Orbital dependent band degeneracy and edge states in single layer and AA bilayer honeycomb lattice systems with p orbital degeneracy

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Abstract
We have investigated band structure and edge states of single and AA bilayer honeycomb lattice systems with p orbital degeneracy which would be relevant for relatively heavy metals such as Pb and Bi. The p electrons, which are triply degenerate in the atomic limit, form quadruple degeneracy at K point in a single layer honeycomb lattice. The spin-orbit interaction splits the quartet at K point into two singlets and one doublet which are mixtures of px, py, and pz orbitals. In the AA bilayer honeycomb lattice, the Dirac node at K point is deformed into circular line node around it. With the intermediate interlayer coupling, there is a degenerate point along Γ⁻K with pz character. A px/pz type degenerate point exists under the strong interlayer coupling. This degenerate point is robust against the spin-orbit interaction and the antiferromagnetic spin arrangement only along the intralayer bonds. Without SOI, localized edge states with px, pz or pz character are created at the zigzag edges both in the single and AA bilayer systems. In the AA bilayer system with SOI, only the px/pz edge states exhibit the Dirac-like dispersion.

1. Introduction
Since the experimental realization of graphene [1] and the theoretical discovery of quantum spin Hall effect in Kane-Mele model [2], the band structure of honeycomb lattice layers has been attracting great interest. The honeycomb lattice harbors Dirac fermions which generate various fascinating physical properties of graphene [3] and two-dimensional topological insulators [4]. On the basis of ground breaking studies on graphene [1, 3], bilayer graphene systems have been explored theoretically and experimentally [5–8]. More recently, the discovery of correlated insulating states and superconductivity in twisted bilayer graphene [9–11] have ignited intensive research activities on twisted bilayer systems [12–23].

Apart from the twisted systems, there are two kinds of graphene bilayer systems which are AA bilayer and AB bilayer [6]. In the AA bilayer graphene, all the carbon atoms of the top layers are located above the carbon atoms of the bottom layer. The AB bilayer graphene where only half of the carbon atoms of the top layer is located above the carbon atoms of the bottom layer, is stable and has been well studied experimentally. Compared to the AB bilayer graphene, electronic structure of AA bilayer systems is less studied. In addition, there is an interesting possibility that atoms along the stacking direction form a A-A dimer and the dimers are arranged in a honeycomb lattice.

In graphene systems, the carbon 2px and 2py orbitals are involved in the sp² hybrids and do not contribute to the conduction bands. In the theoretical models for graphene systems, only the 2px orbitals are considered to discuss the band structure near the Fermi level. Honeycomb lattice layers can be formed by other group 14 elements including Si, Ge, Sn, and Pb. The single honeycomb lattice layers of Si and Ge are known as silicene and germanene, respectively [24–30]. As pointed out in the pioneering work by Takeda and Shiraishi [24], the Si and Ge layer tends to be corrugated indicating that 3s and 4s orbitals play important roles with the tendency to form sp³ hybrids with the 3p and 4p orbitals. The single honeycomb lattice layers of heavier group 14 elements Sn and Pb are known as stanene and plumbene, respectively [31–41]. As analyzed by Liu et al [25], Kaloni et al [35], and
Hattori et al [36, 37], the corrugation also plays important roles in the Sn and Pb systems. On the other hand, in the heaviest Pb system, the 6px and 6py orbitals tend not to form sp3 or sp2 hybrids due to the contraction of the 6s orbital caused by the relativistic Darwin term. Consequently, the px and py orbitals contribute to the electronic states near the Fermi level [39, 40]. In addition to the Pb system, the band structure of BiS2 based superconductors can be well described by a tight binding model of the 6p orbitals [42, 43]. The corrugation would be suppressed and the degeneracy of p orbitals are relatively rare. However, it would be interesting to explore a possible interplay between the atomic orbital degeneracy and the band structure of the honeycomb lattice. In addition, the AA bilayer can be viewed as a honeycomb lattice of the A-A molecule which might be realized by molecule adsorption on a metal surface. Partly because of the lack of corresponding materials, theoretical studies on tight binding models with triply degenerate p orbitals are relatively rare.

In the present work, we investigate electronic structure of single layer and AA stacked bilayer honeycomb lattice systems with px, py, and pz orbitals. The model systems without corrugation would be relevant for honeycomb lattice layers of Bi which are not realized yet. The present calculations indicate that bulk Dirac states and edge states can be formed which are associated with the degeneracy of px and py orbitals.

2. Model Hamiltonian

We use tight-binding models for single layer and AA bilayer honeycomb lattice systems which include the three orbitals per site. We consider in-plane nearest neighbor and interplane hopping. The Hamiltonian is

$$H_{\text{hop}} = \sum_{i,j \sigma} v_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \sum_{i \sigma} t_{\sigma\sigma'}(a_{i\sigma} b_{i\sigma'} + b_{i\sigma} a_{i\sigma'}),$$

where $a_{i\sigma}^\dagger$, $b_{i\sigma}$ are the creation and annihilation operators for an $p$ electron on sublattice A and B. i and j denote the sites on the layer and the sum at the first term takes in-plane nearest neighbor. $\alpha$ denotes the layer, $m$ and $m'$ denote px, py, and pz orbitals, and $\sigma$ denotes the spin states, respectively. The in-plane nearest neighbor and interplane hopping amplitudes are expressed by Slater-Koster parameters $pp\sigma$ and $pp\tau$ [44]. We consider two regimes of the interlayer hopping: intermediate coupling which is applicable to a realistic AA bilayer system and strong coupling where layers are very close to each other. The values of Slater-Koster parameters we used are shown in Table 1. The energies are given in unit of $t = pp\sigma$ in which $pp\sigma$ is for the in-plane nearest neighbor bond. The ratio $pp\tau / pp\sigma$ is fixed to -0.25 following the Harrison’s formulation in the calculations [36, 37, 45].

Since the spin-orbit coupling becomes important for heavier elements such as Sn and Pb, we include the atomic spin-orbit interaction (SOI) in the Hamiltonian. The corresponding Hamiltonian is [37]

$$H_{\text{SO}} = \frac{\Delta_{\text{SO}}}{2} \sum_{i, \sigma} \epsilon_{i\sigma\sigma'} c_{i\sigma}^\dagger (-i\sigma\sigma') c_{i\sigma'},$$

where $c_{i\sigma}$ are the creation and annihilation operators for an $p$ electron at site $i$, the operator $\sigma\sigma'$ is the Pauli matrix($n\sigma'$ denotes $x, y, z$), and $\epsilon_{i\sigma\sigma'}$ is antisymmetric tensor. In this paper, when we include SOI, we set the parameter $\Delta_{\text{SO}}$ to t/9 and t/3. Assuming that $t = 1.5$ eV, $\Delta_{\text{SO}}$ of t/9 and t/3 are about 0.17 eV and 0.045 eV respectively which are close to the values for Sn and Pb estimated by Kaloni et al [35] The atomic values of $\Delta_{\text{SO}}$ are about 0.5eV for Sn and about 1.6 eV for Pb or Bi [48]. Here, it should be noted that $\Delta_{\text{SO}}$ for Sn is set to 0.8 eV in some literatures [25, 36, 37, 49] which is renormalized by factor of ~1.5 from the atomic value. We also consider systems with antiferromagnetic spin arrangements by introducing staggered energy splitting $t/3$ between spin up and spin down states. When we consider these systems, we introduce the Hamiltonian

$$H_{\text{AFM}} = \sum_{i\sigma} \epsilon_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma},$$

Table 1. Slater-Koster parameters for the intermediate and strong interlayer coupling cases.

|          | Inplane (intermediate) | Interplane (intermediate) | Interplane (strong) |
|----------|------------------------|----------------------------|---------------------|
| $pp\sigma / t$ | 1.0                    | 0.18                       | 2.72                |
| $pp\tau / t$   | −0.25                  | −0.045                     | −0.68               |
where $M_{i\sigma}$ causes energy splitting between spin up and spin down states at site $i$. The total Hamiltonian is the sum of the three terms above

$$H = H_{\text{hop}} + H_{\text{SO}} + H_{\text{AFM}}$$

(4)

3. Results and discussion

Figure 1 shows the band dispersion along $\Gamma$-$K$ of a single layer honeycomb lattice. Without SOI, we can see a quadruply degenerate point at $K$. While it is well known that $p_z$ bands are degenerate at $K$, $p_x/p_y$ bands are also degenerate. At the $K$ point, $p_x/p_y$ orbitals form $l_z = +1$ like state at one sublattice and $l_z = -1$ like state at the other sublattice. Since the net transfer integral between these two states at $K$ becomes zero, the $p_x/p_y$ bands are degenerate. We can also see that $p_x/p_y$ bands are degenerate at $\Gamma$ because of threefold symmetry of the system. With SOI, the quadruply degenerate point at $K$ and the doubly degenerate point at $\Gamma$ are removed. The quartet states at $K$ are split into two singlet and one doublet which are mixtures of $p_x$, $p_y$ and $p_z$ orbitals. The $p_x/p_y$ doublet states at $\Gamma$ are split into two singlets.

Figure 2 shows the band dispersion of an AA bilayer honeycomb lattice for the intermediate interlayer coupling. Without SOI, we can see a quadruply degenerate point at $K$. While it is well known that $p_z$ bands are degenerate at $K$, $p_x/p_y$ bands are also degenerate. At the $K$ point, $p_x/p_y$ orbitals form $l_z = +1$ like state at one sublattice and $l_z = -1$ like state at the other sublattice. Since the net transfer integral between these two states at $K$ becomes zero, the $p_x/p_y$ bands are degenerate. We can also see that $p_x/p_y$ bands are degenerate at $\Gamma$ because of threefold symmetry of the system. With SOI, the quadruply degenerate point at $K$ and the doubly degenerate point at $\Gamma$ are removed. The quartet states at $K$ are split into two singlet and one doublet which are mixtures of $p_x$, $p_y$ and $p_z$ orbitals. The $p_x/p_y$ doublet states at $\Gamma$ are split into two singlets.

Consequently, the degenerate point of $p_z$ (at energy zero) is closer to $\Gamma$ than that of $p_x/p_y$. The degenerate points survive with SOI of $t/9$ although the $p_x/p_y$ and $p_z$ orbitals are mixed [figure 2(b)]. The energies of the degenerate
points are different and deviate from zero. With SOI of $t/3$, only the degenerate point with $p_z$ character survives as shown in figure 2(c). Figure 3 shows the band dispersion of an AA bilayer honeycomb lattice for the strong interlayer coupling. In this parameter setting, $p_z$ orbitals couple between the layers so strongly that these bands are located on top and bottom of the energy range, and the degenerate point of $p_z$ in figure 2 disappears. However, the degenerate point of $p_x/p_y$ at energy zero remains. The degenerate point is robust against SOI.

Figure 4 shows the effects of antiferromagnetic spin arrangements on the band structure for the intermediate interlayer coupling. Here, we study three types of antiferromagnetic spin arrangements for the AA bilayer honeycomb lattice. As shown in figures 4(a) and (d-f), without $\Delta_{SO}$, the degenerate points survive under the antiferromagnetic spin arrangements which are staggered along one of the intralayer or interlayer bonds. However, the degenerate points are removed by the spin arrangement which is staggered along the intralayer and

![Figure 3](attachment:image3.png)

Figure 3. Band dispersion along $\Gamma$-$K$ of an AA bilayer honeycomb lattice with the strong interlayer coupling for $\Delta_{SO} = (a) 0$, (b) $t/9$, and (c) $t/3$. The darker colored band has the higher weight of $p_z$ relative to $p_x$ as indicated in the vertical color bar.

![Figure 4](attachment:image4.png)

Figure 4. Band dispersion along $K$-$\Gamma$-$K'$ of an AA bilayer honeycomb lattice for the intermediate interlayer coupling and three different antiferromagnetic spin arrangements. (a-c) and (d-f) are the results without and with $\Delta_{SO} = t/3$. The darker colored band has the higher weight of $p_z/p_y$ relative to $p_z$ as indicated in the vertical color bar.
interlayer bonds [figure 4(c)]. With $\Delta_{SO}$, one of the degenerate points can survive only under the spin arrangement of figure 4(e). Please note that the K and K' points are not equivalent due to the spin arrangement.

Figure 5 shows the effects of antiferromagnetic spin arrangements on the band structure for the strong interlayer coupling. As shown in figures 5(a) and 5(b), without $\Delta_{SO}$, the degenerate point of $p_x/p_y$ survives under the spin arrangements which are staggered along one of the intralayer or interlayer bonds. In contrast, the degenerate point is removed by the spin arrangement which is staggered along the intralayer and interlayer bonds (figure 5(c)). With $\Delta_{SO}$, one of the degenerate points can survive only under the spin arrangement of figure 5(c). This situation is similar to the intermediate interlayer coupling case.

We also consider the electronic states at the zigzag edge in which the Kramers degeneracy is lifted. Figure 6 shows the band dispersion of honeycomb lattice zigzag ribbon. For the honeycomb lattice single layer without SOI (figure 6(a)), it is well known that the flat band of $p_z$ orbital appears among the degenerate points of the $p_z$
bulk bands [50] (at energy zero and at $k_z$ between $2\pi/3a$ and $4\pi/3a$ in figure 6(a)). Here, $k_z$ represents wave number along the edge. In the present system with triply degenerate $p$ orbitals, additional flat bands of $p_x/p_y$ also appear at energy zero and $k_z$ between $0$ and $2\pi/3a$ or $k_z$ between $4\pi/3a$ and $2\pi/a$. In addition, there are $p_x/p_y$ flat bands at energy $\approx \pm t$ which are related to the bulk $p_x/p_y$ degeneracy at $\Gamma$. As shown in figure 6(b), the edge states with $p_x/p_y$ character exhibit spin polarized Dirac like dispersions with degenerate points at $k_z = 0$ and $k_z = \pi/a$ due to weak mixing of $p_x/p_y$ and $p_z$ orbitals by $\Delta_{SO} = t/9$. On the other hand, the effect of SOI is relatively small for the edge state with $p_z$ character which remains almost flat. In figure 6(c) for $\Delta_{SO} = t/3$, the edge state with $p_z$ character exhibits a clear Dirac like dispersion with substantial mixing of $p_z$ and $p_x/p_y$ orbitals.

The various edge states for the AB bilayer systems have been studied in previous works [51–55]. Here, we study edge states at the zigzag edges of the AA bilayer (with strong interlayer coupling) which exhibit complicated behaviors. Without SOI, the flat edge states at $\pm 2t$ and $\pm 3t$ are related to $p_x$ and $p_x/p_y$, respectively (7(a)). These localized edge states are split due to the interlayer hybridization. With SOI, the edge states with $p_x/p_y$ character show clear Dirac like dispersions while those with $p_z$ character remain almost flat (figures 7(b) and (c)). The orbital dependent behavior is associated with the fact that the degeneracy of the $p_z$ and $p_x/p_y$ orbitals can be mixed by the atomic SOI while the $p_z$ orbital is already ostracized due to the interlayer coupling.

In the realistic honeycomb systems, the $p_x/p_y$ degeneracy is broken due to the formation of $sp^2$ hybrids. However, when the energy difference between the $s$ and $p$ orbitals is sufficiently large compared to the transfer integrals between them, the $p_z$, $p_x$, and the corresponding edge states obtained in the present calculations become important.

4. Conclusion

In conclusion, we have investigated bulk and edge states of $p$ electron systems on single layer and AA bilayer honeycomb lattice systems. In the single layer honeycomb lattice, SOI splits the quartet at K point into two singlets and one doublet which are mixtures of $p_x$, $p_y$, and $p_z$ bands. In the AA bilayer honeycomb lattice with the intermediate interlayer coupling, two degenerate points along $\Gamma$–$K$ have $p_x/p_y$ and $p_z$ characters respectively. Only the $p_x/p_y$ type degenerate point survives under the strong interlayer coupling. One of the degenerate points survive against the SOI and the antiferromagnetic spin arrangement which is staggered only along the intralayer bonds. On the other hand, the degenerate points are removed by the SOI and the antiferromagnetic spin arrangement which is staggered only along the interlayer bonds. Without SOI, localized edge states at the zigzag edges also have $p_x/p_y$ or $p_z$ character both in the single layer and the AA bilayer systems. In the AA bilayer with SOI, only the $p_x/p_y$ edges states form the Dirac like band dispersion since the $p_x$ and $p_y$ can be mixed due to SOI. Although corresponding honeycomb lattice systems without corrugations have not been realized yet, the $p_z/p_y$ orbital degeneracy is expected to play significant roles in possible Pb or Bi honeycomb lattice systems.

**Figure 7.** Band dispersion of an AA bilayer honeycomb lattice zigzag ribbon for the strong interlayer coupling for $\Delta_{SO} = (a) 0$, (b) $t/9$, and (c) $t/3$. The width of the ribbon is $N = 200$. $k_x$ represents wave number along the edge, and $a$ is the lattice constant. The darker colored edge state has the higher weight of $p_x/p_y$ relative to $p_z$ as indicated in the vertical color bar.
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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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