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## Supplementary information

# Pseudospin-selective Floquet band engineering in black phosphorus

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# Pseudospin-selective Floquet band engineering in black phosphorus

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1. Supplementary Note on theoretical analysis of the pseudospin selection rules for Floquet band engineering in black phosphorus.
2. Supplementary Table S1: Summary of theoretical analysis on pseudospin selection rules for Floquet band engineering in black phosphorus.
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## Supplementary Note: Theoretical analysis of pseudospin selection rules for Floquet band engineering in black phosphorus

TrARPES measurements show that the Floquet band engineering strongly depends on the pump polarization, which reflects the role of pseudospin selectivity in the Floquet engineering. First of all, we would like to clarify that the pseudospin in the black phosphorus refers to a spin-like degree of freedom for electronic states around the Γ point, which is dictated by the crystal symmetry of black phosphorus and underlies photoemission dipole matrix elements[S1] and optical selection rules[S2,S3]. Based on results discussed in Ref. [S1,S4,S5], we have $\langle c|AC|v\rangle \neq 0$ and $\langle v|ZZ|c\rangle = 0$, where $|c\rangle$ and $|v\rangle$ are the electronic states at the conduction band (CB) and valence band (VB) edges at the Γ point and the AC (ZZ) refers to the pump polarization along the armchair (zigzag) direction of black phosphorus. We note that the optical transition from VB to CB is allowed only for AC pump polarization. These results could be also explained in the physical picture of the pseudospin in black phosphorus.

Herein, the concept of the pseudospin is only well-defined for electronic states of black phosphorus in equilibrium. In the Floquet theory, the light-matter interaction will renormalize the electronic structures of the black phosphorus, while at the same time, the pseudospin selection rules for the electronic state in equilibrium will also influence the Floquet bands.

In the following, we start from the low-energy $\boldsymbol{k}\cdot\boldsymbol{p}$ theory around the Γ point in equilibrium, apply it to the Floquet theory, and demonstrate how equilibrium optical matrix elements affect the Floquet bands of the black phosphorus. The low-energy $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian around the Γ point $H_\Gamma$ for black phosphorus has the form[S5,S6]:

$$H_\Gamma(\boldsymbol{k}) = \begin{pmatrix} E_c + \eta_c k_y^2 + \nu_c k_x^2 & \gamma_1 k_y \\ \gamma_1^* k_y & E_v + \eta_v k_y^2 + \nu_v k_x^2 \end{pmatrix}$$

Herein $E_c$ and $E_v$ are the energies for the conduction and valence band edge at the Γ point, $k_x$ and $k_y$ are the momenta along the ZZ and AC directions in black phosphorus, $\eta_c$, $\nu_c$, $\eta_v$ and $\nu_v$ are parameters with the value of -2.519 eV·Å$^2$, 3.225 eV·Å$^2$, -1.512 eV·Å$^2$, and -2.982 eV·Å$^2$. $\gamma_1 = \langle c|p_y|v\rangle$ is the optical matrix element with the module value of 3.691 eV·Å, which corresponds to the allowed absorption with AC polarization, and the optical matrix element $\gamma_2 = \langle c|p_x|v\rangle = 0$ corresponds to the forbidden absorption with ZZ polarization.

**For a linear polarized pump with AC polarization,** we obtain the time dependent Hamiltonian $H'_\Gamma(t)$ via considering the Peierls substitution ($k_y \rightarrow k_y + A\cos\,\Omega t$):

$$\begin{pmatrix} E_c + \eta_c k_y^2 + \nu_c k_x^2 + 2\eta_c k_y A\cos\ \Omega t & \gamma_1 k_y + \gamma_1 A\cos\ \Omega t \\ \gamma_1^* k_y + \gamma_1^* A\cos\ \Omega t & E_v + \eta_v k_y^2 + \nu_v k_x^2 + 2\eta_v k_y A\cos\ \Omega t \end{pmatrix}$$

According to the Floquet theory, $[H_\Gamma^{F-AC}]_{nm} = \frac{1}{T}\int_0^T \mathrm{H}(t)e^{i(n-m)\Omega t}\,dt - m\hbar\Omega\delta_{mn}$, so we can obtain the Floquet Hamiltonian $[H_\Gamma^{F-AC}]_{nm}$ as

$$\begin{pmatrix} (E_c + \eta_c k_y^2 + \nu_c k_x^2 - m\hbar\Omega)\delta_{mn} + \eta_c k_y A(\delta_{m,n+1} + \delta_{m,n-1}) & \gamma_1 k_y \delta_{mn} + \frac{A\gamma_1}{2}(\delta_{m,n+1} + \delta_{m,n-1}) \\ \gamma_1^* k_y \delta_{mn} + \frac{A\gamma_1^*}{2}(\delta_{m,n+1} + \delta_{m,n-1}) & (E_v + \eta_v k_y^2 + \nu_v k_x^2 - m\hbar\Omega)\delta_{mn} + \eta_v k_y A(\delta_{m,n+1} + \delta_{m,n-1}) \end{pmatrix}$$

Here we choose the truncation as $m, n = \{-1, 0, 1\}$, the $H_\Gamma^{F-AC}$ is shown as

$$\begin{pmatrix} (E_c + \eta_c k_y^2 + \nu_c k_x^2) + \hbar\Omega & \gamma_1 k_y & \eta_c k_y A & \frac{A\gamma_1}{2} & 0 & 0 \\ \gamma_1^* k_y & (E_v + \eta_v k_y^2 + \nu_v k_x^2) + \hbar\Omega & \frac{A\gamma_1^*}{2} & \eta_v k_y A & 0 & 0 \\ \eta_c k_y A & \frac{A\gamma_1}{2} & (E_c + \eta_c k_y^2 + \nu_c k_x^2) & \gamma_1 k_y & \eta_c k_y A & \frac{A\gamma_1}{2} \\ \frac{A\gamma_1^*}{2} & \eta_v k_y A & \gamma_1^* k_y & (E_v + \eta_v k_y^2 + \nu_v k_x^2) & \frac{A\gamma_1^*}{2} & \eta_v k_y A \\ 0 & 0 & \eta_c k_y A & \frac{A\gamma_1}{2} & (E_c + \eta_c k_y^2 + \nu_c k_x^2) - \hbar\Omega & \gamma_1 k_y \\ 0 & 0 & \frac{A\gamma_1^*}{2} & \eta_v k_y A & \gamma_1^* k_y & (E_v + \eta_v k_y^2 + \nu_v k_x^2) - \hbar\Omega \end{pmatrix}$$

The hybridization gap induced by the light-matter interaction (see red arrows shown in Extended Data Fig. 3) is determined by the off-diagonal matrix elements between states with different Floquet index $(m, n)$. Now we focus on the 1-th valence band and the 0-th conduction band as an example to see how the hybridization gap is formed. We show the effective Floquet Hamiltonian for these states as:

$$\begin{pmatrix} (E_v + \eta_v k_y^2 + \nu_v k_x^2) + \hbar\Omega & \frac{A\gamma_1^*}{2} \\ \frac{A\gamma_1}{2} & (E_c + \eta_c k_y^2 + \nu_c k_x^2) \end{pmatrix}$$

Due to the existence of $\gamma_1$, the band renormaliztion is always non-zero for any k point. This fact indicates that the 1-th valence band and the 0-th conduction band are always coupled to each other with a hybridization gap opening when the linear polarized pump light is applied with the oscillation along AC direction.

To confirm such analysis, we consider the pumping light with $\hbar\Omega = 0.44\ eV$ and $0.38\ eV$ for AC and ZZ directions as an example and perform numerical simulations based on the Floquet TB model and the Floquet effective $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian. We consider the momentum lines along the ZZ direction ($k_y = 0$) and AC direction ($k_x = 0$), and always observe the hybridization gaps from both simulations with the TB model and the $\boldsymbol{k}\cdot\boldsymbol{p}$ model as shown in Extended Data Fig. 4a-d.

**For a linear polarized pump light with the oscillation along ZZ direction**, we can obtain the Floquet Hamiltonian $H_\Gamma^{F-ZZ}$ via considering the Peierls substitution ($k_x \rightarrow k_x + A\cos\ \Omega t$)

$$\begin{pmatrix} (E_c+\eta_c k_y^2+\nu_c k_x^2)+\hbar\Omega & \gamma_1 k_y & \nu_c k_x A & 0 & 0 & 0 \\ \gamma_1^* k_y & (E_v+\eta_v k_y^2+\nu_v k_x^2)+\hbar\Omega & 0 & \nu_v k_x A & 0 & 0 \\ \nu_c k_x A & 0 & (E_c+\eta_c k_y^2+\nu_c k_x^2) & \gamma_1 k_y & \nu_c k_x A & 0 \\ 0 & \nu_v k_x A & \gamma_1^* k_y & (E_v+\eta_v k_y^2+\nu_v k_x^2) & 0 & \nu_v k_x A \\ 0 & 0 & \nu_c k_x A & 0 & (E_c+\eta_c k_y^2+\nu_c k_x^2)-\hbar\Omega & \gamma_1 k_y \\ 0 & 0 & 0 & \nu_v k_x A & \gamma_1^* k_y & (E_v+\eta_v k_y^2+\nu_v k_x^2)-\hbar\Omega \end{pmatrix}$$

In the same way, we pick up the 1-th valence band and the 0-th conduction band, and their effective Floquet Hamiltonian has the form

$$\begin{pmatrix} (E_v+\eta_v k_y^2+\nu_v k_x^2)+\hbar\Omega & 0 \\ 0 & (E_c+\eta_c k_y^2+\nu_c k_x^2) \end{pmatrix}$$

Importantly, due to the lattice symmetry restrictions, the off-diagonal element is zero ($\gamma_2 = \langle c|p_x|v\rangle = 0$). In the near resonance pumping case, no band renormalizations can be observed for states at the the Γ point along the armchair and zigzag directions. To confirm such analysis, we consider the pumping light with $\hbar\Omega = 0.44\,eV$ and $0.38\,eV$ for AC and ZZ directions as an example and perform numerical simulation based on the Floquet TB model and the Floquet effective $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian.

We consider the momentum lines along the ZZ direction ($k_y = 0$) and AC direction ($k_x = 0$), and can't observe the hybridization gaps from both simulations with the TB model and the $\boldsymbol{k}\cdot\boldsymbol{p}$ model as shown in Extended Data Fig. 4e-h.

| | **Near resonance pumping** |
|---|---|
| **AC-polarized light** | **There is always a hybridization gap.** |
| **ZZ-polarized light** | **There is almost no hybridization gap.** |

*Supplementary Table S1. Summary of theoretical analysis on pseudospin selection rules for Floquet band engineering in black phosphorus.*

In summary, through the analysis of the Floquet $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian around Γ point, we summarized the results in the Supplementary Table S1. We conclude that the pseudospin selection rules for electronic states of black phosphorus in equilibrium, which is constrained by the crystal symmetry, strongly influence the hybridization gaps in the Floquet electronic structures in black phosphorus.

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