{sp\pi}$ and so on. They are determined by the type of oribitals which are invarible in any material. Then there are two factors that have to do with the hopping parameters. One is the distance of these two oribitals which can be described as a function of d. Usually it appears in d^{-2} scaling like $\frac{V_{sp\sigma}}{d^2}$. That's how lattice constants affect the hopping parameters. The other one is the angle between these two orbitals. We know that σ or π refers to different direction of s and p ortibals. In real situation, if the angle is not exactly the same angle of σ or π, the hopping parameters would be a mixture of them just like the Figure 4 shows. That's how lattice strutcures affect the hopping parameters.

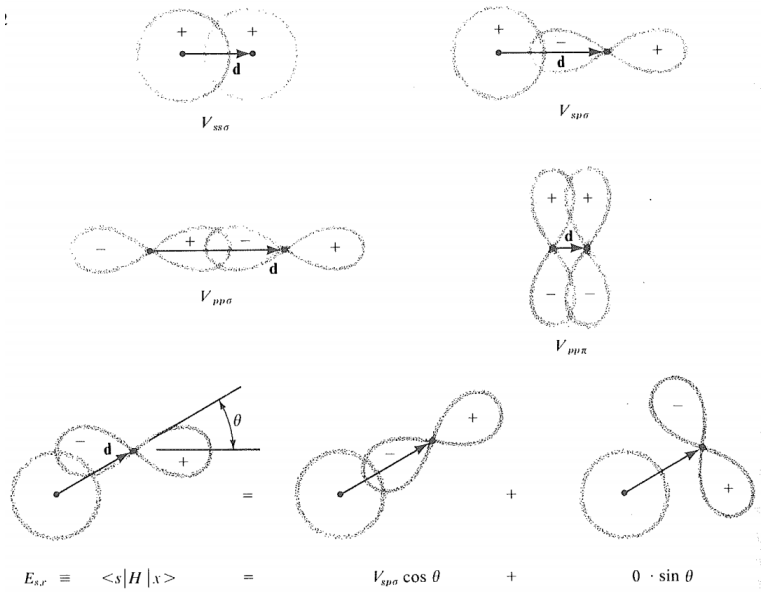


Figure 4: Oribital couplings(from Reference 1)

To some extent I think the question has been answered. So now we come to the question that can we change the hopping parameters in interactive picture in order to find what hopping parameters contribute most to indirect band gap and relate it to real space interaction? From my point of view, it will be very hard to be done. Figure 5 shows some of the hopping parameters of group III-V compounds. We can see that all the parameters suffer a change when the bond length, which means it is almost impossible to extract what are important ones and the band structure change is a co-reaction of all the hopping parameters. To see the contribution of different orbitals, maybe we'd better turn to vasp calculation to see band structure contribution instead of tight binding model.

bond	Si-Si	Ge-Ge	Ge-Si	Al-P	Al-As	Al-Sb	Ga-P	Ga-As	Ga-Sb	In-P	In-As	In-Sb
$V_{s_c s_a \sigma}$	-1.7377	-1.7530	-1.7411	-1.7682	-1.8219	-2.1063	-1.7010	-1.7842	-2.0232	-1.9110	-1.9667	-2.2797
$V_{s_c^* s_a^* \sigma}$	-4.2881	-4.4947	-4.6183	-4.0139	-4.3097	-4.2962	-4.1464	-4.3164	-4.2066	-3.7944	-4.2049	-4.1696
$V_{s_c s_a^* \sigma}$	-1.7587	-1.4865	-1.6734	-2.0131	-2.0242	-1.8153	-1.8778	-1.8820	-1.7410	-2.2047	-2.1482	-1.8748
$V_{s_c p_a \sigma}$	2.9260	2.9146	2.8349	2.9402	3.1045	3.3534	2.8997	2.9935	3.2439	3.0736	3.2715	3.5395
$V_{s_c^* p_a \sigma}$	2.5379	2.3919	2.5087	2.1206	2.1783	2.2283	2.0854	2.1256	2.4986	2.2361	2.2493	2.2701
$V_{s_c d_a \sigma}$	-2.0901	-1.9432	-2.2045	-2.2681	-2.2634	-2.4048	-2.2303	-2.1456	-2.2758	-2.2543	-2.2986	-2.4392
$V_{s_c^* d_a \sigma}$	-0.1627	-0.1556	-0.2007	-0.3042	-0.3051	-0.3387	-0.2808	-0.2812	-0.1848	-0.3446	-0.2867	-0.1813
$V_{p_c p_a \sigma}$	3.7002	3.8013	3.6856	3.5838	3.7366	4.1011	3.5451	3.7312	4.1685	3.6073	3.9261	4.2661
$V_{p_c p_a \pi}$	-1.2896	-1.3517	-1.2686	-1.2121	-1.3318	-1.6433	-1.1631	-1.2992	-1.5846	-1.2755	-1.4074	-1.7708
$V_{p_c d_a \sigma}$	-0.9729	-0.7001	-1.0464	-0.7139	-0.6818	-0.9318	-0.8561	-0.7416	-1.1356	-0.5488	-0.6025	-0.9446
$V_{p_c d_a \pi}$	2.1919	2.1684	1.9985	2.2351	2.2795	2.4007	2.1997	2.2874	2.3716	2.2517	2.2879	2.4045
$V_{d_c d_a \sigma}$	-0.9507	-0.4385	-0.3279	-0.9666	-0.7343	-0.7374	-0.4721	-0.4906	-0.5153	-0.4615	-0.4708	-0.6675
$V_{d_c d_a \pi}$	1.8412	1.5738	1.6931	1.9252	1.8295	1.7864	1.5643	1.4887	1.6402	1.6186	1.6103	1.7524
$V_{d_c d_a \delta}$	-1.3776	-1.6745	-1.6394	-1.5266	-1.6782	-1.8053	-1.4702	-1.6107	-1.8241	-1.6310	-1.8837	-2.0733
$V_{s_a s_c^* \sigma}$			-1.5824	-1.2241	-1.2520	-1.5371	-1.1986	-1.1588	-1.6281	-1.1401	-1.1581	-1.3964
$V_{s_a p_c \sigma}$			2.8553	2.5861	2.5919	2.9884	2.6045	2.7008	3.0092	2.5465	2.6184	3.0903
$V_{s_a^* p_c \sigma}$			2.0593	2.6252	2.6105	2.5435	2.6205	2.5674	2.2691	2.6249	2.6070	2.3266
$V_{s_a d_c \sigma}$			-2.2859	-2.1557	-2.1862	-2.0941	-1.7346	-1.9422	-2.1687	-1.6800	-1.7252	-2.0149
$V_{s_a^* d_c \sigma}$			-0.3354	-0.5445	-0.4197	-0.2418	-0.4906	-0.3828	-0.3829	-0.7584	-0.4789	-0.3659
$V_{p_a d_c \sigma}$			-0.9837	-1.2443	-1.1628	-0.9421	-0.7510	-0.6656	-0.3859	-0.5816	-0.5791	-0.3351
$V_{p_a d_c \pi}$			2.0199	1.8639	1.9673	2.0986	1.8737	2.0486	2.1917	1.8626	1.9421	2.0716

Figure 5: Bond length dependent interactomic coupling parameters for group IV and III-V materials(from Reference 3)

2.2 PythTB

In this section I want to restate why PythTB cannot simulate real band structure. In advanced tight binding model, usually there is more than one parameter in a single element of the Hamiltonian matrix. For example, in the following expression $V_{\alpha_i}\beta_j|m|$ and $\eta_{\alpha_i\beta_j}$ are two variables that need to be specified(from Reference 3).

$$V_{\alpha_i\beta_j|m|}\left(d_{ij}\right) = V_{\alpha_i\beta_j|m|}e^{-\eta_{\alpha_i\beta_j|m|}(d_{ij}+\delta d_{ij}-d_0)} \tag{2.1}$$

I don't quite understand the meaning of $\eta_{\alpha_i\beta_j}$. In some paper they just treat it as a fitting parameter to make it adjust to experimental results. Perhaps it is taken to reproduce the slope of the Harrison's d^{-2} scaling law. Anyway PythTB only provides one parameters in the 'set_hop' functions so it cannot simulate advanced tight binding model. In addition, I notice that in some model the author raises off-diagonal onsite elements or some other complex term, which seems hard to take advantages of existing tools. Besides, I try to contact the author of PythTB but I'm not sure if I get what Prof. Vanderbilt means. I will forward the mail to you.

3 Summary

Up to now, I assume that I have get a understanding of the relationship of tight binding model and indirect band gap. It's time to think about what applications can we use tight binding model to do and if it is a proper tools for

researching indirect band gap. Besides, I find a website that offers tight binding model fitting services, but it is not free. Maybe it will be helpful if we continue using tight binding model. https://www.nanoacademic.com/product-page/ddpy

4 Reference

1. Walter A. Harrison - Electronic Structure and the Properties of Solids
2. E. Cappelluti, R. Rold´an, J. A. Silva-Guill´en, P. Ordej´on, and F. Guinea1, Tight-binding model and direct-gap/indirect-gap transition in single-layer and multilayer MoS2, DOI:10.1103/PhysRevB.88.075409
3. Yaohua Tan, Michael Povolotskyi, Tillmann Kubis, Timothy B. Boykin, and Gerhard Klimeck, Transferable tight-binding model for strained group IV and III-V materials and heterostructures, DOI:10.1103/PhysRevB.94.045311