Atomic frustrated impurity states in Weyl metals

W. N. Mizobata,1 Y. Marques,2 M. Penha,1 J. E. Sanches,1 L. S. Ricco,1 M. de Souza,3 I. A. Shelykh,2,4 and A. C. Seridonio1,3

1São Paulo State University (Unesp), School of Engineering, Department of Physics and Chemistry, 15385-000, Ilha Solteira-SP, Brazil
2ITMO University, St. Petersburg 197101, Russia
3São Paulo State University (Unesp), IGCE, Department of Physics, 13506-970, Rio Claro-SP, Brazil
4Science Institute, University of Iceland, Dunhagi-3, IS-107, Reykjavik, Iceland

We theoretically analyze the effect of the inversion symmetry breaking on the structure of the impurity molecular states in Weyl metals. We show that for the case of a highly noncentrosymmetric Weyl metallic host, the standard picture of the alternating bonding and antibonding orbitals breaks down, and qualitatively different frustrated atomic state emerges. This is a consequence of the pseudogap closing and related delicate Fano interplay between intra- and inter-impurity scattering channels.

Introduction. Dirac-Weyl equation [1], which first appears in the context of the relativistic quantum field theory, where it describes massless fermions, such as neutrinos, recently found its application in the domain of condensed matter physics. The existence of Dirac-Weyl fermions, quasi-relativistic quasiparticles, was unambiguously demonstrated for the family of the gapless binary alloys, such as Na3Bi, Cd3As2, TaAs, NbAs and TaP [2–12]. The pair of the Dirac cones, present in these materials, can be split into two Weyl nodes with opposite chirality, if certain symmetry (inversion or time-reversal) is broken [13–19]. As a result, a topological Weyl material with unusual characteristics, such as Fermi arcs, chiral anomaly and exotic Hall effects [13–19], emerges. The peculiar band structure of Weyl systems has dramatic impact on the electronic structure of impurities [20–26]. In particular, as it was recently shown by some of us, chiral magnetic chemical bounds for a pair of impurities can appear in Weyl semimetals with energy degenerate Weyl nodes shifted in k space with respect to each other [20].

In this communication, we consider the structure of impurity molecular states in Weyl metals, where two Weyl nodes are located at the same k, but are shifted in energy. We demonstrate that in the geometry corresponding to two Anderson-like impurities [27] shown in Fig. 1, bonding and antibonding molecular states evolve into an atomic frustrated state marked by two Hubbard bands [28], with increase of the energy splitting between the two Weyl nodes. In this regime, the closing of the host pseudogap occurs, which leads to the dominance of the destructive Fano interference [29,30] in the intra-impurity scattering channel, which is opposite to what happens in the corresponding inter-impurity channel revealing resonant behavior. The reported crossover can be realized by application of external stress [13] and experimentally detected with use of the STM techniques.

The Model. The Hamiltonian of the system sketched in Fig. 1 can be represented as:

\[
\mathcal{H} = \sum_{\mathbf{k}} \sum_{j} \psi_{\mathbf{k}}^{\dagger}(\mathbf{k})(H_{+} \oplus H_{-})\psi(\mathbf{k}) + \varepsilon_{d} \sum_{j} d_{j}^{\dagger}d_{j} + \sum_{j} \psi_{\mathbf{k}}^{\dagger}(\mathbf{k}) + H.c.,
\]

where \(H_\chi(\mathbf{k}) = \chi(v_F \sigma \cdot \mathbf{k} + \sigma_0 Q_0)\) is the Dirac-Weyl Hamiltonian of the host, corresponding to the two Dirac cones shifted vertically in energy (see Fig. 1(c)), \(\sigma_0\) stands for the vector of Pauli matrices, \(\sigma_0\) is the unity matrix, \(\chi = \pm 1\) corresponds to the Weyl nodes chirality, \(Q_0\) is the characteristic parameter defining the energy splitting.
between the Weyl nodes ($Q_0 \neq 0$ corresponds to a Weyl metal, $Q_0 = 0$ to a Dirac semimetal), $v_F$ is the Fermi velocity, $\psi(k) = (c_{k+\uparrow}, c_{k+\downarrow}, c_{k-\uparrow}, c_{k-\downarrow})^T$ is the four-spinor operator describing the electronic states in the host $\varepsilon_{\chi_{k\sigma}}^{\dagger}, \varepsilon_{\chi_{k\sigma}}$ with wave vector $k$, chirality $\chi$ and spin $\sigma$. The operators $d^\dagger_{j\sigma}, d_{j\sigma}$ describe the electronic states of individual impurities ($j = 1, 2$) with single-particle energies $\varepsilon_j$ and on-site Coulomb correlation energy $U$. The term, containing the two-spinor $d^\dagger_j = (d^\dagger_{j+\downarrow}, d^\dagger_{j+\uparrow})$, couples the impurities to the host, via the matrix

$$V_{jk} = v_0 \begin{pmatrix} e^{i k R_j^\dagger} & 0 & e^{i k R_j} & 0 \\ 0 & e^{i k R_j^\dagger} & 0 & e^{i k R_j} \end{pmatrix},$$

with $v_0$ being the coupling strength.

The electronic characteristics of the system are determined by its Local Density of States (LDOS) $\rho(\varepsilon, r)$, which can be found from the Green’s functions (GF) of the host in the energy domain, $\hat{G}_\chi(\varepsilon, r)$, defined as the time-Fourier transform of $G_{\chi}(t, r) = -i \theta(t) \langle \psi_\chi(t, r), \psi_\chi^\dagger(0, r) \rangle_H$ with $\psi_\chi(t, r) = \sum_k e^{i k \cdot r} c_{\chi k\sigma}(t)$ being the field operator of the host conduction states with spin $\sigma$ and chirality $\chi$. The LDOS reads $\rho(\varepsilon, r) = \frac{1}{\pi} \sum_{\chi, \sigma} \text{Im} \left\langle \hat{G}_\chi(\varepsilon, r) \right\rangle = \rho_0 + \sum_{j'} \delta \rho_{jj'}$, and the first term in this expression describes the host DOS $\rho_0 = \sum_\chi \frac{2 \pi^2}{D^3}$, with $D$ as the energy cutoff and $\varepsilon_\chi^{\text{full}} = \varepsilon - \chi Q_0$, and the second term is the correction to the LDOS induced by the host-impurity coupling:

$$\delta \rho_{jj'}(\varepsilon, r) = -\frac{1}{\pi v_0} \sum_{\chi, \sigma} \text{Im} \left\langle \Sigma^+_{\chi\sigma}(r - R_j) \hat{G}_{j\sigma j'\sigma}(\varepsilon) \right\rangle \times \Sigma^\dagger_{\chi\sigma}(r - R_j'),$$

where the terms with $j' = j$ and $j' \neq j$ correspond to intra- and inter-impurity scattering channels, respectively, and $\Sigma^\pm_{\chi\sigma}(r)$ are the self-energy terms responsible for the spatial modulation of the LDOS.

$\hat{G}_{j\sigma j'\sigma}(\varepsilon)$ is the time-Fourier transform of the impurities GFs, $G_{j\sigma j'\sigma} = -i \theta(t) \langle \{ d_{j\sigma} (t), d^\dagger_{j'\sigma} (0) \} \rangle_H$. Away from the Kondo regime $\Sigma^\dagger_{\chi\sigma}(r)$, Hubbard-I approximation can be applied, which gives:

$$\hat{G}_{j\sigma j'\sigma}(\varepsilon) = \frac{\lambda^\dagger_{j'}}{g_{j\sigma j'\sigma}(\varepsilon)} - \lambda^\dagger_{j'} \Sigma^+_{\chi}(R_{12}) g_{j'\sigma j'\sigma}(\varepsilon) \lambda^\dagger_{j'} \Sigma^-_{\chi}(R_{12}).$$

Here $\sigma = -\sigma$, $j' \neq j$, $R_{12} = R_1 - R_2$, $\Sigma^\pm_{\chi}(r) = \sum_{\chi} \Sigma^\pm_{\chi\sigma}(r)$.

$$g_{j\sigma j'\sigma}(\varepsilon) = \frac{1}{\varepsilon - \varepsilon_{j\sigma} - \Sigma_0}$$

is the single-impurity noninteracting GF,

$$\Sigma_0 = \frac{3\pi^2}{2D^3} \sum_{\chi} \varepsilon^2 \left\langle \ln \left| \frac{D + \varepsilon}{D - \varepsilon} \right| - \frac{2D}{\varepsilon} - i \right\rangle$$

as the local self-energy,

$$\lambda^\dagger_{j'} = 1 + \frac{U}{g_{j'\sigma j'\sigma}(\varepsilon)}$$

is the spectral weight and

$$\langle n_{j\sigma} \rangle = -\frac{1}{\pi} \int_{-\infty}^{+\infty} n^f(\varepsilon) \text{Im} \langle \hat{G}_{j\sigma j'\sigma}(\varepsilon) \rangle d\varepsilon$$

is the impurity occupation. The crossed GF reads

$$\hat{G}_{j\sigma j'\sigma}(\varepsilon) = g_{j\sigma j'\sigma}(\varepsilon) \lambda^\dagger_{j'} \Sigma^+_{\chi}(R_{12}) \hat{G}_{j'\sigma j'\sigma}(\varepsilon),$$

in which the $\pm$ signs correspond to $j = 1, j' = 2$ and $j = 2, j' = 1$, respectively.

In the case of uncorrelated impurities, realized when $|R_{12}| \gg v_F \sqrt{\varepsilon_0^2 / D^3}$, $\Sigma^\dagger_{\chi}(R_{12}) = 0$ and $\delta \rho_{jj'} = 0$, Eq. (6) has two poles (the so-called Hubbard resonant bands $\Sigma_{\chi}(0)$), appearing in $\delta \rho_{jj'}$. The host-mediated inter-impurity correlations lead to the splitting of these poles, which corresponds to the formation of the impurity molecular bands even in the absence of the direct hopping term between the impurities.

Results and Discussion. In our following consideration, we use model parameters: $|R_{12}| = 2 \text{ nm}$, $\varepsilon_d = -0.07D$, $v_0 = -0.14D$, $U = 0.14D$, $v_F \approx 3 \text{ eV}$ and $D \approx 0.2 \text{ eV}$

we suggest that the impurities are buried at the distance of 1 nm below the top surface of the Dirac-Weyl material, and are placed in the points $R_1 = (0, -1, 0) \text{ nm}$ and $R_2 = (0, 1, 0) \text{ nm}$ (see Fig. 1).

Fig. 2 illustrates the evolution of the spatial profiles of the LDOS at the surface of the host, given by Eq. (9), which can be probed by an STM tip, with increase of the parameter $Q_0$, describing the breaking of the inversion symmetry. In panel (a) the case of a Dirac semimetal with degenerated Weyl nodes, corresponding to $Q_0 = 0$, is illustrated. Molecular orbitals of the bonding and antibonding type are formed, and the profile corresponding to the latter one, with maxima of the LDOS centered at the points where the impurities are located, is shown. We stress that due to the peculiarities of the band structure of the Dirac host, the antibonding state has lower energy as compared to the bonding state, as it was demonstrated in Ref. [25]. The increase of the parameter $Q_0$ leads to the broadening of the LDOS peaks. Still, if values of $Q_0$ are moderate, the LDOS profiles remain qualitatively the same as for $Q_0 = 0$, and still can be described in terms of...
Frustration is switched-off
Switching on/off the frustration
Frustration is switched-on

Figure 2. (Color online) Panel (a): Spatial profile of the LDOS, corresponding to the antibonding state of a pair of impurities, placed inside a Dirac semimetal ($Q_0 = 0$). Panel (b): Spatial profile of the LDOS for a pair of impurities, placed inside a Weyl metal with moderate value of $Q_0 = 0.25D$. Panel (c): Spatial profile of the LDOS, corresponding to the frustrated atomic state, for a pair of impurities, placed inside a Weyl metal with large value of $Q_0 = 0.4D$.

Figure 3. (Color online) Impurity-induced contributions to the density of states $\delta \rho_{jj}$ as a function of the energy. Position of the STM tip is fixed at $r = (1, 1, 1)$ nm. Panel (a): The case of a Dirac semimetal host, $Q_0 = 0$. One clearly sees two well resolved pairs of peaks in $\delta \rho_{jj}$, centered around $\varepsilon_d$ and $\varepsilon_d + U$ and corresponding to bonding (indicated by green arrow) and antibonding (indicated by red arrow) molecular orbitals. Panel (b): The case of a Weyl metal host with small value of $Q_0 = 0.1D$. The peaks corresponding to the molecular states become broadened, but are still clearly resolved. Panel (c): The case of a Weyl metal host with moderate value of $Q_0 = 0.25D$. Intermediate Fano structures with merged peaks and dips appear. Panel (d): The case of a Weyl metal host with large value of $Q_0 = 0.4D$. Broad plateau in the density of states flanked by a pair of the merged peaks or dips is formed around $\varepsilon = 0$. Transition to the regime of atomic frustrated state occurs, as seen in Fig. 2(c).

To shed more light on the underlying mechanisms of its formation, we have analyzed separately different contributions to the LDOS induced by the impurities, as illustrated by Figs. 3 and 4.

Fig. 4 shows the plots of $\delta \rho_{jj}$ as a function of the energy for one particular tip position $r = (1, 1, 1)$ nm (the change of this latter does not affect the results qualitatively). Both contributions from intra-impurity ($j = l$) and inter-impurity ($j \neq l$) are shown. In panel (a), corresponding to the case of a Dirac host with $Q_0 = 0$, one clearly sees the presence of the four peaks in $\delta \rho_{jj}$, corresponding to well resolved Hubbard bands and describing the formation of bonding and antibonding molecular orbitals, which stem from single-impurity bands centered around $\varepsilon_d < 0$ and $\varepsilon_d + U > 0$. For the considered parameters, the lowest energy peak corresponds to the antibonding state (pointed by the red arrow) and next peak to the bonding molecular state (pointed by the green arrow). The crossed term $\delta \rho_{jj}$, with $j \neq l$ exhibits two resolved pairs of peaks and Fano dips instead. The increase of the parameter $Q_0$ leads to the broadening of the peaks and Fano dips (panel (b), $Q_0 = 0.1D$). At some point, the peaks corresponding to the bonding and antibonding states merge, giving rise to intermediate Fano lineshapes, with shallow minimum at $\varepsilon = 0$ (panel (c), $Q_0 = 0.25D$). Further increase of $Q_0$ leads to the forma-
tion of a broad plateau in the density of states around \( \varepsilon = 0 \), flanked by a pair of merged peaks for \( j \neq l \), or merged dips for \( j = l \) (panel (d), \( Q_0 = 0.4D \)). The presence of only two resolved Hubbard bands is typical for a pair of uncorrelated impurities. However, in our case the amplitudes \( \delta \rho_{jl} \neq 0 \) for \( j \neq l \), which means that molecular binding still persists, although in the unusual form of an atomic frustrated state. In this configuration, the role of the constructive and destructive Fano interference channels between \( \delta \rho_{jj} \) and \( \delta \rho_{pl} \) becomes inverted with respect to those observed in Dirac hosts, as it can be clearly seen from the comparison between panels (d) and (a). This is the direct outcome of the pseudogap closing in Weyl materials with large \( Q_0 \), for which the host DOS is enhanced at the Fermi energy.

The corresponding total LDOS has very broad maximum at \( \varepsilon = 0 \) and a pair of the broad minima around \( \varepsilon_B \) and \( \varepsilon_B + U \), as it is shown in Fig. 4(a). The crossover between the cases of the standard molecular bonding and antibonding states, and formation of an atomic frustrated state is illustrated by Fig. 4(b), where a phase diagram, showing the total LDOS as function of the energy \( \varepsilon \) and the parameter \( Q_0 \) is presented. With increase of \( Q_0 \) the narrow peaks characteristic to four well resolved Hubbard bands become broadened and finally merge, producing characteristic profile plotted in Fig. 4(a). From the experimental perspective, such transition can be achieved by application of stress, which is expected to break the inversion symmetry [13].

Conclusions. We have demonstrated that the nature of electronic states of a pair of impurities placed inside a Weyl metal strongly depends on the parameter \( Q_0 \), which defines the breaking of the inversion symmetry in the host material. For small values of this parameter one observes the formation of conventional bonding and antibonding molecular orbitals. However, for large values of \( Q_0 \) transition to an atomic frustrated state, characterized by a broad bowl-shape distribution of the LDOS in the real space occurs. This transition should take place under the application of external stress, which allows to propose the concept of a molecular switcher, alternating between ordinary molecular and atomic frustrated states.

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[1] H. Weyl, Zeitschrift für Physik 56, 330 (1929).
[2] Z. Wang et al., Phys. Rev. B 85, 195320 (2012).
[3] Z. K. Liu et al., Science 343, 864 (2014).
[4] Z. Wang, H. Weng, Q. Wu, X. Dai, and Z. Fang, Phys. Rev. B 88, 125427 (2013).
[5] Z. K. Liu et al., Nature Materials 13, 677 EP– (2014).
[6] S.-M. Huang et al., Nature Communications 6, 7373 EP– (2015).
[7] H. Weng, C. Fang, Z. Fang, B. A. Bernevig, and X. Dai, Phys. Rev. X 5, 011029 (2015).
[8] S.-Y. Xu et al., Science 349, 613 (2015).
[9] B. Q. Lv et al., Phys. Rev. X 5, 031013 (2015).
[10] B. Q. Lv et al., Nature Physics 11, 724 EP– (2015).
[11] S.-Y. Xu et al., Science 347, 294 (2015).
[12] N. Xu et al., Nature Communications 7, 11006 EP– (2016).
[13] N. P. Armitage, E. J. Mele, and A. Vishwanath, Rev. Mod. Phys. 90, 015001 (2018).
[14] X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, Phys. Rev. B 83, 205101 (2011).
[15] K.-Y. Yang, Y.-M. Lu, and Y. Ran, Phys. Rev. B 84, 075129 (2011).
[16] P. Hosur, S. A. Parameswaran, and A. Vishwanath, Phys. Rev. Lett. 108, 046602 (2012).
[17] P. Kim, J. H. Ryoo, and C.-H. Park, Phys. Rev. Lett. 119, 266401 (2017).
[18] H. Nielsen, and M. Ninomiya, Physics Letters B 130, 389–396 (1983).
[19] G. Xu , H. Weng, Z. Wang, X. Dai, and Z. Fang, Phys. Rev. Lett. 107, 186806 (2011).
[20] J.-H. Sun, D.-H. Xu, F.-C. Zhang, and Y. Zhou, Phys. Rev. B 92, 195124 (2015).
[21] D. Ma, H. Chen, H. Liu, and X. C. Xie, Phys. Rev. B 97, 045148 (2018).
[22] H.-R. Chang, J. Zhou, S.-X. Wang, W.-Y. Shan, and D. Xiao, Phys. Rev. B 92, 241103 (2015).
[23] A. Principi, G. Vignale, and E. Rossi, Phys. Rev. B 92, 041107 (2015).
[24] S.-H. Zheng, , R.-Q. Wang, M. Zhong, and H.-J. Duan, Scientific Reports 6, 36106 EP– (2016).
[25] Y. Marques, A. E. Obispo, L. S. Ricco, M. de Souza, I. A. Shelykh, and A. C. Serido, Phys. Rev. B 96, 041112 (2017).
[26] Y. Marques, W. N. Mizobata, R. S. Oliveira, M. de Souza, M. S. Figueira, I. A. Shelykh, and A. C. Seri- donio, Scientific Reports 9, 8452 (2019).
[27] P. W. Anderson, Phys. Rev. 124, 41 (1961).
[28] J. Hubbard, Proc. R. Soc. A 276, 238 (1963).
[29] B. U. Fano, Phys. Rev. 124, 1866 (1961).
[30] A. E. Miroshnichenko, S. Flach, and Y. S. Kivshar, Rev. Mod. Phys. 82, 2257 (2010).
[31] H. Bruns and B. Flensberg, Many-Body Quantum Theory in Condensed Matter Physics, An Introduction, Oxford University Press, 2012.
[32] A. C. Hewson, The Kondo problem to Heavy Fermions, Cambridge University Press, 1993.
[33] The Hubbard I is applicable for temperatures \( T \gg T_K \) being \( T_K \) the Kondo temperature. For the evaluation of \( \langle \sigma_\varepsilon \rangle \), \( T \) should not be very high so that we can safely assume the Heaviside step function for the Fermi-Dirac distribution \( n_F(\varepsilon) \).

\[ n_F(\varepsilon) = \frac{1}{1 + e^\frac{\varepsilon - \mu}{T}} \]