Role of Velocity Field and Principal Axis of Tilted Dirac Cones in Effective Hamiltonian of Non-Coplanar Nodal Loop

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Nodal line in single-component molecular conductor [Pd(dddt)$_2$] with a half-filled band has been examined to elucidate properties of Dirac cone on the non-coplanar loop. The velocity of the tilted cone is evaluated at respective Dirac points on the nodal loop, which is obtained by our first-principles band structure calculations [J. Phys. Soc. Jpn. 87 113701 (2018)]. In the previous study, we proposed a new method to derive an effective Hamiltonian with a $2 \times 2$ matrix using two kinds of velocities of the Dirac cone on the nodal line, and the momentum dependence of the Dirac points are fully reproduced only at symmetric points. In this work, we show that our improved method well reproduces reasonable behavior of all the Dirac cones and a very small energy dispersion of 6 meV among the Dirac points on the nodal line, which originate from three-dimensionality of the electronic state. The variation of velocities along the nodal line are shown by using principal axes of the gap function between the conduction and valence bands. Further, the electronic states of the nodal line semimetal is examined by calculating the density of states close to the chemical potential using the effective Hamiltonian.

1. Introduction

A class of three-dimensional (3D) topological semimetals, called nodal line semimetals is a recent topics in condensed matter physics. 1–6 Although the number of band calculations has predicted the existence of nodal line nodal loop near the Fermi level, 7–14 only a few candidate materials are experimentally confirmed by angle-resolved photo emissions and magnetoresistance. 15–18 There are several protection mechanisms, such as a combination of inversion and time-reversal symmetry, mirror reflection symmetry, and nonsymmorphic symmetry. 19 Nodal line takes the form of an extended line running across the Brillouin zone (BZ), closed loop inside the BZ or even form a chain consisting of tangled loops. Such studies originate from accidental degeneracies in the energy bands with an inversion symmetry. 20 The existence of odd or even number of nodal loop inside the BZ corresponds to a condition given by negative or positive sign of a product of parity eigenvalues of filled bands at the time reversal invariant momentum (TRIM), respectively. The condition is valid also for weak spin orbit coupling (SOC) materials with light elements such as molecular conductors. The classification of band nodes is appreciated as an underpinning of topological materials after the discovery of $\mathbb{Z}_2$ topological insulator. 21–23

A noticeable molecular conductor that shows a single nodal-loop semimetal was discovered by the structural analysis and transport measurement under pressure. A single-component molecular conductor [Pd(dddt)$_2$] (dddt = 5,6-dihydro-1,4-dithiin- 2,3-dithiolate) exhibits nearly massless Dirac electrons under high pressure, which has been shown by almost temperature independent electronic resistivity and performing theoretical structural optimization using first-principles calculations based on density functional theory (DFT). 24 Further, the nodal line with a loop of Dirac points has been analyzed using an extended Hückel calculation for the DFT optimized structure. 25 The formation of Dirac points originates from the multi-orbital nature, where the parity is different between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital).

The characteristic property of the nodal line semimetal has been examined to comprehend such nodal line, We have calculated the anisotropic electric conductivity at absolute zero and finite temperatures, 26, 27 and proposed the reduced Hamiltonian with two components. 25, 28 Further, the extensive studies are performed on the topological behavior of the Berry phase, 29 and a method to obtain an effective Hamiltonian directly from the nodal line. 30 As for the condition of the Dirac electrons, 11, 21 the present Dirac nodal line semimetal in 3D system is compared with the previous case of massless Dirac electrons in a two-dimensional molecular conductor. 31, 32, 25, 33 Note that the materials of [Pd(dddt)$_2$] may be regarded as a Dirac electron system with the gapless nodal line, 24, 30 while it turns out to be a strong topological insulator 34 in the presence of the SOC. 22

In the previous work, a reduced model is introduced to analyze such Dirac cone in [Pd(dddt)$_2$]. 30 In fact, an effective Hamiltonian with a $2 \times 2$ matrix has been derived by employing a new method, where two kinds of velocities of the cone are successfully calculated from the momentum dependence of the Dirac points on the nodal line. However, the description of the the matrix element is insufficient to reproduce the quantitative behavior of all the Dirac cone on the nodal line. The direction of both

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the velocity and principal axes of the cone is nontrivial, and the cone is tilted, when the energy of Dirac point depends on the line. Further, it is significant to determine the principal axes of the cone to calculate the correct response to the external field, as seen from the deviation of the current from the electric field for the anisotropic conductivity.\(^{35}\)

In the present paper, by improving the previous method,\(^{30}\) we demonstrate the effective model, which reproduces all the Dirac points obtained in the DFT calculation. In Sect. 2, the velocities of the Dirac cone are calculated from the gradient of matrix elements, while the tilting velocity is obtained from the energy variation of the Dirac point. In Sect. 3, the variation of the Dirac cone along the nodal line is examined by calculating the velocity fields and principal axes of the cone, which are obtained from the gap function between the conduction and valence bands. The effect of the tilting of the cone is shown by calculating a tilting parameter. Further, using the present effective Hamiltonian, the density of states is estimated to understand the characteristics of the nodal line semimetal. Summary is given in Sect. 4.

2. Nodal line and Two-band model

2.1 Effective Hamiltonian

Figure 1 shows the crystal structure of single-component molecular conductor [Pd(dddt)\(_2\)]\(_2\) with HOMO and LUMO. In the molecule, there is an inversion center at Pd atom, where the HOMO and LUMO have the different parity of umergade and gerade symmetries. Since there are four molecules in unit cell, there are eight energy bands \(E_1 \geq E_2 \geq E_3 \geq \cdots \geq E_8\), where upper (lower) four bands are mainly determined by HOMO and LUMO. Under high pressure of 8 GPa, the electronic state shows the Dirac point due to the reverse given by \(E_\pm(k)\) for HOMO and \(E_\pm(k)\) for LUMO close to the \(\Gamma\) point. The tight-binding model shows that the Dirac points \(k_0\) with \(E_\pm(k_0) = E_\mp(k_0)\) form a loop, i.e., a nodal line between the conduction and valence bands.\(^{25}\) Such a line is verified by the first-principles DFT calculation.\(^{30}\)

Figure 2(a) shows a nodal line, which is obtained by the DFT calculation,\(^{30}\) and is utilized in the present calculation. Although the shape of the line is slightly different from that of the tight-binding model, the condition of the Dirac point at the TRIM remains the same.\(^{34}\) In the previous paper,\(^{30}\) it is shown that the Dirac points in Fig. 2(a) can be obtained by a two-band model of the following effective Hamiltonian \(H_{\text{eff}}(k)\) with \(2 \times 2\) matrix,

\[
H_{\text{eff}}(k) = \begin{pmatrix}
E(k) + f_+(k) & -if_2(k) \\
if_2(k) & f_-(k) - f_2(k)
\end{pmatrix},
\]

(1)

The base is given by \(|H(k)| > |L(k)|\), the wave functions of \(H_0(k)\) corresponding to HOMO and LUMO, i.e.,

\[
H_0^\alpha(k) = E_\alpha(k)|\alpha(k)\rangle > ,
\]

(2)

with \(\alpha = H\) and \(L\). \(k = (k_x, k_y, k_z)\) denotes a three-dimensional wave vector. \(k_x, k_y,\) and \(k_z\) correspond to the reciprocal vector for \(a + c, b\) and \(c.\(^{24}\)\) Matrix elements \(f_0(k), f_2(k)\), and \(f_3(k)\) in Eq. (1) are given by

\[
f_2(k) = i < H(k)|H_{\text{int}}|L(k)>,
\]

(3)

\[
f_3(k) = \frac{(E_H(k) - E_L(k))}{2},
\]

(4)

\[
f_0(k) = \frac{(E_H(k) + E_L(k))}{2},
\]

(5)

where \(H_{\text{int}}\) denotes the HOMO-LUMO (H-L) interaction. Although the off-diagonal element is treated by the perturbation, such an effective Hamiltonian is justified for the limiting case of \(f_0(k) \to 0\), which is the present case of finding the Dirac point. The energy of Eq. (1) is calculated as \(E_\pm = f_0 \pm \sqrt{f_2^2 + f_3^2}\), where \(E_+(E_-) = E_+(E_-)\) corresponds to the energy of conduction (valence) band. The Dirac point \(k_0\), which is given by \(E_+ = E_-\), is obtained from

\[
f_2(k_0) = 0,
\]

(6a)

\[
f_0(k_0) = 0.
\]

(6b)

Note that \(f_0(k)\) and \(f_2(k)\) are the even function of \(k\) due to time reversal symmetry and \(f_3(k)\) is the odd function of \(k\) due to HOMO and LUMO having different parity. Instead of calculating Eq. (2) directly, we utilize the numerical results of the DFT calculation as follows. The function \(f_2(k)\) is estimated by projecting the nodal line on the \(k_x - k_z\) plane, while \(f_3(k)\) is estimated by projecting the nodal line on the \(k_x - k_y\) plane.\(^{30}\) Such a method is justified in the present case due to the presence of the inversion symmetry at \(k_y = 0\).

Here we mention about the gap function between the conduction and valence bands, which is estimated from the present effective Hamiltonian of Eq. (1). Close to the Dirac point, we rewrite \(f_j(k)\) as \(f_j(k) \simeq f_j(k_0) + \nu_j \cdot \delta k, (j = 2, 3\text{ and } 0)\) with \(\delta k = k - k_0\), where \(f_2(k_0) = f_3(k_0) = 0\) and \(f_0(k_0) \neq 0\). Diagonalizing Eq. (1), the energy of the Dirac cone is obtained as \(E_\pm(k) \simeq f_0(k_0) + \nu_0 \cdot \delta k \pm \sqrt{(\nu_2 \cdot \delta k)^2 + (\nu_3 \cdot \delta k)^2}\). Thus, the gap function \(\Delta(k)\) is expressed as

\[
\Delta(k) = \sqrt{(\nu_2 \cdot \delta k)^2 + (\nu_3 \cdot \delta k)^2}.
\]

(7)
The matrix elements of Eq. (1) are obtained as,

\[ f_0(k) \simeq b_x k^2_x + b_y k^2_y + b_z k^2_z \]

\[ + b k^2_z k^2_x + d x k^2_y k^2_z + d_z k^2_y k^2_z + C_0 \]  

(8c)

where \( f_0(k_0) = (E_D) \) denotes the energy at the Dirac point \( k_0 \). The Dirac point \( k_0 = (k_{0x}, k_{0y}, k_{0z}) \) is obtained by calculating self-consistently Eqs. (6a) and (6b) with Eqs. (8a) and (8b). Compared with the previous case, the present calculation is improved by adding arbitrary \( C_2 \) and \( C_3 \) in Eqs. (8a) and (8b), and fourth order terms in Eq. (8c). Note that a non-coplanar nodal line is understood from the nonlinear terms in Eq. (8a).

From Eqs. (8a), (8b), and (8c), the velocity of the cone at the Dirac point \( k_0 \) is obtained as \( \mathbf{v}_2 = \nabla_{k_0} f_2 \), \( \mathbf{v}_3 = \nabla_{k_0} f_3 \), and \( \mathbf{v}_0 = \nabla_{k_0} f_0 \). The explicit form of \( f_j \) is given as

\[ v_2 = \nabla_{k_0} f_2 \simeq C_2(1 + 120 b_2 k^4_{0x} - 1900 k^4_{0x} + 0, 1), \quad (9a) \]

\[ v_3 = \nabla_{k_0} f_3 \simeq C_3(2 k_{0x}(1.196^2 + 2 k_{0x} k_{0y})/0.027^2, \]

\[ 2 k_{0y}/0.86^2 + 2 k_{0x} k_{0y}/0.027^2, 0), \quad (9b) \]

\[ v_0 = \nabla_{k_0} f_0 \simeq (2 k_{0x}(b_x + b k_{0x} + d x k_{0y}), \]

\[ 2 k_{0y}(b_y + d x k_{0x} + d_z k_{0y}), \]

\[ 2 k_{0x} (b_z + b d_{0x} + d_b k_{0y}^2)) \]  

(9c)

Although the derivative of \( C_2(k_0) \) and \( C_3(k_0) \) with respect to \( k_0 \) is finite, Eqs. (9a) and (9b) are still valid due to \( f_2(k_0)/C_2 = 0 \) and \( f_3(k_0)/C_3 = 0 \).

Coefficients in Eqs. (8a) and (8b) except for \( C_2 \) and \( C_3 \) are obtained from Eqs. (6a) and (6b) with Dirac points of Fig. 2(a). In fact, we used two Dirac points of \((0, 0.0856, 0) \) (I), \((-0.1967, 0.0, 0.3924) \) (II), and some other Dirac points in the intermediate region in Fig. 2(a). Coefficients \( C_2 \) and \( C_3 \), which also depend on the location of the Dirac point, are determined using the velocities of the Dirac points (I) and (II). From the DFT calculation, the velocities at the point (I) are \( \mathbf{v}_2 = (0.148, 0, 0.148) \) and \( \mathbf{v}_3 = (0, 1.25, 0) \), while the velocity at the Dirac point (II) are \( \mathbf{v}_2 \simeq 0.36 \) and \( \mathbf{v}_z \simeq 0.09 \). Further, using an interpolation between points (I) and (II) we obtain \( C_2 = 0.148(1 - 0.39(k_z/0.392^2)) \)

\[ C_3 = 0.65(1 - 0.53(k_z/0.392^2)) \]

for Eqs. (9a) and (9b).

Figure 2(b) shows the energy of the Dirac points as a function of \( k_z \), where open square denotes the numerical results of the DFT calculation, and is used to fit Eq. (8c). Thus, we obtain that the coefficients in Eq. (8c) are \( b_x = -0.88, b_y = -2.62, b_z = -0.069 \), \( b = 3.7, d_x = -98, \) and \( d_z = 32 \). Note that terms with coefficients \( b_x, b_y, \) and \( b_z \) are added compared with the previous case, since terms with only \( b_x, b_y, \) and \( b_z \) are insufficient to reproduce the open square in Fig. 2(b).

The coefficients \( b_x, b_y, b_z \) and \( b \) in Eq. (6) is determined from \( \delta E_D \equiv (E_D - C_0) \) at the Dirac point (I), and the tiltting velocities \( \mathbf{v}_0 = (0, -0.45, 0) \) and \( \mathbf{v}_0 = (0, 0.12, 0.06) \) at the Dirac points (I) and (II), respectively. \( C_0 \) denotes \( E_D \) at the Dirac point (I). Further, the coefficients \( d_x \) and \( d_z \) are determined from Dirac points (symbols) with \( \delta E_D = -0.0539 \) and -0.0642 close to the minimum in Fig. 2(b). The energy \( E_D \) (solid line) is calculated by substituting the Dirac point into Eqs. (8c), where \( k_0 \) is

Note that the spectrum of the Dirac cone is perpendicular to the nodal line since the tangent of the nodal line is parallel to \( \mathbf{v}_2 \times \mathbf{v}_3 \).  

2.2 Calculation of matrix elements

We examine \( f_2(k), f_3(k), \) and \( f_0(k) \) in terms of the power law of \( k \), where the coefficients of \( f_2(k) \) and \( f_3(k) \) are determined as so to reproduce the Dirac points in Fig. 2(a).  

Hereafter, we take the lattice constant as unity and scale \( k_x, k_y, \) and \( k_z \) by \( 2\pi \), i.e., \( k_{x}/2\pi \to k_{0x} \) for \( \alpha = x, y, \) and \( z \). The unit of energy is taken as eV. The matrix elements of Eq. (1) are obtained as,

\[ f_2(k) \simeq C_2(k_x + k_y + 40k^2_x - 380k^2_z), \quad (8a) \]

\[ f_3(k) \simeq C_3((k_x/0.196)^2 + (k_y/0.086)^2 \]

\[ + (k_x k_y/0.027)^2 - 1) \],  

(8b)

Fig. 2. (Color online) (a) Nodal line in the three-dimensional momentum space \((k_x, k_y, k_z)\), which connects the Dirac point \( k_0 = (k_{0x}, k_{0y}, k_{0z}) \) calculated from first-principles calculation for the optimized structure at 8GPa. \( k_0 \) is taken as \((0.085, 0.075, 0.108) \) and \((-0.191, 0.019, 0.372) \).
and cone (8b). Using these Dirac points, the velocities of the Dirac self-consistently Eqs. (6a) and (6b) with Eqs. (8a) and v potential first-principles calculation (open square). The chemical val region of 2.3 Velocities by the alternation of the hole and electron pockets, e.g., the half-filled band, which is shown later. It is found that the function of k̂ is the odd function of x̂. In order to consider the orthogonal basis on the e2-e3 plane, we introduce e⊥ (= e1 × e2⊥), which is orthogonal to both e1 and e2. They are expressed as

\begin{align}
e_2 &= v_2/v_3 = (v_{2z}, 0, v_{2z}/v_3), \tag{10a} \\
e_3 &= v_3/v_3 = (v_{3z}, v_{3y}, 0)/v_3, \tag{10b} \\
e_1 &= e_2 \times e_3/|e_2 \times e_3|, \tag{10c} \\
e_\perp &= e_1 \times e_2, \tag{10d}
\end{align}

where v2 = \sqrt{v_{2x}^2 + v_{2z}^2} and v3 = \sqrt{v_{3x}^2 + v_{3y}^2}. Figure 4(a) shows components of e1 as the function of k2, e1y is odd while e1x and e1z are even. With increasing k2, e1y changes from 1 to -1, while the sign of e1x and e1z remains unchanged. Note that e1 with k_y < 0 (small symbols in Fig. 2(a)) is obtained from e1 with k_y > 0 by the replacement of (k_\text{ox}, k_\text{oy}, k_\text{o}_z) → (-k_\text{ox}, k_\text{oy}, -k_\text{o}_z).

3. Properties of Dirac Cone

3.1 Unit vector along nodal line

Since v2 is not orthogonal to v3 except for k_{0z} = 0, we calculate principal axes to understand clearly the Dirac cone for arbitrary Dirac point on the nodal line. First, we introduce a set of three orthogonal unit vectors, e1, e2, and e⊥. Quantities e2, e3, and e1 are unit vectors parallel to v2, v3 and v2 × v3, respectively. Since the direction of e1 is the tangent of the nodal line, the vectors of principal axes for the Dirac cone are located on the plane perpendicular to e1, i.e., on the e2-e3 plane. In order to consider the orthogonal basis on the e2-e3 plane, we introduce e⊥ (= e1 × e2⊥), which is orthogonal to both e1 and e2. They are expressed as

\begin{align}
e_2 &= v_2/v_2 = (v_{2x}, 0, v_{2z}/v_2), \tag{11a} \\
e_3 &= v_3/v_3 = (v_{3x}, v_{3y}, 0)/v_3, \tag{11b} \\
e_1 &= e_2 \times e_3/|e_2 \times e_3|, \tag{11c}
\end{align}

where v2 = \sqrt{v_{2x}^2 + v_{2z}^2} and v3 = \sqrt{v_{3x}^2 + v_{3y}^2}. Figure 4(a) shows components of e1 as the function of k2, e1y is odd while e1x and e1z are even. With increasing k2, e1y changes from 1 to -1, while the sign of e1x and e1z remains unchanged. Note that e1 with k_y < 0 (small symbols in Fig. 2(a)) is obtained from e1 with k_y > 0 by the replacement of (k_\text{ox}, k_\text{oy}, k_\text{o}_z) → (-k_\text{ox}, k_\text{oy}, -k_\text{o}_z).

3.2 Principal axes and values

Next, we examine the principal axes of the gap function of Eq. (7), which is expressed in terms of e2 and e⊥. Since v2 is not orthogonal to v3 except for k_{0z} = 0, we introduce φ as an angle between v2 and v3,

\[ \cos \phi = (v_2 \cdot v_3)/(v_2 v_3). \tag{11a} \]

In Fig. 5, φ as a function of k_z is shown by the dashed line, where φ = π/2 is the odd function of k_z and |cos ϕ| increases monotonously by the increase of |k_z|. To calculate the gap function Δ(q) given by Eq. (7), we introduce q = k - k_0 = q_1e_1 + q_2e_2 + q_3e_3. Noting that cos ϕ = e_2 · e_3, v_2 = v_2 v_3 and v_3 = v_3 cos(ϕ)e_2 + v_3 sin(ϕ)e_⊥, we obtain

\begin{align}
v_2 \cdot q &= v_2 q_2, \tag{11b} \\
v_3 \cdot q &= v_3 q_3 \cos \phi + v_3 q_3 \sin \phi. \tag{11c}
\end{align}

Thus, the explicit form of the gap function Δ(q) is written as

\[ \Delta(q)^2 = (v_2 \cdot q)^2 + (v_3 \cdot q)^2 \]

= Aq_2^2 + 2Cq_2q_3 + Bq_3^2, \tag{12a} \\
A &= v_2^2 + (v_3 \cos \phi)^2, \tag{12b} \\
B &= v_3^2(\sin \phi)^2. \tag{12c} \]
The principal axes are obtained by a rotation of the axis on the \( q_2 - q_3 \) plane to eliminate the second term being proportional to \( q_2 q_3 \). The result is obtained as

\[
\Delta(q)^2 = V_2^2 q_2^2 + V_3^2 q_3^2 ,
\]

\[
V_2^2 = \frac{1}{2} \left[ A + B \pm \sqrt{(A - B^2) + 4C^2} \right]
\]

\[
\tan(2\theta) = \frac{2C}{A - B} = \frac{v_2^2 \sin 2\phi}{v_2^2 + v_3^2 \cos 2\phi} ,
\]

where \( q_+ \) and \( q_- \) are rotated coordinates of principle axes given by

\[
e_+ = q_1 e_1 + q_+ e_+ + q_- e_- ,
\]

\[
e_- = \cos \theta e_2 + \sin \theta e_3 ,
\]

\[
e_+ = -\sin \theta e_2 + \cos \theta e_3 .
\]

In Fig. 5, \( \theta \) is shown by the dot dashed line, where \( \theta \) is an angle between \( e_- \) and \( e_2 \) and is chosen as \(|\theta| \leq \pi/2 \).

Figures 4(b) and 4(c) show \( k_z \) dependence of the unit vector, \( e_z \), which corresponds to respective principal axes. Figure 4(b) shows the component of \( e_- = (e_{-x}, e_{-y}, e_{-z}) \). As a function of \( k_z, e_{-x} \) and \( e_{-z} (>0) \) are even and \( e_{-y} \) is odd. \( e_{-z} \) takes a minimum and \( \approx 1 \) for \( k_z = \pm 0.3924 \), while \( e_{-x} \) takes a maximum and decreases almost to zero for \(|k_z| \approx 0.3924 \). With increasing \(|k_z|, e_{-y} \) increases linearly followed by a sudden decrease to zero at \(|k_z| \approx 0.3924 \). Figure 4(c) shows \( k_z \) dependence of the component for \( e_+ = (e_{+x}, e_{+y}, e_{+z}) \). \( e_{+y} \) is even function where \( e_{+y} = 1 \) at \( k_z = 0 \) and decreases to zero monotonously with \(|k_z| \) increasing to \( 0.3924 \). \( e_{+x} \) and \( e_{+z} \) are odd function, \( e_{+x} \) changes from \( \approx 1 \) to \( \approx -1 \). The variation of \( e_{+z} \) is much smaller than that of \( e_{+y} \). The rotation of \( e_+ \) with increasing \( k_z \) from \( k_z = 0 \) to \( k_z = 0.3924 \) is also reasonable compared with that of \( e_- \) due to \( e_+ \cdot e_+ = 0 \).

The cross section for \( \Delta(k) = E_0 \) shows an ellipse with the radius of the minor (major) axis, which is calculated as \( a = E_0 / V_+ \) \( b \) \( = E_0 / V_- \). Using principal values \( V_+ \) and \( V_- \), we estimate the area of the ellipse, \( S \) given by the gap \( 2E_0 = E_+ - E_- \). For arbitrary Dirac point, where \( S \) is determined by \( v_2 \) and \( v_3 \). In fact, the area of the ellipse, \( S \) with the gap \( 2E_0 \) is given by

\[
S(k_0) = \pi ab = \pi E_0^2 / (V_+ V_-) = \pi E_0^2 / \sqrt{AB-C^2} = \pi E_0^2 / (v_2 v_3 |\sin \theta|) .
\]

The \( k_z \) dependence of \( S(x S' = 1/|v_2 v_3|) \) is shown in Fig. 5 which takes a minimum with increasing \(|k_z| \).

Figure 6 shows velocities \( V_\pm \) of Eq. (13b), which are the principal values of the gap function. The principal axes of the ellipsoid are obtained by a rotation of \( \theta \) (in Fig. 5) from the \( q_2 - q_3 \) plane to the \( q_- q_+ \) plane. The quantity \( \theta \) is odd with respect to \( k_z \) and becomes \( \approx \pm \pi/2 \) for \( k_z = \pm 0.3924 \). The principal value \( V_+ \) decreases monotonously but \( V_- \) takes a maximum with increasing \(|k_z| \). Principal values \( V_\pm (V_+ > V_-) \) show a large anisotropy, where \( V_+/V_- \) takes a maximum \((\approx 6.0)\) at \( k_z = 0 \) and a minimum \((\approx 2.3)\) at \(|k_z| = 0.324 \).

3.3 Effect of tilting

We briefly mention the Dirac cone in the presence of the tilting velocity \( v_0 \). On the basis of \( e_\pm \), the tilting velocity is rewritten as

\[
v_0 = v_{0,1} e_1 + v_{0,-} e_- + v_{0,+} e_+ , \quad (15a)
\]

\[
v_0 \pm = v_0 \mp e_0 , \quad (15b)
\]

with \( v_{0,1} = v_0 \cdot e_1 \). In Fig. 6, \( v_0 \pm \) is shown, where \( v_0 - (v_{0,0}) \) is the odd (even) function with respect to \( k_z \). By taking account of \( v_0 \cdot q \) with \( q = q_- e_- + q_+ e_+ \), the energy of the upper band \( E_+(q) = E \) is written as

\[
(\sqrt{(V_- q_-)^2 + (V_+ q_+)^2} + v_0 - q_- + v_0 + q_+ = E . \quad (16)
\]

Defining \( \vec{q}_\pm = V_\pm q_\pm \), we examine the tilting on the plane of \( \vec{q}_- \) and \( \vec{q}_+ \). Equation (16) is rewritten as

\[
\vec{q}_-^2 + \vec{q}_+^2 + \vec{\delta} \cdot (\vec{q}_- e_- + \vec{q}_+ e_+) = E , \quad (17a)
\]

\[
\vec{\delta} = (v_0 - V_-) e_- + (v_0 + V_+) e_+ , \quad (17b)
\]

\[
\eta = |\vec{\delta}| = \sqrt{(v_0 - V_-)^2 + (v_0 + V_+)^2} . \quad (17c)
\]

The quantity \( \eta \) denotes a tilting parameter and the \( k_z \) dependence is shown in Fig. 6. The Dirac cone is tilted but not overtilted due to \( \eta < 1 \). Defining \( \theta' \) by \( e_- \sin \theta' = \cdots \)
Fig. 6. (Color online) Velocities $V_\perp$ and $V_-$ for principal axes of the Dirac cone without tilting, which is obtained by the gap function Eq. (13a). Note that $\eta$ denotes a tilting parameter given by \(\eta = (v_{0,-}/V_-)^2 + (v_{0,+}/V_+)^2\). The quantity $\eta$ denotes the tilting parameter given by $\eta = ((v_{0,-}/V_-)^2 + (v_{0,+}/V_+)^2)^{1/2}$, which is shown in Eq. (17c).

$e^+ \cos \theta' = \tilde{\delta}/\tilde{d}_i$, Eq. (17a) is rewritten as

\[
(1 - \eta^2)Q^2 + (1 - \eta^2) \left( Q_+ \frac{E\eta}{1 - \eta^2} \right)^2 = E^2,
\]

where

\[
\tilde{q}_- e_- + \tilde{q}_+ e_+ = Q_-e_{\delta 2} + Q_+e_{\delta 1}, \tag{18b}
\]

\[
e_{\delta 2} = \cos \theta' e_- + \sin \theta' e_+, \tag{18c}
\]

\[
e_{\delta 1} = -\sin \theta' e_- + \cos \theta' e_+, \tag{18d}
\]

\[
\sin \theta' = \frac{(v_{0,-}/V_-)}{\eta}. \tag{18e}
\]

Equation (18a) shows an ellipsoid with a radius $E(1 - \eta^2)^{-1} (E_2(1 - \eta^2)^{-1/2})$ for $Q_+/Q_-$. The center is located at $[E\eta/(1 - \eta^2)][-\sin \theta', \cos \theta']$ on the plane of $\tilde{q}_-$ and $\tilde{q}_+$. The phase $\theta'$ is an angle between $e_{\delta 2}$ and $e_-$, where $e_{\delta 1}$ and $e_{\delta 2}$ are orthogonal each other due to $e_+ e_- = 0$. For $k_z = 0$, the principal axis is given by $e_+ = e_{\delta 1}$, i.e., $\tilde{q}_+ = Q_+$ with $\theta' = 0$ due to $v_{0,-} = 0$. Thus the rotation angle of the axis of the ellipsoid is obtained as $\theta'$, i.e., $Q_- = \tilde{q}_- \cos \theta' + \tilde{q}_+ \sin \theta'$, and $Q_+ = -\tilde{q}_- \sin \theta' + \tilde{q}_+ \cos \theta'$ from Eqs. (18b), (18c), and (18d).

Note that it is straightforward to calculate the anisotropic conductivity by projecting the electric field on the axes of $e_{\delta 1}$ and $e_{\delta 2}$.

3.4 Density of states

We calculate the chemical potential $\mu$, which is measured from $E_D$ at the Dirac point (I) with $k = (0, 0.086, 0)$. For this purpose, from Eqs. (12b), (12c), (12d), (13a), and (13b), we note a fact that the area of the ellipse of the Dirac cone with a gap $2E_0$ is given by $S(k_0) = \pi E_2^2/(V_+ V_-) = \pi E_2^2/(|v_2| v_3) \sin \phi)$. Further, the area in the presence of the tilting is modified as $S/(1 - \eta^2)^{3/4}$ from Eq. (18a). Thus, the deviation of the total number, $\delta N(\mu)$, from the half-filled band and the density of states (DOS) are calculated as

\[
\delta N(X) = \int_{C_1} ds \cdot e_1 \left( E_D(k_0) - X \right)^2 \times \frac{2\pi \text{sgn}(\delta E_D(k_0) - X)}{v_2 v_3 |\sin(\phi)| (1 - \eta^2)^{3/4}}, \tag{19a}
\]

\[
D(\omega) = \frac{\partial \delta N}{\partial X} |_{X=\omega}, \tag{19b}
\]

where $\mu$ and $\omega$ are measured from $E_D$ at $k_z = 0$ in Fig. 2(b). $C_1$ denotes a path along the nodal line with $k_y > 0$, and the integral is performed using $\int ds \cdot e_1 = \int dz/e_{1z}$. The quantity $\delta N$ as a function of $k_z$ is shown.
in the inset of Fig. 7, where \( \delta N = 0 \) gives \( \mu = -0.0041 \). DOS is obtained by substituting Eq. (19a) into Eq. (19b). In Fig. 7, DOS is shown as a function of \( \omega \) by the solid line, which is measured from \( E_D \) at the Dirac point (I). The dashed line denotes DOS without tilting, i.e., \( \eta = 0 \), which is lower than the solid line since the tilting increases \( S \) of the area of the ellipsoid with the fixed energy \( E_D \). Within the numerical accuracy, one finds a relation, 

\[
D(\omega - \mu) \propto |\mu - \omega|, \tag{19c}
\]

for \( 0.005 < |\omega - \mu| \), while there is a slight deviation for \( 0 < |\omega - \mu| < 0.005 \). This comes from the non-monotonous variation of \( E_D \) with respect to \( k_z \) as seen from Fig. 2(b).

Finally, we compare the solid line in Fig. 7 with the DOS calculated from the first-principles DFT calculation of DFT (symbol). For the DOS calculations, Kohn-Sham equations are self-consistently solved in a scalar-relativistic fashion using all-electron full-potential linearized augmented plane wave (FLAPW) method\(^{26-36}\) within a exchange-correlation functional of a generalized gradient approximation (GGA).\(^{39}\) \( k \)-point meshes was set to be 16 \times 32 \times 16 for the DFT optimized structure under the pressure of 9GPa.\(^{24,30}\) The finite DOS even for small \( \omega \) suggests a metallic behavior, which is consistent with the experiment\(^{27}\) and also that of Fig. 7. Although a behavior close to the minimum shows a deviation from the solid line, the linear dependence in the interval region \( 0.005 < \omega - \mu < 0.02 \) is compatible with that of Eq. (19c). Thus the present calculation in terms of the effective model may provide reasonable results as a nodal line semimetal.

4. Summary

In summary, we examined an effective Hamiltonian of two-band model, which describes the Dirac cone close to the nodal line of molecular conductor \( \text{[Pd(dddt)2]+} \) with a half-filled band. The energy with a dispersion perpendicular to the nodal line is evaluated using the Dirac points obtained by the DFT calculation. The gap function between the conduction and valence bands is calculated to obtain the principal values and the principal axes, which rotate along the nodal line. Further, the effect of the tilting on the Dirac cone is examined, where the mutual relation between the principal axis and the tilting direction is clarified. The Dirac cone obtained by the variation of the nodal line gives reasonable energies, since the density of states showing characteristics of the nodal line semimetal is compatible with that of the DFT calculation. The determination of the tilting axis of the respective Dirac cone in terms of the original momentum space \( \mathbf{k} \) is useful to calculate the response to the external field with arbitrary direction. Finally, we note that the present method of deriving the effective Hamiltonian for the Dirac cone could be applied to other systems of the nodal line with an inversion symmetry.

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