Three-band tight binding model for transition metal dichalcogenide monolayers

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1 Three-band tight binding method

The time-independent Schrödinger equation for an electron in the crystal has the form

$$\left[-\frac{\hbar^2\nabla^2}{2m} + U_0(\mathbf{r})\right]\psi_{\lambda,\mathbf{k}}(\mathbf{r}) = \varepsilon_\lambda(\mathbf{k})\psi_{\lambda,\mathbf{k}}(\mathbf{r}), \tag{1}$$

where $U_0(\mathbf{r})$ is the periodic lattice potential, $\psi_{\lambda,\mathbf{k}}(\mathbf{r})$ is the Bloch wavefunction of an electron in band λ with wave vector $\mathbf{k}$, and $\varepsilon_\lambda(\mathbf{k})$ is the band structure.

In the tight binding (TB) model, the single-electron Bloch wavefunction can be expressed in terms of atomic orbitals as follows

$$\psi_{\lambda,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{j,i} C^\lambda_{ji}(\mathbf{k})\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot(\mathbf{R}+\mathbf{r}_i)}\phi_j(\mathbf{r}-\mathbf{R}-\mathbf{r}_i), \tag{2}$$

where $\phi_j(\mathbf{r}-\mathbf{R}-\mathbf{r}_i)$ is the orbital j of an atom i localized on a lattice site $\mathbf{R}$, in which $\mathbf{r}_i$ is the relative position of the atom i in the unit cell, and $C^\lambda_{ji}(\mathbf{k})$ are the coefficients of linear expansion.

The unit cell of transition metal dichalcogenide (TMDC) monolayers consists of 1 transition metal atom M and 2 chalcogenide atoms X. The three-band TB model considers a basis set consisting of only three d orbitals of atom M, namely d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ [1]

$$|\phi_1\rangle = |d_{z^2}\rangle,\ |\phi_2\rangle = |d_{xy}\rangle,\ |\phi_3\rangle = |d_{x^2-y^2}\rangle. \tag{3}$$

The Bloch wavefunction in this model has the form

$$\psi_{\lambda,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{j=1}^{3} C^\lambda_{j}(\mathbf{k})\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\phi_j(\mathbf{r}-\mathbf{R}). \tag{4}$$

The coefficients $C^\lambda_j(\mathbf{k})$ are the solutions of the eigenvalue equation

$$\sum_{j'=1}^{3}\left[H_{jj'}(\mathbf{k}) - \varepsilon_\lambda(\mathbf{k})S_{jj'}(\mathbf{k})\right]C^\lambda_{j'}(\mathbf{k}) = 0, \tag{5}$$

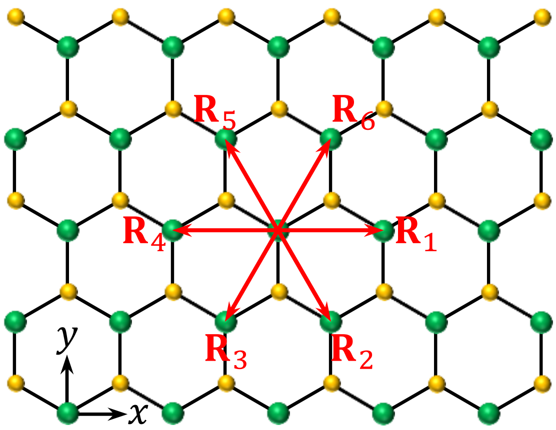

Figure 1: Top view of monolayer MX_2.

where

$$H_{jj'}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \langle \phi_j(\mathbf{r})| \left[-\frac{\hbar^2\nabla^2}{2m} + U_0(\mathbf{r}) \right] |\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle \tag{6}$$

and

$$S_{jj'}(\mathbf{k}) = \sum_{\mathbf{R}} \langle \phi_j(\mathbf{r})|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle \simeq \delta_{jj'}. \tag{7}$$

If we only consider the nearest-neighbor hoppings, the matrix elements of the TB Hamiltonian (6) are

$$\begin{aligned} H^{\mathrm{NN}}_{jj'}(\mathbf{k}) = \mathcal{E}_{jj'}(\mathbf{0}) &+ e^{i\mathbf{k}\cdot\mathbf{R}_1}\mathcal{E}_{jj'}(\mathbf{R}_1) + e^{i\mathbf{k}\cdot\mathbf{R}_2}\mathcal{E}_{jj'}(\mathbf{R}_2) + e^{i\mathbf{k}\cdot\mathbf{R}_3}\mathcal{E}_{jj'}(\mathbf{R}_3) \\ &+ e^{i\mathbf{k}\cdot\mathbf{R}_4}\mathcal{E}_{jj'}(\mathbf{R}_4) + e^{i\mathbf{k}\cdot\mathbf{R}_5}\mathcal{E}_{jj'}(\mathbf{R}_5) + e^{i\mathbf{k}\cdot\mathbf{R}_6}\mathcal{E}_{jj'}(\mathbf{R}_6), \end{aligned} \tag{8}$$

where

$$\mathcal{E}_{jj'}(\mathbf{R}) = \langle \phi_j(\mathbf{r})| \left[-\frac{\hbar^2\nabla^2}{2m} + U_0(\mathbf{r}) \right] |\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle \tag{9}$$

and

$$\begin{aligned} &\mathbf{R}_1 = (a,0)\,, \;\; \mathbf{R}_2 = \left(\frac{a}{2}, -\frac{a\sqrt{3}}{2}\right), \;\; \mathbf{R}_3 = \left(-\frac{a}{2}, -\frac{a\sqrt{3}}{2}\right), \\ &\mathbf{R}_4 = (-a,0)\,, \;\; \mathbf{R}_5 = \left(-\frac{a}{2}, \frac{a\sqrt{3}}{2}\right), \;\; \mathbf{R}_6 = \left(\frac{a}{2}, \frac{a\sqrt{3}}{2}\right). \end{aligned} \tag{10}$$

Here, $\mathbf{R}_{1-6}$ are the positions of the nearest neighboring M atoms, see Fig. 1.

g_n	x'	y'	z'	z'^2	$x'y'$	$\frac{1}{2}(x'^2-y'^2)$
E	x	y	z	z^2	xy	$\frac{1}{2}(x^2-y^2)$
$C_3\left(\frac{-2\pi}{3}\right)$	$-\frac{1}{2}x+\frac{\sqrt{3}}{2}y$	$-\frac{\sqrt{3}}{2}x-\frac{1}{2}y$	z	z^2	$-\frac{1}{2}xy+\frac{\sqrt{3}}{4}(x^2-y^2)$	$-\frac{\sqrt{3}}{2}xy-\frac{1}{4}(x^2-y^2)$
$C_3\left(\frac{-4\pi}{3}\right)$	$-\frac{1}{2}x-\frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x-\frac{1}{2}y$	z	z^2	$-\frac{1}{2}xy-\frac{\sqrt{3}}{4}(x^2-y^2)$	$\frac{\sqrt{3}}{2}xy-\frac{1}{4}(x^2-y^2)$
σ_v	$-x$	y	z	z^2	$-xy$	$\frac{1}{2}(x^2-y^2)$
σ_v'	$\frac{1}{2}x-\frac{\sqrt{3}}{2}y$	$-\frac{\sqrt{3}}{2}x-\frac{1}{2}y$	z	z^2	$\frac{1}{2}xy-\frac{\sqrt{3}}{4}(x^2-y^2)$	$-\frac{\sqrt{3}}{2}xy-\frac{1}{4}(x^2-y^2)$
σ_v''	$\frac{1}{2}x+\frac{\sqrt{3}}{2}y$	$\frac{\sqrt{3}}{2}x-\frac{1}{2}y$	z	z^2	$\frac{1}{2}xy+\frac{\sqrt{3}}{4}(x^2-y^2)$	$\frac{\sqrt{3}}{2}xy-\frac{1}{4}(x^2-y^2)$

Table 1: Some symmetry operations of the D_{3h} point group on basis functions taking (x, y, z) into (x', y', z'). $C_3(\frac{-2\pi}{3})$ and $C_3(\frac{-4\pi}{3})$ are the rotations by $\frac{-2\pi}{3}$ and $\frac{-4\pi}{3}$ around the z axis, respectively. σ_v, σ_v', σ_v'' are mirror planes parallel to the z axis, that are perpendicular to and bisect the line segments connecting $\mathbf{R}_1$ and $\mathbf{R}_4$, $\mathbf{R}_1$ and $\mathbf{R}_2$, $\mathbf{R}_1$ and $\mathbf{R}_6$, respectively.

One parameterizes the matrices $\mathcal{E}(\mathbf{0})$ and $\mathcal{E}(\mathbf{R}_1)$ by

$$\mathcal{E}(\mathbf{0}) = \begin{pmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & \epsilon_2 \end{pmatrix} \text{ and } \mathcal{E}(\mathbf{R}_1) = \begin{pmatrix} t_0 & t_1 & t_2 \\ -t_1 & t_{11} & t_{12} \\ t_2 & -t_{12} & t_{22} \end{pmatrix}. \tag{11}$$

Given $\mathcal{E}(\mathbf{R}_1)$, the matrix $\mathcal{E}(\mathbf{R}_{2-6})$ corresponding to all neighboring sites $\mathbf{R}_{2-6}$ can be generated by

$$\mathcal{E}(g_n\mathbf{R}_1) = D(g_n)\mathcal{E}(\mathbf{R}_1)D^\dagger(g_n), \tag{12}$$

where $D(g_n)$ is the matrix of the irreducible representation, g_n are symmetry operations of D_{3h} point group, $\{E, 2C_3, 3C_2, 2S_3, \sigma_h, 3\sigma_v\}$. In particular, we have $\mathcal{E}(\mathbf{R}_2) = \mathcal{E}\left(\sigma_v'\mathbf{R}_1\right)$, $\mathcal{E}(\mathbf{R}_3) = \mathcal{E}\left(C_3(\frac{-2\pi}{3})\mathbf{R}_1\right)$, $\mathcal{E}(\mathbf{R}_4) = \mathcal{E}\left(\sigma_v\mathbf{R}_1\right)$, $\mathcal{E}(\mathbf{R}_5) = \mathcal{E}\left(C_3(\frac{-4\pi}{3})\mathbf{R}_1\right)$, and $\mathcal{E}(\mathbf{R}_6) = \mathcal{E}\left(\sigma_v''\mathbf{R}_1\right)$.

Table 1 shows the transformation of the basis functions under the action of symmetry operations. From Table 1 we obtain irreducible matrices as follows

$$D\left(C_3\left(\tfrac{-2\pi}{3}\right)\right) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix}, \quad D\left(C_3\left(\tfrac{-4\pi}{3}\right)\right) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{pmatrix},$$
$$D\left(\sigma_v\right) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad D\left(\sigma_v'\right) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/2 & -\sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix},$$
$$D\left(\sigma_v''\right) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/2 & \sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{pmatrix}. \tag{13}$$

Therefore, we have

$$\begin{aligned}\mathcal{E}(\mathbf{R}_2) &= D(\sigma_v')\mathcal{E}(\mathbf{R}_1)D^\dagger(\sigma_v') \\ &= \begin{pmatrix} t_0 & \frac{1}{2}t_1 - \frac{\sqrt{3}}{2}t_2 & -\frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 \\ -\frac{1}{2}t_1 - \frac{\sqrt{3}}{2}t_2 & \frac{1}{4}t_{11} + \frac{3}{4}t_{22} & -\frac{\sqrt{3}}{4}t_{11} - t_{12} + \frac{\sqrt{3}}{4}t_{22} \\ \frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 & -\frac{\sqrt{3}}{4}t_{11} + t_{12} + \frac{\sqrt{3}}{4}t_{22} & \frac{3}{4}t_{11} + \frac{1}{4}t_{22} \end{pmatrix},\end{aligned} \tag{14}$$

$$\begin{aligned}\mathcal{E}(\mathbf{R}_3) &= D\left(C\left(\tfrac{-2\pi}{3}\right)\right)\mathcal{E}(\mathbf{R}_1)D^\dagger\left(C\left(\tfrac{-2\pi}{3}\right)\right) \\ &= \begin{pmatrix} t_0 & -\frac{1}{2}t_1 + \frac{\sqrt{3}}{2}t_2 & -\frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 \\ \frac{1}{2}t_1 + \frac{\sqrt{3}}{2}t_2 & \frac{1}{4}t_{11} + \frac{3}{4}t_{22} & \frac{\sqrt{3}}{4}t_{11} + t_{12} - \frac{\sqrt{3}}{4}t_{22} \\ \frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 & \frac{\sqrt{3}}{4}t_{11} - t_{12} - \frac{\sqrt{3}}{4}t_{22} & \frac{3}{4}t_{11} + \frac{1}{4}t_{22} \end{pmatrix},\end{aligned} \tag{15}$$

$$\mathcal{E}(\mathbf{R}_4) = D(\sigma_v)\mathcal{E}(\mathbf{R}_1)D^\dagger(\sigma_v) = \begin{pmatrix} t_0 & -t_1 & t_2 \\ t_1 & t_{11} & -t_{12} \\ t_2 & t_{12} & t_{22} \end{pmatrix}, \tag{16}$$

$$\begin{aligned}\mathcal{E}(\mathbf{R}_5) &= D\left(C\left(\tfrac{-4\pi}{3}\right)\right)\mathcal{E}(\mathbf{R}_1)D^\dagger\left(C\left(\tfrac{-4\pi}{3}\right)\right) \\ &= \begin{pmatrix} t_0 & -\frac{1}{2}t_1 - \frac{\sqrt{3}}{2}t_2 & \frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 \\ \frac{1}{2}t_1 - \frac{\sqrt{3}}{2}t_2 & \frac{1}{4}t_{11} + \frac{3}{4}t_{22} & -\frac{\sqrt{3}}{4}t_{11} + t_{12} + \frac{\sqrt{3}}{4}t_{22} \\ -\frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 & -\frac{\sqrt{3}}{4}t_{11} - t_{12} + \frac{\sqrt{3}}{4}t_{22} & \frac{3}{4}t_{11} + \frac{1}{4}t_{22} \end{pmatrix},\end{aligned} \tag{17}$$

$$\begin{aligned}\mathcal{E}(\mathbf{R}_6) &= D(\sigma_v'')\mathcal{E}(\mathbf{R}_1)D^\dagger(\sigma_v'') \\ &= \begin{pmatrix} t_0 & \frac{1}{2}t_1 + \frac{\sqrt{3}}{2}t_2 & \frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 \\ -\frac{1}{2}t_1 + \frac{\sqrt{3}}{2}t_2 & \frac{1}{4}t_{11} + \frac{3}{4}t_{22} & \frac{\sqrt{3}}{4}t_{11} - t_{12} - \frac{\sqrt{3}}{4}t_{22} \\ -\frac{\sqrt{3}}{2}t_1 - \frac{1}{2}t_2 & \frac{\sqrt{3}}{4}t_{11} + t_{12} - \frac{\sqrt{3}}{4}t_{22} & \frac{3}{4}t_{11} + \frac{1}{4}t_{22} \end{pmatrix}.\end{aligned} \tag{18}$$

The nearest-neighbor TB Hamiltonian Eq. (8) can now be written as

$$H^{\mathrm{NN}}(\mathbf{k}) = \begin{pmatrix} h_0 & h_1 & h_2 \\ h_1^* & h_{11} & h_{12} \\ h_2^* & h_{12}^* & h_{22} \end{pmatrix}, \tag{19}$$

where

$$\begin{aligned} h_0 &= \epsilon_1 + 2\left(\cos(2\alpha) + 2\cos(\alpha)\cos(\beta)\right)t_0, \\ h_1 &= -2\sqrt{3}\sin(\alpha)\sin(\beta)t_2 + 2i\left(\sin(2\alpha) + \sin(\alpha)\cos(\beta)\right)t_1, \\ h_2 &= 2\left(\cos(2\alpha) - \cos(\alpha)\cos(\beta)\right)t_2 + 2\sqrt{3}i\cos(\alpha)\sin(\beta)t_1, \\ h_{11} &= \epsilon_2 + \left(2\cos(2\alpha) + \cos(\alpha)\cos(\beta)\right)t_{11} + 3\cos(\alpha)\cos(\beta)t_{22}, \\ h_{12} &= \sqrt{3}\sin(\alpha)\sin(\beta)\left(t_{22} - t_{11}\right) + 2i\left(\sin(2\alpha) - 2\sin(\alpha)\cos(\beta)\right)t_{12}, \\ h_{22} &= \epsilon_2 + 3\cos(\alpha)\cos(\beta)t_{11} + \left(2\cos(2\alpha) + \cos(\alpha)\cos(\beta)\right)t_{22}, \end{aligned} \tag{20}$$

and $\alpha = \frac{1}{2}k_x a$, $\beta = \frac{\sqrt{3}}{2}k_y a$.

We now consider a new basis consisting of three eigenfunctions of the angular momentum operators L^2 and L_z, for $l = 2, m = 0, \pm 2$,

$$|\tilde{\phi}_1\rangle = |d_{m=0}\rangle,\ |\tilde{\phi}_2\rangle = |d_{m=+2}\rangle,\ |\tilde{\phi}_3\rangle = |d_{m=-2}\rangle. \tag{21}$$

The new basis can be obtained from the old one by the transformation

$$|\tilde{\phi}_j\rangle = \sum_{j'} W_{jj'}|\phi_{j'}\rangle, \tag{22}$$

where

$$W = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \end{pmatrix}. \tag{23}$$

The TB Hamiltonian in new basis reads

$$\begin{aligned}\tilde{H}^{\mathrm{NN}}(\mathbf{k}) &= WH^{\mathrm{NN}}(\mathbf{k})W^\dagger \\ &= \begin{pmatrix} h_0 & \frac{1}{\sqrt{2}}(h_1 - ih_2) & \frac{1}{\sqrt{2}}(h_1 + ih_2) \\ \frac{1}{\sqrt{2}}(h_1^* + ih_2^*) & \frac{1}{2}(h_{11} + h_{22} + 2\mathrm{Im}(h_{12})) & \frac{1}{2}(h_{11} - h_{22} + 2i\mathrm{Re}(h_{12})) \\ \frac{1}{\sqrt{2}}(h_1^* - ih_2^*) & \frac{1}{2}(h_{11} - h_{22} - 2i\mathrm{Re}(h_{12})) & \frac{1}{2}(h_{11} + h_{22} - 2\mathrm{Im}(h_{12})) \end{pmatrix}.\end{aligned} \tag{24}$$

2 Spin-orbit coupling

The spin-orbit coupling (SOC) is modeled by

$$H_{\mathrm{SOC}} = \frac{\lambda}{2}\mathbf{L}\cdot\boldsymbol{\sigma}, \tag{25}$$

where $\mathbf{L}$ and $\boldsymbol{\sigma}$ are anglar momentum and Pauli matrices, respectively. Using the bases $\{|d_{z^2},\uparrow\rangle, |d_{xy},\uparrow\rangle, |d_{z^2-y^2},\uparrow\rangle, |d_{z^2},\downarrow\rangle, |d_{xy},\downarrow\rangle, |d_{z^2-y^2},\downarrow\rangle\}$ we get

$$H_{\mathrm{SOC}} = \frac{\lambda}{2}\begin{pmatrix} L_z & L_x - iL_y \\ L_x + iL_y & -L_z \end{pmatrix}. \tag{26}$$

In bases of d_{z^2}, d_{xy}, and $d_{x^2-y^2}$, the components L_x and L_y are zeros and

$$L_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 2i \\ 0 & -2i & 0 \end{pmatrix}. \tag{27}$$

Therefore the three-band TB Hamiltonian with SOC reads

$$H_{6\times 6}(\mathbf{k}) = \begin{pmatrix} H_{3\times 3}(\mathbf{k}) + \frac{\lambda}{2}L_z & 0 \\ 0 & H_{3\times 3}(\mathbf{k}) - \frac{\lambda}{2}L_z \end{pmatrix}. \tag{28}$$

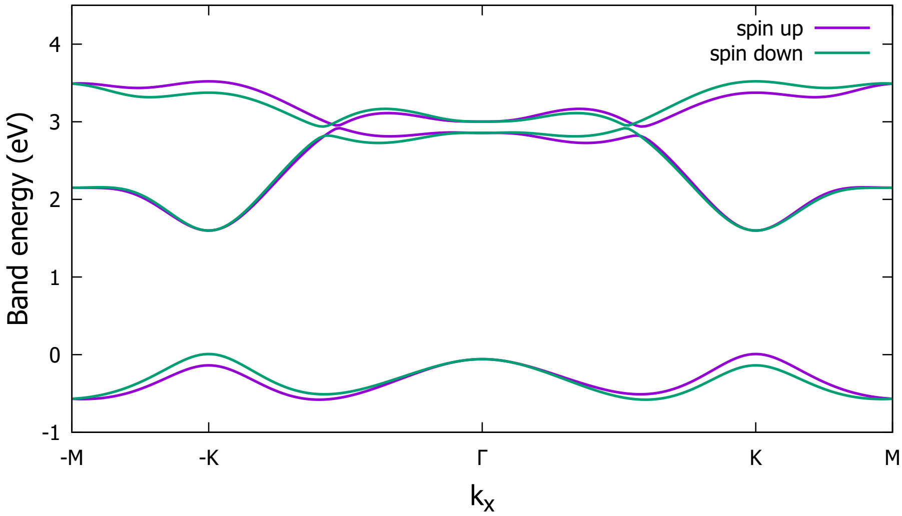

Figure 2: TB band structure of monolayer MoS_2 using following parameters: $\epsilon_1 = 1.045$ eV, $\epsilon_2 = 2.104$ eV, $t_0 = -0.184$ eV, $t_1 = 0.401$ eV, $t_2 = 0.507$ eV, $t_{11} = 0.218$ eV, $t_{12} = 0.338$ eV, $t_{22} = 0.057$ eV, $a = 3.19$ Å, $\lambda = 0.073$ eV [1].

3 Optical matrix elements

The matrix element of the electron position is given by

$$\langle \psi_{\lambda,\mathbf{k}} | \mathbf{r} | \psi_{\lambda',\mathbf{k}} \rangle = \frac{1}{N} \sum_{j,j'} C_j^{\lambda *}(\mathbf{k}) C_{j'}^{\lambda'}(\mathbf{k}) \sum_{\mathbf{R},\mathbf{R}'} e^{i\mathbf{k}(\mathbf{R}'-\mathbf{R})} \langle \phi_j(\mathbf{r}-\mathbf{R}) | \mathbf{r} | \phi_{j'}(\mathbf{r}-\mathbf{R}') \rangle. \tag{29}$$

In the tight binding model, the overlapping of orbitals belonging to different atoms is assumed to be small, one has

$$\langle \phi_j(\mathbf{r}-\mathbf{R}) | \mathbf{r} | \phi_{j'}(\mathbf{r}-\mathbf{R}') \rangle = (\mathbf{R}\delta_{jj'} + \mathbf{d}_{jj'})\, \delta_{\mathbf{R}\mathbf{R}'}, \tag{30}$$

where $\mathbf{d}_{jj'} = \langle \phi_j(\mathbf{r}) | \mathbf{r} | \phi_{j'}(\mathbf{r}) \rangle$ is the intra-atomic dipole matrix element between different orbitals.

Using the relation $\mathbf{p} = i\frac{m}{\hbar}[H, \mathbf{r}]$, where $H = -\frac{\hbar^2\nabla^2}{2m} + U_0(\mathbf{r})$, we obtain the matrix element of the electron momentum

$$\begin{aligned}
\langle\psi_{\lambda,\mathbf{k}}|\mathbf{p}|\psi_{\lambda',\mathbf{k}}\rangle =& i\frac{m}{\hbar}\frac{1}{N}\sum_{j,j'}C_j^{\lambda*}(\mathbf{k})C_{j'}^{\lambda'}(\mathbf{k})\sum_{\mathbf{R},\mathbf{R}'}e^{i\mathbf{k}(\mathbf{R}'-\mathbf{R})}\langle\phi_j(\mathbf{r}-\mathbf{R})|[H,\mathbf{r}]|\phi_{j'}(\mathbf{r}-\mathbf{R}')\rangle \\
=& i\frac{m}{\hbar}\frac{1}{N}\sum_{j,j'}C_j^{\lambda*}(\mathbf{k})C_{j'}^{\lambda'}(\mathbf{k})\sum_{\mathbf{R},\mathbf{R}'}e^{i\mathbf{k}(\mathbf{R}'-\mathbf{R})} \\
&\times\Bigg[\sum_{j''}\langle\phi_j(\mathbf{r}-\mathbf{R})|H|\phi_{j''}(\mathbf{r}-\mathbf{R}')\rangle\langle\phi_{j''}(\mathbf{r}-\mathbf{R}')|\mathbf{r}|\phi_{j'}(\mathbf{r}-\mathbf{R}')\rangle \\
&-\sum_{j''}\langle\phi_j(\mathbf{r}-\mathbf{R})|\mathbf{r}|\phi_{j''}(\mathbf{r}-\mathbf{R})\rangle\langle\phi_{j''}(\mathbf{r}-\mathbf{R})|H|\phi_{j'}(\mathbf{r}-\mathbf{R}')\rangle\Bigg] \\
=& i\frac{m}{\hbar}\frac{1}{N}\sum_{j,j'}C_j^{\lambda*}(\mathbf{k})C_{j'}^{\lambda'}(\mathbf{k})\sum_{\mathbf{R},\mathbf{R}'}e^{i\mathbf{k}(\mathbf{R}'-\mathbf{R})}\Bigg[(\mathbf{R}'-\mathbf{R})\langle\phi_j(\mathbf{r}-\mathbf{R})|H|\phi_{j'}(\mathbf{r}-\mathbf{R}')\rangle \\
&+\sum_{j''}\left(\langle\phi_j(\mathbf{r}-\mathbf{R})|H|\phi_{j''}(\mathbf{r}-\mathbf{R}')\rangle\mathbf{d}_{j''j'}-\mathbf{d}_{jj''}\langle\phi_{j''}(\mathbf{r}-\mathbf{R})|H|\phi_{j'}(\mathbf{r}-\mathbf{R}')\rangle\right)\Bigg].
\end{aligned} \tag{31}$$

Note that $e^{i\mathbf{k}(\mathbf{R}'-\mathbf{R})}(\mathbf{R}'-\mathbf{R}) = -i\nabla_{\mathbf{k}}e^{i\mathbf{k}(\mathbf{R}'-\mathbf{R})}$, $\langle\psi_{\lambda,\mathbf{k}}|H = \langle\psi_{\lambda,\mathbf{k}}|\varepsilon_\lambda(\mathbf{k})$, and $H|\psi_{\lambda',\mathbf{k}'}\rangle = \varepsilon_{\lambda'}(\mathbf{k}')|\psi_{\lambda',\mathbf{k}'}\rangle$, Eq. (31) reduces to

$$\begin{aligned}
\langle\psi_{\lambda,\mathbf{k}}|\mathbf{p}|\psi_{\lambda',\mathbf{k}}\rangle =& \frac{m}{\hbar}\sum_{j,j'}C_j^{\lambda*}(\mathbf{k})C_{j'}^{\lambda'}(\mathbf{k})\nabla_{\mathbf{k}}H_{jj'}(\mathbf{k}) \\
&+i\frac{m}{\hbar}\sum_{j,j'}C_j^{\lambda*}(\mathbf{k})C_{j'}^{\lambda'}(\mathbf{k})\left(\varepsilon_\lambda(\mathbf{k})-\varepsilon_{\lambda'}(\mathbf{k})\right)\mathbf{d}_{jj'}.
\end{aligned} \tag{32}$$

If we ignore the second term on the right-hand side of Eq. (32) which is proportional to the intra-atomic dipole $\mathbf{d}_{jj'}$, the momentum matrix element is simply given by the $\mathbf{k}$-gradient of the Hamiltonian that is similar as in the $\mathbf{k}\cdot\mathbf{p}$ theory. Although the intra-atomic term is usually considered to be infinitesimal, it can nevertheless be important for some materials. To evaluate this term, we need a comparison with accurate results obtained by other methods [2].

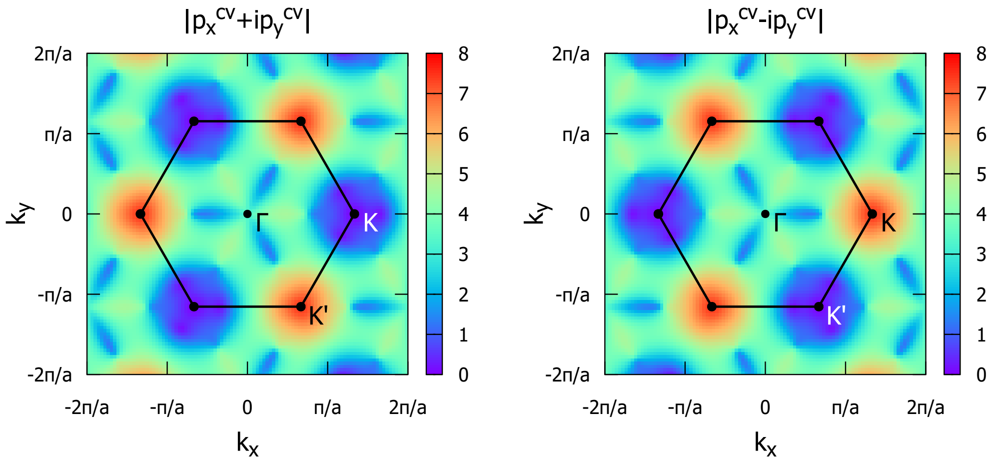

Figure 3: The absolute values of momentum operators $p_+^{cv} = p_x^{cv} + ip_y^{cv}$ and $p_-^{cv} = p_x^{cv} - ip_y^{cv}$ as a function of $\mathbf{k}$.

4 Three-band tight binding method in the presence of a magnetic field

Under a magnetic field described by a vector potential $\mathbf{A}(\mathbf{r})$ the single electron Hamiltonian changes into

$$H = \frac{(-i\hbar\boldsymbol{\nabla} + e\mathbf{A}(\mathbf{r}))^2}{2m} + U_0(\mathbf{r}) + g^*\mu_B\mathbf{B}\cdot\mathbf{L} \tag{33}$$

where $\mu_B = \frac{e\hbar}{2m}$ is Bohr magneton, g^* is an effective g factor, $\mathbf{B} = \nabla\times\mathbf{A}$ is the magnetic field, and $\mathbf{L}$ is the angular momentum. The TB wavefunction Eq. (4) has an additional phase factor

$$\psi_{\lambda,\mathbf{k}}(\mathbf{r}) = \sum_{j=1}^{3} C_j^\lambda \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} e^{i\theta_{\mathbf{R}}(\mathbf{r})}\phi_j(\mathbf{r}-\mathbf{R}) \tag{34}$$

The TB Hamiltonian Eq. (6) now reads

$$H_{jj'}(\mathbf{k}) = H'_{jj'}(\mathbf{k}) + H^Z_{jj'}(\mathbf{k}), \tag{35}$$

where

$$\begin{aligned} H'_{jj'}(\mathbf{k}) &= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_j(\mathbf{r})|e^{-i\theta_0(\mathbf{r})}\left[\frac{(-i\hbar\boldsymbol{\nabla} + e\mathbf{A}(\mathbf{r}))^2}{2m} + U_0(\mathbf{r})\right]e^{i\theta_{\mathbf{R}}(\mathbf{r})}|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle \\ &= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_j(\mathbf{r})|e^{i(\theta_{\mathbf{R}}(\mathbf{r})-\theta_0(\mathbf{r}))}\left[\frac{(-i\hbar\boldsymbol{\nabla} + e\mathbf{A}(\mathbf{r}) + \hbar\boldsymbol{\nabla}\theta_{\mathbf{R}}(\mathbf{r}))^2}{2m} + U_0(\mathbf{r})\right]|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle \end{aligned} \tag{36}$$

and

$$H^Z_{jj'}(\mathbf{k}) = g^*\mu_B\mathbf{B}\cdot\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_j(\mathbf{r})|e^{i(\theta_{\mathbf{R}}(\mathbf{r})-\theta_{\mathbf{0}}(\mathbf{r}))}\mathbf{L}|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle. \tag{37}$$

By choosing $\theta_{\mathbf{R}}(\mathbf{r}) = -\frac{e}{\hbar}\int_{\mathbf{R}}^{\mathbf{r}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'$ (Peierls substitution) we have

$$\begin{aligned} H'_{jj'}(\mathbf{k}) &= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_j(\mathbf{r})|e^{-\frac{ie}{\hbar}\int_{\mathbf{R}}^{\mathbf{r}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'+\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{r}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\left[-\frac{\hbar^2\nabla^2}{2m}+U_0(\mathbf{r})\right]|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle \\ &= \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\langle\phi_j(\mathbf{r})|e^{-\frac{ie}{\hbar}\Phi_{\mathbf{R},\mathbf{r},\mathbf{0}}}\left[-\frac{\hbar^2\nabla^2}{2m}+U_0(\mathbf{r})\right]|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle, \end{aligned} \tag{38}$$

where $\int_{\mathbf{0}}^{\mathbf{R}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'$ is the path integral along the line joining the two sites and $\Phi_{\mathbf{R},\mathbf{r},\mathbf{0}} = \oint_{\mathbf{R},\mathbf{r},\mathbf{0}}\mathbf{A}(\mathbf{r})\cdot d\mathbf{r}$ is the flux of $\mathbf{A}$ through the triangle formed by three points $\mathbf{R},\mathbf{r},\mathbf{0}$. It is showed that the flux term is negligibly small [**?**] and thus we have

$$H'_{jj'}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\langle\phi_j(\mathbf{r})|\left[-\frac{\hbar^2\nabla^2}{2m}+U_0(\mathbf{r})\right]|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle, \tag{39}$$

$$H^Z_{jj'}(\mathbf{k}) = g^*\mu_B\mathbf{B}\cdot\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\langle\phi_j(\mathbf{r})|\mathbf{L}|\phi_{j'}(\mathbf{r}-\mathbf{R})\rangle. \tag{40}$$

Considering only nearest neighbor hoppings, Eq. (39) becomes

$$\begin{aligned} H'^{\mathrm{NN}}_{jj'}(\mathbf{k}) &= \mathcal{E}_{jj'}(\mathbf{0}) + e^{i\mathbf{k}\cdot\mathbf{R}_1}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}_1}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\mathcal{E}_{jj'}(\mathbf{R}_1) \\ &+ e^{i\mathbf{k}\cdot\mathbf{R}_2}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}_2}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\mathcal{E}_{jj'}(\mathbf{R}_2) + e^{i\mathbf{k}\cdot\mathbf{R}_3}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}_3}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\mathcal{E}_{jj'}(\mathbf{R}_3) \\ &+ e^{i\mathbf{k}\cdot\mathbf{R}_4}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}_4}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\mathcal{E}_{jj'}(\mathbf{R}_4) + e^{i\mathbf{k}\cdot\mathbf{R}_5}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}_5}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\mathcal{E}_{jj'}(\mathbf{R}_5) \\ &+ e^{i\mathbf{k}\cdot\mathbf{R}_6}e^{\frac{ie}{\hbar}\int_{\mathbf{0}}^{\mathbf{R}_6}\mathbf{A}(\mathbf{r}')\cdot d\mathbf{r}'}\mathcal{E}_{jj'}(\mathbf{R}_6). \end{aligned} \tag{41}$$

We consider a uniform magnetic field perpendicular to the plane of TMDC monolayer, $\mathbf{B} = (0,0,B)$. Using Landau gauge $\mathbf{A} = (0,Bx,0)$ and substituting $x = na$, we obtain

$$\begin{aligned} H'^{\mathrm{NN}}_{jj'}(\mathbf{k}) &= \mathcal{E}_{jj'}(\mathbf{0}) + e^{i\mathbf{k}\cdot\mathbf{R}_1}\mathcal{E}_{jj'}(\mathbf{R}_1) + e^{-i2\pi n\frac{\Phi}{\Phi_0}}e^{i\mathbf{k}\cdot\mathbf{R}_2}\mathcal{E}_{jj'}(\mathbf{R}_2) + e^{-i2\pi n\frac{\Phi}{\Phi_0}}e^{i\mathbf{k}\cdot\mathbf{R}_3}\mathcal{E}_{jj'}(\mathbf{R}_3) \\ &+ e^{i\mathbf{k}\cdot\mathbf{R}_4}\mathcal{E}_{jj'}(\mathbf{R}_4) + e^{i2\pi n\frac{\Phi}{\Phi_0}}e^{i\mathbf{k}\cdot\mathbf{R}_5}\mathcal{E}_{jj'}(\mathbf{R}_5) + e^{i2\pi n\frac{\Phi}{\Phi_0}}e^{i\mathbf{k}\cdot\mathbf{R}_6}\mathcal{E}_{jj'}(\mathbf{R}_6), \end{aligned} \tag{42}$$

where $\Phi_0 = \frac{h}{e}$ and $\Phi = \frac{\sqrt{3}}{2}Ba^2$. The Hamiltonian depends on the site index n and is not invariant under translation of a lattice vector along the x axis. To restore translational invariance we need to expand the unit cell in the

x direction. For the case $\Phi/\Phi_0 = p/q$, a unit cell consisting of q M-atoms along the x direction will satisfy the periodicity. We define a new basis set of $3q$ atomic orbitals $\{\phi_j(na, y)\}$ where $j = 1, 2, 3$ and $n = 1, 2, ..., q$. Note that $e^{ik_x a}\phi_j(na, y) = \phi_j((n+1)a, y)$ and $e^{-ik_x a}\phi_j(na, y) = \phi_j((n-1)a, y)$, the Hamiltonian matrix in the new basis is written as

$$\begin{aligned} H'^{\mathrm{NN}}_{jnj'n'}(\mathbf{k}) &= \mathcal{E}_{jj'}(\mathbf{0})\delta_{n,n'} + \mathcal{E}_{jj'}(\mathbf{R}_1)\delta_{n-1,n'} + e^{-i2\pi n\frac{p}{q}} e^{i(\alpha-\beta)}\mathcal{E}_{jj'}(\mathbf{R}_2)\delta_{n,n'} \\ &+ e^{-i2\pi n\frac{p}{q}} e^{i(-\alpha-\beta)}\mathcal{E}_{jj'}(\mathbf{R}_3)\delta_{n,n'} + \mathcal{E}_{jj'}(\mathbf{R}_4)\delta_{n+1,n'} \\ &+ e^{i2\pi n\frac{p}{q}} e^{i(-\alpha+\beta)}\mathcal{E}_{jj'}(\mathbf{R}_5)\delta_{n,n'} + e^{i2\pi n\frac{p}{q}} e^{i(\alpha+\beta)}\mathcal{E}_{jj'}(\mathbf{R}_6)\delta_{n,n'}. \end{aligned} \tag{43}$$

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