Electronic properties of bilayer graphene strongly coupled to
interlayer stacking and an external electric field

Changwon Park\textsuperscript{1}, Junga Ryou\textsuperscript{2}, Suklyun Hong\textsuperscript{2}, Bobby Sumpter\textsuperscript{1}, Gunn Kim\textsuperscript{2}, Mina Yoon\textsuperscript{1}

\textsuperscript{1}Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.

\textsuperscript{2}Department of Physics and Graphene Research Institute and Sejong University, Seoul, 143-747, Korea

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1. Hopping parameters extracted from the maximally localized Wannier function

Following the Wannier interpolation scheme \cite{1}, we extract hopping parameters that exactly reproduce the original first-principles eigenvalues. These parameters show exponential decaying behavior as hopping distances increase; this behavior is due to a localization process in the construction of Wannier functions. The obtained intralayer hopping parameters are respectively -2.88 eV and -0.24 eV for nearest and next-nearest pairs, and they remain essentially constant with respect to stacking configurations (their variations are within 0.004 and 0.002 eV, for each). On the other hand, interlayer hopping parameters are strongly stacking dependent; for instance, their variations for selected pairs are presented in Fig. S1(a). In an effective Hamiltonian in k-space, $\mathcal{\gamma}$ denotes the Fourier transformation of the real-valued hopping parameter $\gamma$. Figure S1(b)–(d) presents changes of independent $\gamma$ values ($\mathcal{\gamma}_{AA}$, $\mathcal{\gamma}_{AB}$, and $\mathcal{\gamma}_{BA}$) with respect to stacking configurations, where $\mathcal{\gamma}_{BB}$ is equivalent to $\mathcal{\gamma}_{AA}$ for all translated stacking configurations in the
absence of a rotation. The relation between $\gamma$’s and the band structure will be further discussed in Section 2.

During the translation from AA to AA’ stacking (Fig. S1(b)), $\gamma_{AA}$ becomes smaller in magnitude as we move away from AA stacking due to the increased hopping distance. $\gamma_{AB}$ is equivalent to $\gamma_{BA}$ in this case because of the preserved sublattice symmetry. At the start of AA stacking, threefold symmetry keeps three nearest interlayer hopping parameters ($\gamma$’s) same. Thus, $\gamma_{AB}$ becomes zero due to the relative phase difference $(1 + \exp(2\pi i/3) + \exp(-2\pi i/3) = 0)$, and this holds when we include $n$th-nearest neighbors. As the stacking changes toward AA’ stacking, $\gamma_{AB}$ increases. During the translation from AA to AB stacking (Fig. S1(c)), all $\gamma$’s become purely real due to cancellation of the complex part by reflection symmetry about the $x$-axis. As we will see later, $\gamma_{AB} + \gamma_{BA}$ and $\gamma_{AB} - \gamma_{BA}$ have clear physical meanings related to a Dirac cone shift and coupling. For example, the size of the bandgap is proportional to $\gamma_{AB} + \gamma_{BA}$. During the translation along AA’ to AB stacking (Fig. S1(d)), $\gamma$’s lie on the same line in the complex plane as shown in Fig. S2(f). This reflects the fact that by changing the relative phase of the upper and lower layers by $2\pi/3$, all interlayer hopping can be made purely real. This is related to the reflection symmetry in $\gamma$ about $x$-axis and ensures their reality in this phase-shifted basis.

2. Perturbation analysis of the bandgap in bilayer graphene

In this section we will derive the analytic expression for the bandgaps shown in Table 1. We treat small translations and the E-field as perturbations to high-symmetry stackings (AA, AA’ and AB stacking). In AA stacking, the wavefunctions on each decoupled Dirac cone can be written in the sublattice bonding $(A_{up} + A_{dn}, B_{up} + B_{dn})$ and antibonding basis $(A_{up} - A_{dn}, B_{up} - B_{dn})$ as

$$
\psi_{e(h)}^a(\theta_k) = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & \exp(-i\theta_k/2) \\ 0 & \pm\exp(i\theta_k/2) \end{bmatrix}, \quad \psi_{e(h)}^b(\theta_k) = \frac{1}{\sqrt{2}} \begin{bmatrix} \exp(-i\theta_k/2) & 0 \\ \pm\exp(i\theta_k/2) & 0 \end{bmatrix}
$$
where upper index $a$ ($b$) denotes antibonding (bonding), lower index $e$ ($h$) denotes electron (hole) wavefunction, and $\theta_k \equiv \tan^{-1}(-k_x/k_y)$ when $k_x$ and $k_y$ are the relative crystal momentum at each Dirac point. Translational perturbation $V_T$ can be written as a $4 \times 4$ matrix in this basis, and the change in interlayer hopping is described by eight complex variables in a $2 \times 2$ off-diagonal block. Only three of them are independent, owing to the equivalence of A-A and B-B hopping and the hermiticity. Thus any translational perturbation can generally be written as a linear combination of the following three matrices:

\[
V_T^0 = \begin{bmatrix}
0 & 0 & \delta y_0 & 0 \\
0 & 0 & 0 & \delta y_0 \\
\delta y_0^* & 0 & 0 & 0 \\
0 & \delta y_0^* & 0 & 0
\end{bmatrix},
\]

\[
V_T^{\text{sym}} = \begin{bmatrix}
0 & 0 & 0 & \tilde{\delta} y_s \\
0 & 0 & \tilde{\delta} y_s & 0 \\
0 & \tilde{\delta} y_s^* & 0 & 0 \\
\tilde{\delta} y_s^* & 0 & 0 & 0
\end{bmatrix},
\]

\[
V_T^{\text{asym}} = \begin{bmatrix}
0 & 0 & 0 & \delta y_a \\
0 & 0 & 0 & -\delta y_a \\
0 & -\delta y_a^* & 0 & 0 \\
\delta y_a^* & 0 & 0 & 0
\end{bmatrix},
\]

where $\delta y_0 = (\delta y_{AA} + \delta y_{BB})/2 = \delta y_{AA}, \delta y_s = (\delta y_{AB} + \delta y_{BA})/2$, and $\delta y_a = (\delta y_{AB} - \delta y_{BA})/2$. Note that $V_T^{\text{asym}}$ becomes nonzero only in sublattice-asymmetric translation. Perturbations induced by an E-field can be represented as a potential energy difference $U$ between two layers as

\[
V_E = \frac{1}{2} \begin{bmatrix}
U & 0 & 0 & 0 \\
0 & U & 0 & 0 \\
0 & 0 & -U & 0 \\
0 & 0 & 0 & -U
\end{bmatrix}.
\]

In the sublattice bonding and antibonding basis, these are transformed into

\[
V_T^{0'} = \begin{bmatrix}
\text{Re}(\delta y_0) & 0 & -i \cdot \text{Im}(\delta y_0) & 0 \\
0 & \text{Re}(\delta y_0) & 0 & -i \cdot \text{Im}(\delta y_0) \\
i \cdot \text{Im}(\delta y_0) & 0 & -\text{Re}(\delta y_0) & 0 \\
0 & i \cdot \text{Im}(\delta y_0) & 0 & -\text{Re}(\delta y_0)
\end{bmatrix}.
\]
Hereafter, primes on the perturbation matrix denote matrix representations in this transformed basis. Matrix elements in the $2 \times 2$ diagonal block shift the Dirac cone in energy and $k$-space while those in the off-diagonal block couple two Dirac cones. Changes to band structures will be discussed based on these two effects.

Around AA stacking, the hole band of one Dirac cone and the electron band of the other Dirac cone intersect at the Fermi level. A bandgap can emerge as a result of the change of this intersection when translations or an E-field are applied. First, we will consider the effect of sublattice-symmetric translation $V^0_T + V^\text{sym}_T$. $\delta \gamma_0$ and $\delta \gamma_s$ can be read from Fig. S1(b). $\text{Re} (\delta \gamma_0)$ decreases the energy separation of two Dirac points $\Delta D_E$, and $\text{Re} (\delta \gamma_s)$ increases the $k$ separation of two Dirac points $\Delta D_k$ from zero along the $k_y$-direction. The shifted geometry of two Dirac cones is shown in Fig. S2(a). The intersection becomes a tilted ellipse and its projection to $k$ plane is a circle. The wavefunctions on this ellipse can be indexed with $\theta_1$ and $\theta_2$ which are graphically defined in the projected circle of Fig. S2(a). The coupling of two Dirac cones comes from $\text{Im} (\delta \gamma_0)$ and $\text{Im} (\delta \gamma_s)$. The former is negligibly small, thus we just consider the following Dirac cone coupling matrix by separating the $2 \times 2$ block diagonal part, which is responsible for the shift of the Dirac cone.
By use of degenerate second-order perturbation theory, the doubly degenerated states on the ellipse are split by 

\[
2 < \psi_a^h | V' | \psi_e^b > = 2 i \text{m} \left( \delta \gamma_s \right) \sin \left( \frac{\theta_1 + \theta_2}{2} \right).
\]

At \( \theta_1 = \theta_2 = 0 \) and \( \pi \), the splitting becomes zero, which insures that no bandgap opens by sublattice-symmetric translation. Under the sublattice-asymmetric translation from AA to AB stacking, all \( \delta \gamma \)'s are real. As in sublattice-symmetric translation,\( Re \left( \delta \gamma_0 \right) \) decreases the energy separation of two Dirac points \( \Delta D_e \), and \( Re \left( \delta \gamma_s \right) \) increases the \( k \) separation of two Dirac points \( \Delta D_k \) from zero along the \( k_y \)-direction. The Dirac cone coupling matrix becomes

\[
V' = \begin{bmatrix}
0 & 0 & 0 & -i \cdot \text{Im} \left( \delta \gamma_s \right) \\
0 & -i \cdot \text{Im} \left( \delta \gamma_s \right) & 0 & 0 \\
i \cdot \text{Im} \left( \delta \gamma_s \right) & 0 & 0 & 0 \\
i \cdot \text{Im} \left( \delta \gamma_s \right) & 0 & 0 & 0
\end{bmatrix}
\]

and the energy splitting at the ellipse becomes

\[
2 < \psi_a^h | V' | \psi_e^b > = 2 Re \left( \delta \gamma_0 \right) \cos \left( \frac{\theta_1 + \theta_2}{2} \right).
\]

At \( \theta_1 + \theta_2 = \pi \) and \( 3\pi \), the splitting becomes zero. Schematic energy levels are shown as red lines in Fig. S2(b). In general translation, it can be shown that the zero coupling points rotate on the ellipse and no bandgap opens by a translation alone.

The split states under both translations can be written as \( \psi_\pm = \frac{1}{\sqrt{2}} (\psi_a^h \pm \psi_e^b) \). The E-field further splits these states. The effect of E-field \( V'_E \) on these states is the same for both types of translation, and the additional splitting becomes

\[
2 < \psi_- | V'_E | \psi_+ > = i \text{U} \sin \left( \frac{\theta_1 - \theta_2}{2} \right).
\]

For the sublattice-symmetric bilayer graphene, the zero splitting points of both perturbations coincide so that bandgap opens; however, for the sublattice-asymmetric type, an E-field opens a bandgap (blues lines in Fig. S2(b)). The size of a bandgap is

\[
| \text{U} \sin \left( \frac{\theta_1 - \theta_2}{2} \right) | \approx U \Delta D_k / R
\]

where the \( k \) separation of the Dirac points \( \Delta D_k = Re \left( \delta \gamma_s \right) \), the radius of the projected circle \( R \approx \frac{\gamma_{AA}}{2\hbar v_F} \), and \( \hbar v_F \) is the slope of the Dirac cone.
Now we turn to the band structure around AA’ stacking. Two Dirac cones intersect as in Fig. S2(c), and their line of intersection becomes a tilted hyperbola composed of the intersection points of two growing circles of different radius $R_1$ and $R_2$. Note that $R_1^0 + R_2^0 = \Delta D_k$ and $R_2^0 - R_1^0 = \Delta D_E/(\hbar v_F)$, where $R_1^0$ and $R_2^0$ are the minimum radii for the intersection of two circles. From consideration of the geometry, tilt angle $\alpha$ becomes $\tan^{-1}\left( \frac{R_2^0 - R_1^0}{R_2^0 + R_1^0} \right) \frac{1}{\hbar v_F}$.

The bandgap is related to the change in band structure around each Dirac point. They are well pronounced along the $\theta_1 = \theta_2 = 0$ plane (the second and fourth rows of the AA’ block in Fig. 2). Of the four bands in those planes, perturbations only couple different Dirac cones, which ensures the robustness of the crossing behavior under each single perturbation. Actually, bandgap (pseudogap) openings at the Dirac points are a second-order effect and only possible when the sublattice-asymmetric translation is combined with an E-field, as will be explained.

Under sublattice-symmetric translation or an E-field, only parallel-band pairs of each Dirac cone are coupled, whereas only non-parallel-band pairs of each cone are coupled under the sublattice-asymmetric translation as illustrated in Fig. S2(d) and (e). Though crossing points in the Dirac cones do not open, each Dirac cone’s crossing band now has a small component of the opposite Dirac cone.

Formally, we can write the wavefunctions in Fig. S2(d) and (e) as

$$\psi_1 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix}, \psi_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 1 \\ 1 \\ 0 \end{bmatrix}, \psi_3 = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 0 \\ 1 \\ -1 \end{bmatrix},$$

where the difference in the energy levels of $\psi_2$ and $\psi_3$ is infinitesimally small. One remaining band is energetically so distant that we will neglect it. In sublattice-symmetric translation, perturbed wavefunctions $\psi'_2$ and $\psi'_3$ can be written as $\psi'_2 \approx \psi_2 + \alpha \psi_1$ and $\psi'_3 \approx \psi_3$, where the mixing parameter $\alpha = \frac{\langle \psi_2 | V_{sym}^{\text{eff}} | \psi_1 \rangle}{\Delta D_E}$. When an E-field is applied, the coupling between them becomes $\langle \psi'_2 | V_{E}^{\text{eff}} | \psi'_3 \rangle = \alpha \langle \psi_1 | V_{E}^{\text{eff}} | \psi_3 \rangle = 0$ and the crossing behavior is preserved. In contrast, in sublattice-asymmetric translation,
perturbed wavefunctions $\psi'_2$ and $\psi'_3$ become $\psi'_2 \approx \psi_2$ and $\psi'_3 \approx \psi_3 + \beta \psi_1$, where mixing parameter 

$$\beta = \frac{\langle \psi_3 | \tilde{\psi}_3^{\text{sym}} | \psi_1 \rangle}{\Delta D_E}.$$  

The coupling induced by an E-field is $\langle \psi'_2 | V'_E | \psi'_3 \rangle = \beta \langle \psi_2 | V'_E | \psi_1 \rangle = \beta \frac{U}{2}$. This makes a bandgap $\beta U = Re \left( e^{\frac{2\pi i}{3} \delta \gamma_a} \right) U/\Delta D_E$ on each Dirac point.

References

[1] Nicola Marzari, Arash A. Mostofi, Jonathan R. Yates, Ivo Souza, and David Vanderbilt, Rev. Mod. Phys. 84, 1419 (2012)
FIGURE S1 (Color online). (a) Effect on interlayer hopping parameters $\gamma$ from changes in stacking configurations. In the three panels at right, considered pairs are denoted by a blue dot in the upper layer (dark gray) and a red dot in the lower layer (light gray). (b)-(d) Snapshot of stacking configurations (upper) and accompanying changes in $\tilde{\gamma}$ (lower) when one layer translates on the other layer. Two sublattices of the upper layer (red) are denoted as $A_{up}$ and $B_{up}$, while those of the lower layer (black) are denoted as $A_{dn}$ and $B_{dn}$. The translational directions are (b) from AA (tail of the arrow) to AA’ stacking (tip of the arrow), (c) from AA to AB stacking, and (d) from AA’ (tail of arrow) to AB stacking (tip of arrow). Dots are calculated points for uniform translation spacing.
FIGURE S2 (Color online). (a) Geometry of two non-interacting Dirac cones when $\Delta D_E/\Delta D_k$ is smaller than the slope of the cones. $\Delta D_{E(k)}$ denotes energy (crystal momentum) separation of two Dirac points. Each Dirac point is projected on the plane enclosed by the line of intersection (thick solid black). The wavefunctions on this ellipse can be indexed by the angular variables $\theta_1$ and $\theta_2$. (b) The energy splitting of degenerated states on the ellipse (black) are drawn according to the translation type and the presence of an E-field. (c) Geometry of two noninteracting Dirac cones when $\Delta D_E/\Delta D_k$ is larger than the slope of the cones. The line of intersection is composed of the intersection points of two growing circles and becomes a hyperbola tilted by $\alpha$. The geometry of intersecting circles and the definitions of variables are shown at right. Coupling band pairs are drawn with the same types of lines (solid and dashed) when sublattice-symmetric translation is applied (d) and sublattice-asymmetric translation is applied (e).