Van Hove singularity and ferromagnetic instability in phosphorene

A. Ziletti,1 S. M. Huang,2,3,† D. F. Coker,1 and H. Lin2,3,‡

1Department of Chemistry, Boston University, 590 Commonwealth Avenue, Boston Massachusetts 02215, USA
2Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore 117546
3Department of Physics, National University of Singapore, Singapore 117542

Using Wannier function-based interpolation techniques, we present compelling numerical evidence for the presence of a van Hove singularity at the Γ point near the phosphorene Fermi energy. We show that in proximity of the van Hove singularity the spin susceptibility presents the logarithmic temperature dependence typical of Lifshitz phase transitions. Furthermore, we demonstrate that the critical temperature for the ferromagnetic transition can be greatly increased (up to 0.05 K) if strain along the zigzag ridges is applied. Although the ferromagnetic state would be very difficult to experimentally reach, the logarithmic temperature behaviour of the spin susceptibility due to the van Hove singularity is found to persist at much higher temperatures (up to ∼97 K).

PACS numbers: 73.20.At,73.61.Cw,73.20.-r

I. INTRODUCTION

Van Hove singularities (VHSs) originate from saddle points in the band structure, around which the band curvature has opposite signs along two orthogonal directions. In two dimensions, the density of states (DOS) diverges at the VHS, and therefore arbitrary weak interactions can produce large effects in the electronic behaviour, giving rise to instabilities in many aspects such as charge, spin, and/or pairing susceptibilities. Once the Fermi energy approaches a VHS, ferromagnetism, antiferromagnetism, and/or superconductivity can be substantially enhanced.

The VHS is a topological critical point of the Fermi surface, across which the quantum Lifshitz phase transition takes place. The Lifshitz transition for non-interacting systems is continuous and does not break symmetry. For interacting systems, however, the Lifshitz transition may become discontinuous and accompany symmetry breaking. In cuprates, Hall coefficient measurements provide evidence for the Fermi surface topology change. The Lifshitz transition is also proposed to change the Fermi liquid into the marginal Fermi liquid and the VHS is thus argued to be responsible for the linear temperature (T) dependence of resistivity and the T-independent thermopower observed in this regime. Moreover, in the so-called “van Hove scenario”, the presence of a VHS near the Fermi energy is argued to play a major role in the high-Tc superconductivity of cuprates. Given the strong influence of VHSs on the properties of materials, it is important to identify the presence and understand the role of these singularities, especially for technologically promising low-dimensional materials like phosphorene.

Phosphorene, a single layer of black phosphorus, is the most recent addition to the growing family of two dimensional (2D) materials. It is a semiconductor with high potential for applications in electronic and optoelectronic devices. Despite the relative infancy of the field, few-layer phosphorene field effect transistors exhibit very high on-off current ratios (exceeding 10^5) and ambipolar behaviour together with the highest hole mobility ever (4000 cm^2/Vs) for a 2D material apart from graphene. Phosphorene’s pliable waved structure also allows for strain engineering of both effective masses and band gaps. Strain can even induce a semiconductor to metal transition.

In this article, we show that a VHS is present at the phosphorene Fermi energy, and we investigate the consequent ferromagnetic instability in both the unstrained and strained cases.

The article is organized as follows: after introducing the computational methodology, in Sec. III A we present the electronic structure of phosphorene near the VHS, in Sec. III B we study the ferromagnetic instability (without strain), and finally in Sec. III C we investigate the effect of strain on the critical temperature Tc of the ferromagnetic transition.

II. COMPUTATIONAL DETAILS

The calculations involve the following three steps. (i) A density functional theory (DFT) calculation is performed with a plane wave basis set, as implemented in the Quantum ESPRESSO package. We use the PBEsol exchange functional for the exchange and correlation energy. A plane wave basis set with a kinetic energy cutoff of 70 Ry (280 Ry) is used to represent the electronic wave function (charge density). The core electrons are described via the projected-augmented wave (PAW) method; 12.9 Å of vacuum are added in the direction normal to the monolayer to avoid spurious interactions between periodic replicas. Both lattice parameters and atomic positions are relaxed until the forces on each atom are less than 10^{-3} eV/Å and the pressure is less than 1 kbar. After lattice relaxation, the phosphorene crystal parameters are a_x =3.28 Å and a_y=4.44 Å, in agreement with a previous study. The optimized configuration of the phosphorene monolayer is presented in Fig. 1(a). In this DFT
calculation, the Brillouin Zone (BZ) is sampled through a Γ-centered 60×48×1 Monkhorst-Pack (MP) grid. This calculation will serve as a benchmark for the Wannier interpolation of the band structure [Fig. 1(b) and Fig. 1(c)].

(ii) Using the self-consistent charge density obtained from step (i), we evaluate the required input quantities for the Wannier calculation (energy eigenvalues, overlap matrices and projections) on a relatively coarse 10×8×1 mesh for the unstrained case (Secs. III A and III B), and a 30×8×1 mesh for the strained case (Sec. III C). These k-point meshes are fine enough to provide converged Wannier functions. The calculations are performed with QUANTUM ESPRESSO and its post-processing subroutine PW2WANNIER90. The aim of the two previous steps is to obtain the maximally localized Wannier functions (MLWFs) to be later used for the very dense k-point sampling around the VHS.

(iii) With the energy eigenvalues, overlap matrices and projections obtained from step (ii), we construct the MLWFs according to the procedure presented in Ref. 5 and Ref. 56. The resulting Wannier functions consist of three p-orbitals centered on each P atom, leading to the wannierization of 6 valence and 6 conduction bands (there are four P atoms in the phosphorene unit cell).

One of the main advantages of the maximally localized Wannier representation of the DFT orbitals is that quantities calculated on a coarse reciprocal-space grid can be used to interpolate on a much finer grid with low computational cost. The Wannier interpolation is particularly useful when a fine BZ sampling is required to converge the quantity of interest. In this work, such quantities are the DOS and the valence band in a small region around the VHS. For the DOS calculation, an extremely dense Wannier interpolated mesh of 4·10⁴×3.2·10⁴×1 – corresponding to ~1.3 billion k-points in the BZ - is used to capture the sharp peak in the DOS due to the VHS. We use a smearing of 7×10⁻⁴ eV. Similarly, a Wannier interpolation with a reciprocal lattice spacing of Δkₓ,y=2·10⁻³×2π/αₓ,y corresponding to a 500×500×1 MP grid is employed for the contour plot of the valence band around the VHS. All MLWF calculations are performed with the WANNIER90 package.

III. RESULTS AND DISCUSSION

A. Electronic band structure and van Hove singularity

Phosphorene is a semiconductor with a nearly-direct bandgap. The bandgap is underestimated (0.72 eV) at the PBEsol level (a well-known deficiency of local and semilocal DFT functionals), and enlarged at 1.6 – 2.0 eV when GW corrections are included. The electronic band structure of phosphorene, calculated with the PBEsol functional, is shown in Fig. 1(b). The black solid line represents a standard plane wave DFT calculation, while the red dotted line is the band structure obtained through a Wannier interpolation. Our Wannier interpolation is very accurate, over a broad range of energies. In particular, at Γ point, the DFT band structure and the Wannier interpolation differ by less than 10⁻⁵ eV.

In agreement with recent studies, we find that the top of the valence band is slightly away from the Γ point for all the exchange-correlation approximations used (LDA, PBE, and PBEsol). The detailed symmetry analysis presented in Ref. 58 attributes the absence of direct band gap to the counteracting effects (in the k · p approximation) of states of different symmetries on the valence band around the zone center.

A magnification of the valence band maximum is shown in Fig. 1(c). It is evident that the top of the valence band is displaced from Γ along the Γ-X direction, which is the direction along the phosphorene zigzag ridges [see Fig. 1(a)]. In particular, we find that the valence band maximum is located at kₓ,y=(0.105 Å⁻¹,0)=(kₓ,y,0) and it is 6.6 meV higher than its value at the Γ point.

From Fig. 1(c), we notice that the valence band has a saddle point at Γ. In the reciprocal space neighbourhood of this point, the principal curvature is electron-like along the Γ-X path [from the left in Fig. 1(c)], while it is hole-like in the Γ-Y path [from the right in Fig. 1(c)]. Thus, at the Γ point there is a crossover from electron-like to hole-like conduction that originates at the VHS. The DOS, calculated on an ultrafine grid of ~1.3 billion k-points, is shown in Fig. 1(d). It exhibits a divergent behaviour...
at the energy position of the VHS, as expected for a 2D lattice. In contrast to the saddle point behaviour at Γ, the valence band has a maximum at \( k_{\text{max}} \) and therefore the DOS shows a step-like drop to zero at this point.\[^{17}\] Therefore, due to the anisotropy of the phosphorene band structure, the VHS has an extended character that might amplify its effects on the material properties.

### B. Ferromagnetic instability

As mentioned in the introduction, the presence of a VHS at the Fermi energy can create ferromagnetic, antiferromagnetic or superconducting instabilities. In contrast to cuprates where the VHS points are at \((\pi,0)\) and \((0,\pi)\), in phosphorene the VHS point is at Γ and therefore we can exclude antiferromagnetism since no inter-VHS scattering can induce this instability. Furthermore, for highly anisotropic masses (see Sec. III A), \( m_x/m_y \gg 1 \), similar to the \( t-t' \) Hubbard model with large \( t'/t \) (\( \gg 0.276 \)), the ferromagnetic instability will win over other instabilities.\[^{17,22}\] As a result, we can omit also superconductivity and consider only ferromagnetism.

The extremely fine structure of the VHS in phosphorene requires a very high resolution calculation of the band structure. To make the calculation accessible, instead of using the band structure from the Wannier interpolation, we approximate it here by an analytic single-band model. Consistent with Fig. 1(c) and Fig. 2, the low-energy physics in the neighbourhood of the VHS can be described by

\[
E(k_x, k_y) = \frac{1}{2} \alpha k_x^2 - \frac{1}{4} \beta k_y^2 - \frac{1}{2} \alpha' k_y^2, \quad (1)
\]

which characterizes the saddle point at Γ (opposite signed band masses along \( k_x \) and \( k_y \)) and band inflection along \( k_x \). As in the previous section, the VHS energy at Γ, \( E_{\text{VHS}} \), is set to zero while the band maximum at \( k_{\text{max}} \) is \( E_{\text{max}} \). To fit the DFT calculations, the band parameters follow the relations: \( \alpha'/\alpha = m_x/m_y = 27.02 \), \( \sqrt{\alpha/\beta} = |k_{\text{max}}| = 0.104 \text{ Å}^{-1} \) and \( \alpha^2/4\beta E_{\text{max}} = 6.6 \text{ meV} \).

This simple model captures the energy dispersion behaviour near the VHS and, since the parameters of the model are determined directly from the DFT calculation, it allows us to investigate the magnetic instability quantitatively.

Given the energy dispersion in Eq. (1), it is possible to derive an exact analytical expression for the DOS, \( N(E) \) (see Appendix A for a complete derivation):

\[
N(E) = \begin{cases} \\
\frac{2}{\beta} a_0 a_0 K \left( \sqrt{1-p^2} \right) & \text{if } E \geq 0 \\
\frac{2}{\beta} a_0 a_0 \frac{1}{\sqrt{|p|^2+1}} K \left( \frac{1}{\sqrt{1+|p|^2}} \right) & \text{if } E < 0
\end{cases}
\]

(2)

where we have defined

\[
k_\pm = k_{\text{max}} \sqrt{1 \pm \sqrt{1 - E/E_{\text{max}}}} \quad p^2 = \frac{k_x^2}{k_\pm^2}
\]

(3)

and \( K(k) \) is the complete elliptic integral of the first kind. Since we are mainly interested in the behaviour of the...
DOS at the VHS, we take the limit $E \to 0$ in Eq. (2) to obtain (see Appendix A)

$$N(E \to 0) = \frac{\alpha_k \alpha_y}{2\pi^2 \sqrt{\alpha \alpha'}} [\ln (E_{\text{max}}/E) + \mathcal{O}(1)]$$

(4)

The model of Eq. (1) therefore exhibits a logarithmically divergent DOS and it is proportional to the geometric mean mass, $\sqrt{m_x m_y} \propto 1/\sqrt{\alpha}$, so in the limit of small energies we can approximate the DOS as

$$N(E) \approx N_0 \ln (\Lambda/E)$$

(5)

where $N_0 = \frac{\alpha_k \alpha_y}{2\pi^2 \sqrt{\alpha \alpha'}} = 0.0588 \text{ eV}^{-1}$, and $\Lambda$ is an energy cutoff of the order of $E_{\text{max}}$. We also set the Boltzmann constant $k_B$ to unity. The logarithmic divergence at low temperatures [Eq. (7)] is confirmed by explicit calculation of the spin susceptibility using Eq. (6), as shown in Fig. 3(a).

Notably, the susceptibility will deviate from the logarithmic dependence at higher temperatures, $T > T^* \sim 17 \text{ K}$ (1.5 meV), which can be understood to be the energy scale related to $E_{\text{max}}$. We have checked this fact by comparing susceptibilities for different band parameters $\beta$ (and thus $E_{\text{max}}$) in Eq. (1), and we indeed see proportionality between $T^*$ and $E_{\text{max}}$ (not shown). It is also found that the susceptibility increases with $E_{\text{max}}$ as expected from the energy cutoff and fitting constant dependence in Eqs. (5) and (7) respectively.

Next, we examine the effect of doping on the ferromagnetic instability, considering various chemical potential shifts $\mu$. The susceptibility was calculated numerically and the results are presented in Fig. 3(b), in which the Fermi energy is shifted to $\mu$ above $E_{\text{VHS}}$ (the energy of the VHS, or $\Gamma$). Fig. 3(b) shows that even away from the VHS point, the logarithmic-$T$ behaviour of the susceptibility is still preserved for $T < T^*$. However, for each value of $\mu$, we see that the logarithmic increase of $\chi$ with decreasing $T$ stops at $\mu$, below which the susceptibility become constant suggesting a transition to Pauli paramagnetism at low temperatures. This different behaviour for large and small $T$ (with respect to $\mu$) can thus be understood directly from the expression of the bare spin susceptibility as outlined in Appendix B.

It is in fact possible to obtain analytical estimates for $\chi$ in both regimes (please refer to Appendix B for a complete derivation). For $T \gg \mu$, the susceptibility has the form

$$\chi (T \gg \mu) \approx N_0 \ln (\omega_D/T) \cosh^{-2}(\mu/2T).$$

(8)

We observe the logarithmic-$T$ behaviour, typical of Lifshitz phase transitions. Moreover, for $\mu/T \to 0$, $\cosh^{-2}(\mu/2T) \to 1$ and therefore, in this limit, $\chi$ for the doped system has precisely the same behaviour as in the undoped case, as confirmed by the numerical results presented in Fig. 3(b). In contrast, for $T \ll \mu$ the suscepti-
bility is found to be independent of $T$:

$$\chi (T \ll \mu) \approx N_0 \ln(\Lambda/\mu)$$

(9)

where $\Lambda$ is an energy cutoff $\Lambda < E_{\text{max}}$. This saturation of $\chi$ agrees well with the numerical results presented in Fig. 3(b), and it originates from the infrared cutoff of the excitations due to the shifted thermal distribution (see Appendix B).

Now we estimate the ferromagnetic transition temperature. Let us assume a Hubbard interaction of strength $U$ between intra-orbital spins. According to the Stoner criterion the magnetic transition occurs when $U\chi(T)=1$. Here $U\chi$, which is defined by $U$ times the average weight $W_\nu$ at the Fermi energy for a particular orbital $\nu$, is regarded as the effective interaction of orbital $\nu$. From the Stoner criterion, the critical temperature follows the BCS form:

$$T_c = \frac{\omega_D}{\pi} \exp(-1/N_0 U\chi)$$

(10)

where the geometric mean mass, appearing in $N_0$ as outlined above, determines the DOS at the Fermi energy. With this BCS formula, one can obtain the magnetization directly.

The effective interaction $U\chi$ can be evaluated using the Kohn-Sham orbitals from the DFT calculation. Let us define orbital operators $\psi_\nu$ and band operators $\phi_\nu$. The relation between them is a unitary transformation $\psi_\nu(k) = \sum_\nu A_{\nu,\nu}(k) \phi_\nu(k)$ where $A(k)$ is the unitary matrix that diagonalizes the Bloch Hamiltonian. The Hubbard onsite (intra-orbital) interaction is

$$U_\nu = \left. U \sum_{R} \sum_{m} \psi^\dagger_{m\uparrow}(R) \psi_{m\uparrow}(R) \psi^\dagger_{m\downarrow}(R) \psi_{m\downarrow}(R) \right|_{\nu=\nu_\text{F}}$$

(11)

where $R$ is the real space lattice vector and $\psi_{m\uparrow,\downarrow}$ are the Kohn-Sham spin-orbitals.

Since only the valence band (VB) is included in our low-energy model [Eq. (1)], we include only the intra-band scattering terms from the Hubbard model. Moreover, at $T=0$, only states from the Fermi surface contribute to the susceptibility. After these considerations, the effective interaction $U_\nu$ is

$$U_\nu = U W_\nu \approx \left. U \sum_{k \in k_F} \sum_m |A_{\nu,\nu}(k)|^4 \right|_{\nu=\nu_\text{F}}$$

(12)

where $k_F$ is the Fermi wave vector.

From the DFT results, we obtain an average weight, $W_\nu$, for the contributing orbitals of about 0.2. This orbital weight significantly reduces the critical temperature. For example, using the criterion $U\chi(T_c)=0.8$ and at $U=4$ eV, the critical temperature $T_c$ for ferromagnetism is only about 4 $\mu$K.

Doping can destroy ferromagnetism even at zero temperature when $N_0 U_\nu \ln(\omega_D/\mu)<1$. Although inter-orbital interactions might slightly enhance $T_c$, the Stoner criterion applied to the bare susceptibility typically overestimates the critical temperature since particle-particle correlations would give large corrections to the self-energy. As a result, this ferromagnetic state would be difficult to reach.

C. Effect of strain on the van Hove singularity and on the critical temperature

Strain can have a large effect on phosphorene’s pliable waved structure, and therefore it represents a natural way to tune the band parameters of the VHS, in order to increase $T_c$. In particular, from Eq. (10) we notice that, for a fixed effective interaction $U_\nu$, the critical temperature can be varied in two ways. One way is to increase $\omega_D$ (or equivalently $E_{\text{max}}$, see Sec. III B) so that $T_c$ will linearly increase. The second and more prominent way is to increase $N_0$ such that $T_c$ will increase exponentially; for instance, by reducing the dispersion in both $x$ and $y$ directions near the $\Gamma$ point [see Eqs. (1) and (5)].

We find that strain along the armchair direction [$y$-axis in Fig. 1(a)] does not alter significantly the critical temperature, with a modest ninefold increase in $T_c$ (~36 $\mu$K) for a tensile strain of 3%.

The situation, however, is significantly different for strain along the zigzag ridge direction [$x$-axis in Fig. 1(a)]. The most relevant quantities for representative $x$-strain values are listed on Table I.

**Table I:** Parameters related to the VHS for different strains on the zigzag direction [$x$-axis in Fig. 1(a)]. For $T<T^*$, the susceptibility follows the logarithmic temperature dependence of Eq. (6).

| $x$-strain  | -4%   | 0     | +4%   |
|-------------|-------|-------|-------|
| $k_{\text{max}}$ (1/Å) | (0.175,0) | (0.105,0) | (0.033,0) |
| $E_{\text{max}}$ (meV) | 27.8 | 6.6 | 0.1 |
| $N_0$ (eV$^{-1}$) | 0.0374 | 0.0588 | 0.1909 |
| $T^*$ (K) | 97 | 17 | 0.23 |
| $T_c$ (K) | $5\times10^{-7}$ | $4\times10^{-6}$ | $5\times10^{-2}$ |

Compressive $x$-strain reduces $N_0$ (see Table I), and since $T_c$ depends exponentially on $N_0$, the critical temperature is only 0.5 $\mu$K for a compressive strain of 4%.

In contrast to $N_0$, $E_{\text{max}}$ increases (see Table I). Due to the proportionality between $E_{\text{max}}$ and $T^*$, the spin susceptibility starts to follow the logarithmic-$T$ behaviour - signature of the VHS - at higher temperatures than the unstrained case. For example, a compressive $x$-strain of 4% leads to $T^*$ of about 97 K (8.4 meV) [see Fig. 1(a), yellow squares]. Due to the relatively high temperatures involved, the logarithmic-$T$ behaviour in the spin susceptibility could in principle be observed experimentally, thus providing compelling evidence for the presence of the VHS.

In contrast, tensile $x$-strain has the opposite effect
on the band parameters: while $E_{\text{max}}$ diminishes, $N_0$ is greatly enhanced. Notably, the critical temperature exhibits an exponential dependence on tensile strain, as depicted in Fig. 4(b). For a 4% strain, the critical temperature is about 0.05 K. Even though this corresponds to a $10^4$-fold increase in $T_c$ with respect to the unstrained case, this magnetic state will hardly be seen experimentally due to the very low temperatures required. We also observe that the logarithmic divergence becomes the dominant contribution at around $T^* \sim 0.23$ K (0.002 meV) [Fig. 4(a), orange crosses], a much lower value compared to the unstained case resulting from the flattening of the valence band (and consequently diminished $E_{\text{max}}$), caused by the applied stress.

Finally, we observe that the critical temperature still follows the exponential law of Eq. (10), even if strain is applied, as shown in Fig. 4(c). For higher stress, $T_c$ could deviate from Eq. (10), since $E_{\text{max}}$ diminishes ($\sim 10^{-4}$ eV for a 4% tensile strain) and therefore narrows the VHS divergence, limiting the increase of the critical temperature.

**IV. CONCLUSIONS**

We have used Wannier function-based interpolation techniques to investigate the VHS at the $\Gamma$ point near the phosphorene Fermi energy with more than a billion $k$-points. Thanks to this extreme resolution, we are able to present compelling numerical evidence for the presence of a VHS near the phosphorene Fermi energy. Seen its close proximity to the valence band maximum, the VHS can be reached with a hole doping concentration of approximately $1.4 \times 10^{12}$ cm$^{-2}$, easily achievable by chemical doping or gating.

Furthermore, we have calculated an exact expression for the DOS near the VHS, and we have demonstrated that the spin susceptibility presents a logarithmic-$T$ behaviour, signature of the VHS, and consequent Lifshitz phase transition.

We have also shown that the critical temperature can be increased up to 0.05 K by applying a modest strain to the phosphorene pliable waved structure. Although this ferromagnetic state would be very difficult to experimentally reach, the logarithmic temperature behaviour of the spin susceptibility due to the presence of the VHS could be observed because it persists at higher temperatures ($T^* \sim 17$ K for the unstrained case, and $T^* \sim 97$ K for a 4% tensile strain along the zigzag ridges).

There are numerous experimental techniques able to detect the presence of VHSs. For example, the scanning tunnelling microscope (STM) measures the tunnelling differential conductance, which is proportional to the local DOS and therefore represents an ideal tool to detect VHSs. This technique has been used to observe VHSs in other 2D materials like twisted multilayer graphene or the cuprate superconductor Bi-2201. Furthermore, angle-resolved photoemission spectroscopy (ARPES) can detect saddle points in the single-particle energy dispersion, as employed for numerous cuprate compounds and doped graphene. Finally, the Knight shift in nuclear magnetic resonance experiments could provide evidence for the change in spin susceptibility in proximity of the VHS.

**ACKNOWLEDGEMENTS**

A.Z. and D.F.C. acknowledge NSF grant CHE-1301157 and also an allocation of computational resources from Boston University’s Office of Information Technology and Scientific Computing and Visualization. H.L. acknowledges the Singapore National Research Foundation for the support under NRF Award No. NRF-NRFF2013-03.

**Appendix A: Exact derivation of the density of states**

In this section, we present an analytical derivation of the DOS for phosphorene around the VHS. According to Eq. (11), the dispersion relation of the valence band around the $\Gamma$ point has the form

$$E_k = \frac{1}{2} \alpha k_x^2 - \frac{1}{4} \beta k_x^4 - \frac{1}{2} \alpha' k_y^2$$  \hspace{1cm} (A1)

with $\alpha, \beta, \alpha' > 0$. The valence band has its energy extreme at $E_{\text{max}} = \frac{\alpha^2}{4\beta}$ when $(k_x, k_y) = (k_{\text{max}}, 0)$ and...
\[ k_{\text{max}} = \sqrt{\alpha/\beta}. \] Moreover, there is a VHS at energy \( E_{\text{VHS}} = 0 \) originating from states near \( k_x = 0 \).

By definition, the DOS per spin per unit area is

\[
N(E) = \frac{1}{(2\pi)^2} \int \frac{dk_x dk_y}{\partial k_x E_k} \delta(E - E_k)
\]

\[ = \frac{1}{(2\pi)^2} \int_{k_y \geq 0} \frac{dk_y}{\partial k_y E_k} \delta(k_y - k_y^E)
\]

\[ = \frac{1}{\sqrt{2\alpha'\pi^2}} \int_{k_y \geq 0} \frac{dk_y}{\sqrt{\frac{\alpha}{\beta} k_y^2 - \frac{\beta}{4} k_y^4 - E}}.
\]

where \( k_y^E \) satisfies \( E = \frac{1}{2} \alpha k_y^2 - \frac{1}{4} \beta k_y^4 - \frac{1}{2} \alpha' (k_y^E)^2 \).

The integration range is limited by the fact that the square root term has to be real. After some algebra, one can show that the integral range is \( k \in [\max(0, k_-), k_+] \) with

\[
k_{\pm} = \sqrt{\frac{\alpha' \pm \sqrt{\left(\frac{\alpha}{\beta}\right)^2 - \frac{4E}{\beta}}} \} = k_{\text{max}} \sqrt{1 \pm \sqrt{1 - E/E_{\text{max}}}}.
\]

(A3)

Thus, if \( E < 0 \), \( k_- \) is not purely real, and the lower bound is zero. Therefore, we have

\[
\int_{k_-}^{k_+} dk_x \frac{1}{\sqrt{\frac{\beta}{4} k_x^2 - \frac{\beta}{4} k_x^4 + E}} = F(\arcsin(u), p)
\]

(A4)

\[
= \int_{k_-}^{k_+} dk_x \frac{1}{\sqrt{\left(\frac{\beta}{2}\right) (k_x^2 - k_x^4) (k_x^2 - k_x^4)}}
\]

\[
= -2i \int_{p_-}^{1} dp \sqrt{\left(1 - p^2\right) (1 - p^2 x^2)} = -2i \int_{p_-}^{1} dp \sqrt{\left(1 - p^2\right) \sqrt{\left(1 - p^2\right)}} = -2i \frac{F\left(\frac{\pi}{2}, \sqrt{1 - p^2}\right)}{p}.
\]

where we have defined

\[ p^2 = \frac{k_x^2}{k^2} = \frac{E_{\text{max}}}{E} \left(1 + \sqrt{1 - \frac{E}{E_{\text{max}}}}\right)^2 \]

(A5)

and introduced \( F(\phi, k) \) the incomplete elliptic integral of the first kind and \( K(k) \) the complete elliptic integral of the first kind. They are related here by \( F\left(\frac{\pi}{2}, k\right) = K(k) \).

On the other hand, if \( E > 0 \) \( (k_- > 0) \), the lower bound is \( k_- \) and we will deal with

\[
\int_{k_-}^{k_+} dk_x \frac{1}{\sqrt{\frac{\beta}{4} k_x^2 - \frac{\beta}{4} k_x^4 + E}}
\]

(A6)

\[
= \int_{k_-}^{k_+} dk_x \frac{1}{\sqrt{\left(\frac{\beta}{2}\right) (k_x^2 - k_x^4) (k_x^2 - k_x^4)}}
\]

\[
= -2i \int_{1}^{p_-} dp \sqrt{\left(1 - p^2\right) (1 - p^2 x^2)} = -2i \int_{1}^{p_-} dp \sqrt{\left(1 - p^2\right) \sqrt{\left(1 - p^2\right)}} = -2i \frac{F\left(\frac{\pi}{2}, \sqrt{1 - p^2}\right)}{p}.
\]

In Eqs. (A4) and (A6), we have used the integral formulae:

\[
\int_{0}^{u} dx \frac{1}{\sqrt{(1 - x^2)(1 - p^2 x^2)}} = \frac{1}{2} \int_{0}^{u} dz \frac{1}{\sqrt{z(1 - z)(1 - p^2 z)}} = F(\arcsin(u), p)
\]

(A7)

\[
\int_{u}^{1} dx \frac{1}{\sqrt{(1 - x^2)(1 - p^2 x^2)}} = \frac{1}{2} \int_{u}^{1} dz \frac{1}{\sqrt{z(1 - z)(1 - p^2 z)}} = \frac{i}{p} F\left(\arcsin\left(\frac{1 - u^2}{1 - p^2}\right), \sqrt{1 - p^2}\right).
\]

(A8)

For negative energies, \( E < 0 \),

\[
k_- = i \sqrt{1 + \frac{|E|}{E_{\text{max}}}} = i |k_-|
\]

(A9)

\[
p = i \sqrt{\frac{E_{\text{max}}}{|E|}} \left(1 + \sqrt{1 + \frac{|E|}{E_{\text{max}}}}\right) = i |p|
\]

(A10)

and therefore we will use the relation

\[
K(ik) = \frac{1}{\sqrt{k_x^2 + 1}} K\left(\sqrt{\frac{k_x^2}{k_x^2 + 1}}\right)
\]

(A11)
in Eq. [A4].

In conclusion, the density of states for $E < 0$ and $E > 0$ are, respectively,

$$N(E < 0) = \frac{1}{\sqrt{2}\alpha'^2} \int_{0}^{k_{\pi}} dk_{x} \frac{1}{\sqrt{2k_{x}^{2} - 2k'_{x}^{2} - E}}$$

(A12)

$$=- i \sqrt{\frac{2}{3\alpha'^2 i |k_{-}|}} K(k|p|)$$

and

$$N(E > 0) = \frac{1}{\sqrt{2}\alpha'^2} \int_{k_{-}}^{k_{\pi}} dk_{x} \frac{1}{\sqrt{2k_{x}^{2} - 2k'_{x}^{2} - E}}$$

(A13)

$$=- \sqrt{\frac{2}{3\alpha'^2 i k_{+}}} K(k|1-p^{-2}|)$$

The final step is to analyze the asymptotic behaviour of the DOS. Since $K$ will show a logarithmic divergence when

$$K(k = 1-\eta) \stackrel{\eta \to 0}{\longrightarrow} \frac{1}{2} \ln |\eta| + O(1),$$

(A14)

for $E \to 0$, both the quantities $\sqrt{\frac{1}{1+|p|^{-2}}}$ and $\sqrt{1-p^{-2}}$ approach one. By using $k_{\pm} \to \sqrt{2}k_{\max}$, $|k_{-}| \to k_{\max} \sqrt{\frac{|E|}{2E_{\max}}}$, $|p| \to \frac{2}{\sqrt{E_{\max}/|E|}}$, and $\frac{1}{\sqrt{|p|^{2}+1}} \to \frac{1}{2} \sqrt{\frac{|E|}{E_{\max}}}$, we obtain the DOS at the VHS as:

$$N(E \to 0-) = \frac{1}{2\pi^{2}} \frac{1}{\alpha'^2} \left[ \ln \left( \frac{E_{\max}}{|E|} \right) + O(1) \right]$$

(A15)

and similarly,

$$N(E \to 0+) = \frac{1}{2\pi^{2}} \frac{1}{\alpha'^2} \left[ \ln \left( \frac{E_{\max}}{E} \right) + O(1) \right]$$

(A16)

After multiplication by the unit cell area $a_{x} \times a_{y}$, we obtain the result reported in Eq. [A1].

Appendix B: Bare spin susceptibility at the VHS and the effect of doping

Firstly, we derive the bare susceptibility when the Fermi energy is at $E_{\text{VHS}}=0$ ($\mu=0$). The spin susceptibility is given by

$$\chi(T) = \frac{a_{x}a_{y}}{(2\pi)^{2}} \int d^{2}k \frac{1}{4T} \cosh^{-2} \left( \frac{E_{k}}{2T} \right)$$

$$= \frac{1}{4T} \int_{-\infty}^{E_{\max}} dE N(E) \cosh^{-2} \left( \frac{E}{2T} \right)$$

$$\approx \frac{1}{4T} \int_{-\Lambda}^{\Lambda} dE N_{0} \left( \frac{\Lambda}{|E|} \right) \cosh^{-2} \left( \frac{E}{2T} \right)$$

$$= \frac{1}{2} N_{0} \int_{-\Lambda/2T}^{\Lambda/2T} dx \ln \left( \frac{\Lambda}{2T} \right) \cosh^{-2} x$$

$$= - N_{0} \int_{0}^{\Lambda/2T} dx \ln x + \frac{1}{2} N_{0} \ln \left( \frac{\Lambda}{2T} \right) \int_{0}^{\Lambda/2T} dx \cosh^{-2} x$$

where we have considered only the contribution from the VHS and the logarithmic behaviour applies when $|E| < \Lambda$ and $\Lambda$ is another energy cutoff $\Lambda < E_{\max}$.

If we then consider the limit $\Lambda \gg T$ and use the following formulae:

$$\int_{0}^{\infty} dx \ln x \cosh^{-2} x = \log \frac{\pi}{4} - \gamma_{e} \equiv -C = -0.8188$$

(B1)

($\gamma_{e}$ is the Euler-Mascheroni constant)

$$\int_{0}^{\Lambda/2T} dx \cosh^{-2} x = \tanh \frac{\Lambda}{2T} \approx 1$$

(B2)

we obtain the following expression for the bare susceptibility

$$\chi(T) \approx N_{0} C + N_{0} \ln \left( \frac{\Lambda}{2T} \right) \approx N_{0} \ln (\omega_{D}/T)$$

(B3)

which is Eq. [7] in the main text.

Then, we discuss the effect of doping on the susceptibility. When we shift the Fermi energy from zero ($E_{\text{VHS}}$) to $\mu$, the VHS will change to $-\mu$, and therefore we can replace the DOS by $N(E) \approx N_{0} \ln \left( \frac{\Lambda}{|E| + \mu} \right)$ for $|E + \mu| < \Lambda$. The susceptibility thus becomes

$$\chi(T) \approx \frac{1}{4T} N_{0} \int_{-\Lambda-\mu}^{\Lambda-\mu} dE N_{0} \ln \left( \frac{\Lambda}{|E + \mu|} \right) \cosh^{-2} \left( \frac{E}{2T} \right)$$

(B4)

$$= \frac{1}{4T} N_{0} \int_{-\Lambda}^{\Lambda} dE N_{0} \ln \left( \frac{\Lambda}{|E|} \right) \cosh^{-2} \left( \frac{E - \mu}{2T} \right).$$

We will now consider two regimes: $T \gg \mu$ and $T \ll \mu$. Let us start with the case $T \gg \mu$. By using the expansion

$$\cosh \left( \frac{E - \mu}{2T} \right) = \cosh \left( \frac{E}{2T} \right) \cosh \left( \frac{\mu}{2T} \right) +$$

$$- \sinh \left( \frac{E}{2T} \right) \sinh \left( \frac{\mu}{2T} \right),$$

(B5)
and the approximation
\[ \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \approx \cosh^{-2}\left(\frac{E}{2T}\right) \cosh^{-2}\left(\frac{\mu}{2T}\right), \quad (B6) \]
the susceptibility can be written as
\[ \chi(T \gg \mu) \approx \frac{1}{4T} N_0 \int_{-\Lambda}^{\Lambda} dE \ln \frac{\Lambda}{|E|} \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \times \cosh^{-2}\left(\frac{\mu}{2T}\right) \]
\[ = N_0 \ln (\omega_D/T) \cosh^{-2}\left(\frac{\mu}{2T}\right) \approx N_0 \ln (\omega_D/T) \quad (B8) \]
and therefore, in this regime, the susceptibility is the same as the undoped case [compare to Eq. [B3]].

On the other hand, when \( T \ll \mu \), the function \( \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \) decreases proportionally to \( \exp\left(\frac{\mu - E}{T}\right) \) for \( |E - \mu| \gg T \). Therefore it is a good approximation to replace \( \ln \frac{\Lambda}{|E|} \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \) by \( \ln \frac{\Lambda}{|\mu|} \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \) in the integrand in Eq. [B4]. As a result,
\[ \chi(T \ll \mu) \approx \frac{1}{4T} N_0 \int_{-\Lambda}^{\Lambda} dE \ln \frac{\Lambda}{|E|} \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \]
\[ = \frac{1}{4T} N_0 \int_{0}^{\Lambda} dE \ln \frac{\Lambda}{|E|} \left[ \cosh^{-2}\left(\frac{E + \mu}{2T}\right) + \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \right] \]
\[ \approx \frac{1}{4T} N_0 \int_{0}^{\Lambda} dE \ln \frac{\Lambda}{|\mu|} \left[ \cosh^{-2}\left(\frac{E - \mu}{2T}\right) + \cosh^{-2}\left(\frac{E + \mu}{2T}\right) \right] \quad (B9) \]

Then, using
\[ \int_{0}^{\Lambda} dE \cosh^{-2}\left(\frac{E \pm \mu}{2T}\right) = 2T \left[ \tanh\left(\frac{\Lambda \pm \mu}{2T}\right) \pm \tanh\left(\frac{\mu}{2T}\right) \right] \quad (B10) \]
we obtain
\[ \chi(T \ll \mu) = \frac{1}{2} N_0 \ln \frac{\Lambda}{|\mu|} \left[ \tanh\left(\frac{\Lambda + \mu}{2T}\right) + \tanh\left(\frac{\Lambda - \mu}{2T}\right) \right] \]
\[ = \frac{1}{2} N_0 \ln \frac{\Lambda}{|\mu|} \left[ \sinh\frac{\Lambda}{T} \tanh\frac{\Lambda}{2T} \cosh\frac{\Lambda - \mu}{2T} \right] \approx N_0 \ln \frac{\Lambda}{|\mu|} \approx N_0 \ln \frac{\Lambda}{T} \approx N_0 \ln \frac{\Lambda}{\mu} \quad (B11) \]

The final result of Eq. [B11] indicates that, in this regime, the bare spin susceptibility is independent of temperature, as shown in Fig. 3(b). This behavior originates from the infrared cutoff of the excitations due to the thermal distribution. Let us in fact consider the integrand in Eq. [B9]:
\[ \ln \frac{\Lambda}{|E|} \left[ \cosh^{-2}\left(\frac{E - \mu}{2T}\right) + \cosh^{-2}\left(\frac{E + \mu}{2T}\right) \right] \quad (B12) \]
\[ \approx \ln \frac{\Lambda}{|E|} \cosh^{-2}\left(\frac{E - \mu}{2T}\right) \]

Due to the chemical potential shift \( \mu \), the thermal distribution function, \( \cosh^{-2}\left(\frac{E \mp \mu}{2T}\right) \sim \exp\left(\frac{\mu - E}{T}\right) \), is now centered at \( E = \mu \) and not at \( E = 0 \) like in the undoped case. Therefore, the integration around \( E = 0 \), where the logarithmic function diverges, now makes essentially no contribution to the total integral, giving rise to the flattening of the susceptibility observed for \( T \ll \mu \).

* A. Ziletti and S. M. Huang contributed equally to this work.

† nilnish@gmail.com

1 L. Van Hove, Phys. Rev. 89, 1189 (1953).
2 M. Fleck, A. M. Oles, and L. Hedin, Phys. Rev. B 56, 3159 (1997).
3 R. Hlubina, S. Sorella, and F. Guinea, Phys. Rev. Lett. 78, 1343 (1997).
4 H. Q. Lin and J. E. Hirsch, Phys. Rev. B 35, 3359 (1987).
5 W. Kohn, and J. M. Luttinger, Phys. Lett. 15, 524 (1965).
6 J. E. Hirsch and D. J. Scalapino, Phys. Rev. Lett. 56, 2732 (1986).
7 C. Honerkamp and M. Salmhofer, Phys. Rev. Lett. 87, 187004 (2001).
8 I. M. Lifshitz, Sov. Phys. JETP 11, 1130 (1960).
9 Y. Yamaji, T. Misawa, and M. Imada, J. Phys. Soc. Jpn. 75, 094719 (2006).
10 N. S. Vidhyadhiraja, A. Macridin, C. Sen, M. Jarrell, and M. Ma, Phys. Rev. Lett. 102, 206407 (2009).
11 K.-S. Chen, S. Pathak, S. X. Yang, S. Q. Su, D. Galanakis, K. Mikelsons, M. Jarrell, and J. Moreno Phys. Rev. B 84, 245107 (2011).
