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# Role of nematicity in controlling spin fluctuations and superconducting $T_c$ in bulk FeSe

Swagata Acharya,<sup>1,2</sup> Dimitar Pashov,<sup>2</sup> and Mark van Schilfgaarde<sup>2,3</sup>

<sup>1</sup>*Institute for Molecules and Materials, Radboud University, NL-6525 AJ Nijmegen, The Netherlands*

<sup>2</sup>*King's College London, Theory and Simulation of Condensed Matter, The Strand, WC2R 2LS London, UK\**

<sup>3</sup>*National Renewable Energy Laboratories, Golden, CO 80401, USA*

FeSe undergoes a transition from a tetragonal to a slightly orthorhombic phase at 90 K, and becomes a superconductor below 8 K. The orthorhombic phase is sometimes called a nematic phase because quantum oscillation, neutron, and other measurements detect a significant asymmetry in  $x$  and  $y$ . How nematicity affects superconductivity has recently become a matter of intense speculation. Here we employ an advanced *ab-initio* Green's function description of superconductivity and show that bulk tetragonal FeSe would, in principle, superconduct with almost the same  $T_c$  as the nematic phase. The mechanism driving the observed nematicity is not yet understood. Since the present theory underestimates it, we simulate the full nematic asymmetry by artificially enhancing the orthorhombic distortion. For benchmarking, we compare theoretical spin susceptibilities against experimentally observed data over all energies and relevant momenta. When the orthorhombic distortion is adjusted to correlate with observed nematicity in spin susceptibility, the enhanced nematicity causes spectral weight redistribution in the Fe-3d<sub>xz</sub> and d<sub>yz</sub> orbitals, but it leads to at most 10-15% increment in  $T_c$ . This is because the d<sub>xy</sub> orbital always remains the most strongly correlated and provides most of the source of the superconducting glue. Nematicity suppresses the density of states at Fermi level; nevertheless  $T_c$  increases, in contradiction to both BCS and BEC theories. We show how the increase is connected to the structure of the particle-particle vertex. Our results suggest while nematicity may be intrinsic property of bulk FeSe, is not the primary force driving the superconducting pairing.

## INTRODUCTION

Bulk FeSe superconducts up to 8 K, deep inside an orthorhombic phase that sets in at a much higher temperature, 90 K.<sup>1</sup> The normal bulk tetragonal phase does not superconduct unless it is doped<sup>2-6</sup> or forms a monolayer.<sup>7,8</sup> A non-alloy bulk tetragonal superconducting FeSe does not yet exist. This raises the question whether nematicity facilitates superconductivity in the bulk or not.<sup>9-11</sup> Further recent studies have suggested that spin fluctuations are strongly anisotropic, possibly originating from electronic nematicity inside the detwinned orthorhombic phase.<sup>12</sup> This enhanced electronic anisotropy shows up in the inelastic neutron scattering (INS), in resistivity measurements,<sup>13</sup> in angle resolved photo-emission spectroscopic studies<sup>14-16</sup> and in several other measurements.<sup>17</sup> How such spin fluctuations affect the superconducting instability is a subject of intensive study.

Here we take an *ab initio* Green's function approach to compare spin fluctuations and superconductivity in the orthorhombic phase with the tetragonal phase of bulk FeSe. This enables us to directly probe what role nematicity plays in governing these observed properties. To validate the theory we perform rigorous benchmarking against existing susceptibility data from INS measurements.<sup>18</sup> Using the as-given orthorhombic structure, we show that spin susceptibilities are nearly indistinguishable for the two phases. To mimic the true nematicity, we enhance the small observed orthorhombic distortion by a factor of five, to simulate the best possible agreement against the existing INS data inside the orthorhombic

phase. While this enhanced structural nematicity has a different physical origin (most likely originating from a  $k$  dependent vertex in the spin channel, or in the electron-phonon interaction) it provides a similar contribution to nematicity by adding an effective potential from a different source. As we show below, it enhances nematicity and generates a spin susceptibility that fairly well replicates nematicity observed in neutron measurements. We can then assess its impact on superconductivity, since spin fluctuations are the primary driving force for superconductivity, and we find that enhanced nematicity has only very moderate effect.

## METHODS

We believe findings are conclusive because they are obtained from a high fidelity, *ab initio* description of spin fluctuations and superconductivity that depends only minimally on model assumptions. Our theory couples (quasi-particle) self consistent *GW* (QSGW) with dynamical mean field theory (DMFT).<sup>19-22</sup> Merging these two state-of-the-art methods captures the effect of both strong local dynamic spin fluctuations (captured well in DMFT), and non-local dynamic correlation<sup>23,24</sup> effects captured by QSGW.<sup>25</sup> On top of the DMFT self-energy, charge and spin susceptibilities are obtained from vertex functions computed from the two-particle Green's function generated in DMFT, via the solutions of non-local Bethe Salpeter equation (BSE). Additionally, we compute the particle-particle vertex functions and solve the ladder particle-particle BSE<sup>21,26,27</sup> to compute the super-

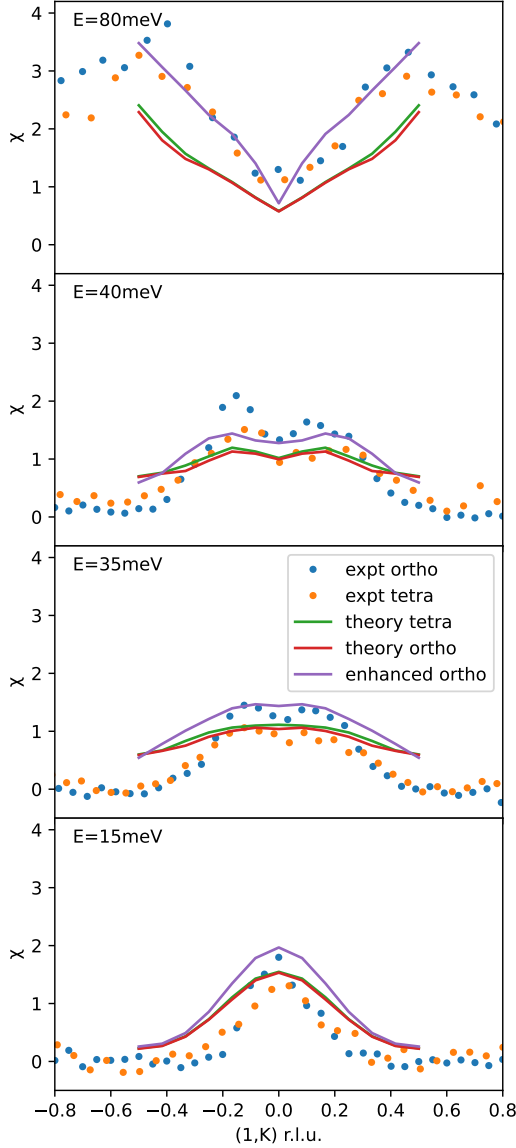


FIG. 1. Imaginary part of the dynamic spin susceptibility  $\text{Im}\chi(q, \omega)$  plotted along the line  $\mathbf{q}=(H=1, K=L=0)$  in reciprocal lattice (r.l.u) units of one Fe-atom unit cell.  $(H, K, L)$  is the standard notation used to identify reciprocal lattice directions. Experimentally it is well established that the low energy peak in  $\text{Im}\chi(q, \omega)$  is at  $\mathbf{q}=(1, 0, 0)$  in the same notation. Different energy cuts are taken and plotted against the observed  $\text{Im}\chi(q, \omega)$  in inelastic Neutron scattering (INS) experiment.<sup>18</sup> The experimental data is reproduced with the raw data received from Wang et al. We plot our computed  $\text{Im}\chi(q, \omega)$  at  $\omega=15, 35, 40$  and  $80$  meV against INS data. Theoretically, the data for the tetragonal (green continuous line) and orthorhombic (red continuous line) phases are nearly indistinguishable and both of them deviate from the experimental data (the latter is plotted as orange (tetra) and blue (ortho) circular points). The theoretical data for the enhanced orthorhombic distortion (purple continuous line) remarkably agrees with the experimental INS data for all energies and momentum.

conducting susceptibilities and eigenvalues of superconducting gap instabilities.

Single particle calculations (LDA, and energy band calculations with the static quasiparticlized QSGW self-energy  $\Sigma^0(k)$ ) were performed on a  $16 \times 16 \times 16$   $k$ -mesh while the (relatively smooth) dynamical self-energy  $\Sigma(k)$  was constructed using a  $8 \times 8 \times 8$   $k$ -mesh and  $\Sigma^0(k)$  is extracted from it. The same mesh is used for DFT. We use Questaal's all-electron implementation for all the calculations here; it is explained in detail in a recent methods paper.<sup>24</sup> For LDA we use a Barth-Hedin exchange-correlation functional (QSGW does not depend on the LDA, but we nevertheless present LDA results to show how QSGW incorporates missing correlations from LDA and renormalizes the electronic bands further.) The QSGW approximation, including the all-electron product basis used to make the polarizability and self-energy is described in detail in Ref. 25. Our one-particle basis set was constructed of 110 orbitals, including *spdfspd* orbitals centered on Fe augmented with local orbitals on the 4d, and *spdfspd* on Se. The product basis in the augmentation spheres was expanded to  $l = 8$ , and included 520 orbitals; for the Coulomb interaction in the interstitial a plane wave cutoff of 2.3 Ry was used. The polarizability is computed with the tetrahedron method; for the self-energy a smearing of 0.003 Ry was used. For frequency integration, we used a mesh with 0.01 Ry spacing at low energy, gradually increasing at higher energy. Six points were used on the imaginary axis contribution to the self-energy. The charge density was made self-consistent through iteration in the QSGW self-consistency cycle: it was iterated until the root mean square change in  $\Sigma^0$  reached  $10^{-5}$  Ry. Thus the calculation was self-consistent in both  $\Sigma^0(k)$  and the density. At the end of QSGW cycles, we use the quasi-particlized electronic band structures as the starting point of our DMFT calculations. The impurity Hamiltonian is solved with continuous time Quantum Monte Carlo solver.<sup>28,29</sup> For projectors onto the Fe d subspace, we used projectors onto augmentation spheres, following the method described in this reference.<sup>30</sup> DMFT is solved for all five Fe-3d orbitals using Continuous Time Quantum Monte Carlo (CTQMC) on a rotationally invariant Coulomb interaction. The double counting correlations are implemented using fully localized limit approximation. The DMFT for the dynamical self energy is iterated, and converges in 30 iterations. Calculations for the single particle response functions are performed with  $10^9$  QMC steps per core and the statistics is averaged over 128 cores. The two particle Greens functions are sampled over a larger number of cores (40000-50000) to improve the statistical error bars. The local effective interactions for the correlated impurity Hamiltonian are given by  $U$  and  $J$ . These are calculated within the constrained RPA<sup>31</sup> from the QSGW Hamiltonian using an approach<sup>21</sup> similar to that of Ref 32, but using projectors from Ref. 30. For bulk FeSe we find  $U=3.5$  eV and  $J=0.6$  eV from our constrained RPA calculations.  $J/U=0.17$  suggests that the

system is in strong Hund's metallic limit as we have discussed in a prior work.<sup>33</sup>

## RESULTS

### Computational details for magnetic susceptibility

We compute the local polarization bubble from the local single-particle Green's function computed from DMFT. We extract  $\Gamma_{loc}^{irr}$ , by solving the local Bethe-Salpeter equation which connects the local two-particle Green's function ( $\chi_{loc}$ ) sampled by CTQMC, with both the local polarization function ( $\chi_{loc}^0$ ) and  $\Gamma_{loc}^{irr}$ .

$$\Gamma_{loc, \alpha_3, \alpha_4}^{irr, m(d)}(i\nu, i\nu')_{i\omega} = [(\chi_{loc}^0)^{-1}_{i\omega} - \chi_{loc}^{m(d)-1}]_{\alpha_1, \alpha_2}^{-1}(i\nu, i\nu')_{i\omega}. \quad (1)$$

$\Gamma$  is the local irreducible two-particle vertex functions computed in magnetic (m) and density (d) channels.  $\Gamma$  is a function of two fermionic frequencies  $\nu$  and  $\nu'$  and the bosonic frequency  $\omega$ .

Spin ( $\chi^m$ ) and charge ( $\chi^d$ ) susceptibilities are computed by solving the momentum dependent Bethe-Salpeter equations in magnetic (spin) and density (charge) channels by dressing the non-local polarization bubble  $\chi^0$  with local irreducible vertex functions  $\Gamma$  in their respective channels:

$$\chi_{\alpha_3, \alpha_4}^{m(d)}(i\nu, i\nu')_{\mathbf{q}, i\omega} = [(\chi^0)^{-1}_{\mathbf{q}, i\omega} - \Gamma_{loc}^{irr, m(d)}]_{\alpha_1, \alpha_2}^{-1}(i\nu, i\nu')_{\mathbf{q}, i\omega}. \quad (2)$$

$\chi^0$  is computed from single-particle DMFT Green's functions embedded in a *QSGW* bath. Susceptibilities  $\chi^{m(d)}(\mathbf{q}, i\omega)$  are computed by summing over frequencies ( $i\nu, i\nu'$ ) and orbitals ( $\alpha_{1,2}$ ).

### Benchmarking of magnetic susceptibilities against experimental observations

In Fig. 1 we plot the imaginary part of  $\text{Im}\chi(q, \omega)$  along the  $q=(1, K)$  line of the one-atom Brillouin zone  $\text{Im}\chi(q, \omega)$  is computed in tetragonal and nematic phases and compared against the inelastic neutron scattering (INS) data received from Wang et al.<sup>18</sup>  $\text{Im}\chi(q, \omega)$  is plotted for slices  $\omega = 15, 35, 40$  and  $80$  meV. The ratio  $a/b$  in the orthorhombic phase ( $a=5.3100$  Å,  $b=5.3344$  Å) differs by only 0.4% from unity and the area is only slightly smaller than the tetragonal phase  $a=3.779$  Å,  $\sqrt{2}a=5.3443$  Å). Consequently,  $\text{Im}\chi(q, \omega)$  changes little between tetragonal and orthorhombic phases. Most remarkably, the entire momentum dependence of  $\text{Im}\chi(q, \omega)$  is rather well reproduced for the tetragonal phase at all energies. This is a testimony to the fact that the essential elements that are required to produce the momentum and energy structures for  $\text{Im}\chi(q, \omega)$  are already present in the three-tier *QSGW*+DMFT+BSE approximation. Nevertheless, our computed  $\text{Im}\chi(q, \omega)$  does not

adequately reflect the effect of nematicity as is apparent in deviations of our theoretical data (red solid lines) from the experimental curves.

These calculations show that nematicity probably originates from a momentum dependent self energy which contains a longer range vertex beyond the single site approximation in DMFT. Our DMFT spin vertex is local and also we do not have the ability to include the electron-phonon interaction *ab initio*; one of which is likely to be responsible for the enhancement of the nematicity. We, instead, mimic the effective potential originating from either of these sources by modifying the crystal-field splitting, enlarging the orthorhombic splitting by a factor of five to ( $a=5.3100$  Å,  $b=5.4344$  Å). In the rest of the paper we use 'ortho-enhanced' to identify this particular structure. We find that the resulting  $\text{Im}\chi(q, \omega)$  is enhanced in intensity and produces very good agreement with the INS data over all energies and momentum.

The precise nature of the boson that Cooper pairs in FeSe is debated, though generally the primary mechanism is believed to be magnetic fluctuations. This is supported by the observation of negligible isotope effect in bulk FeSe.<sup>34</sup> Since the normal phase just above  $T_c=8$  K is orthorhombic, there has been much speculation that nematicity can be the mechanism driving superconductivity, though heavily debated. This is the question we consider within the *QSGW*+DMFT theory. While it is conceivable that our fictitious inducement of nematicity does not yield the proper modification of superconductivity, the true mechanism would have to occur via some unknown process that does not involve the spin susceptibility (which we adequately reproduce, as we have shown). Thus we believe modifying the effective potential via enhancing the orthorhombic distortion is a sufficient proxy to reliably pursue this question.

### Effect of the nematic distortion of density of states

First, we study the effects of nematicity on the local density of states (DOS). The primary effect of non-local charge correlations included within *QSGW* is to reduce the band width (see Fig. 2(a,b)) of FeSe compared to LDA. We show results only for the orthorhombic phase of FeSe, but it is true irrespective of the structural phase considered. The effect nematicity on  $d_{yz}$  and  $d_{xz}$  are mirror images of each other (Fig. 2(d,e)); this includes the change in DOS at  $E_F$ ,  $\rho(E_F)$ . However, the enhanced orthorhombic distortion only weakly reduces the  $d_{xy}$  kinetic energy (Fig. 2(c)) and does not alter the  $xy$  contribution to  $\rho(E_F)$ . The Se-p states remain negligibly small within an energy range of  $\pm 1$  eV around  $E_F$  in all cases. In Fig. 2(b) the Se-p DOS is shown scaled by a factor of 10 to make it visible. The effect of such distortions are negligible on the Se-p states as well and these states remain irrelevant for the low energy physics of FeSe.

Fig. 2(f) plots the *QSGW*+DMFT DOS for the three

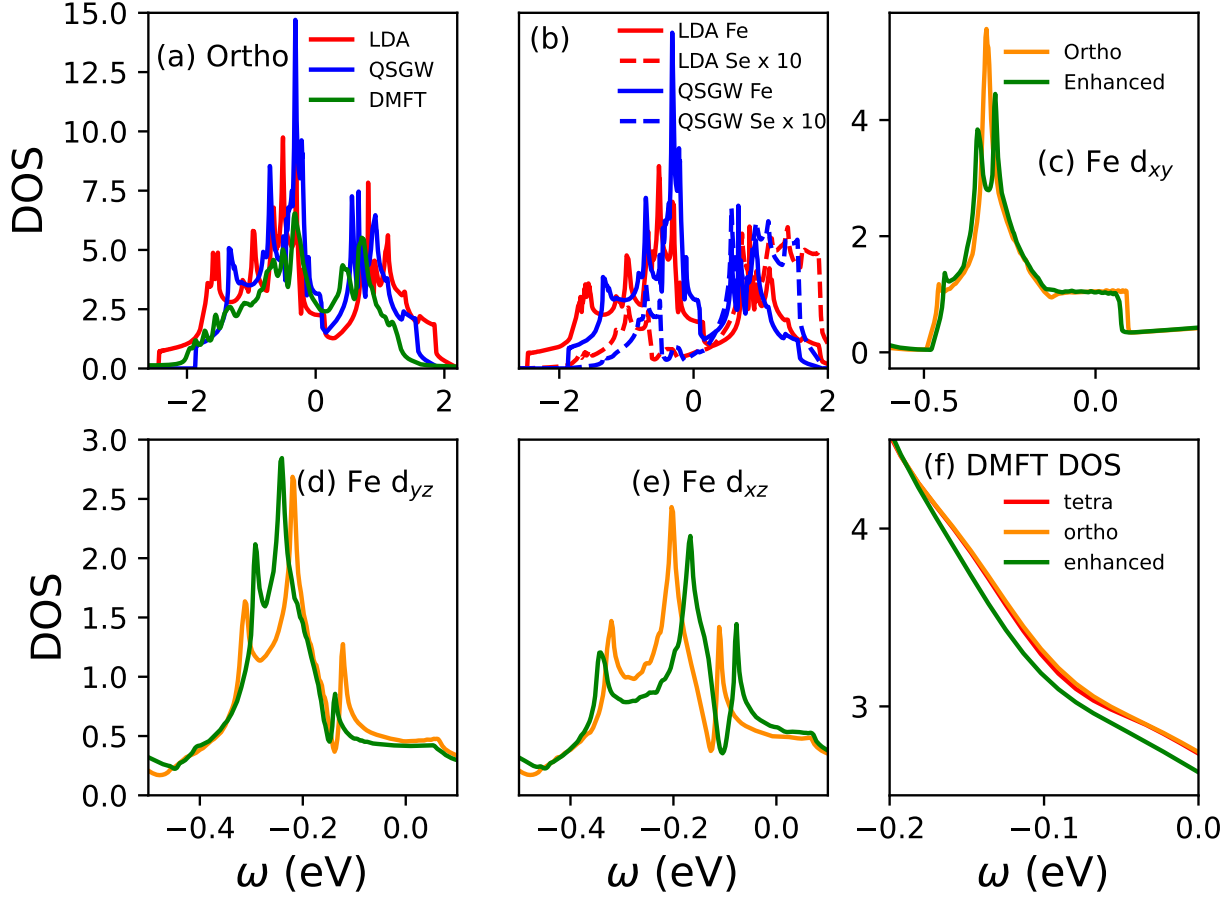


FIG. 2. (a) QSGW total local density of states (DOS) for FeSe is narrower compared to LDA. **DMFT narrows the bands compared to QSGW.** (b) Both Fe-3d states and Se-p states get narrowed within QSGW, although the Se-p states are negligibly small around  $E_F$ . (c) The artificially enhanced nematic distortion reduces the Fe- $d_{xy}$  band width weakly compared to the original nematic phase, however, its effect on (d)  $d_{yz}$  and (e)  $d_{xz}$  orbitals are opposite, in one case DOS at  $E_F$  drops and in the other case it enhances. (f) The total QSGW+DMFT local density of states (DOS) for FeSe in tetragonal, orthorhombic and orthorhombic phase with enhanced distortion are shown.

systems; tetragonal, orthorhombic and ortho-enhanced. Note that the QSGW Green's functions are renormalized in the presence of the self-consistent single-site DMFT self energy. For all phases there is a significant drop in  $\rho(E)$  at  $\omega = 0$ , and it is also seen that enhanced nematicity modestly suppresses  $\rho(E_F)$  (i.e.  $\omega=0$ ). This observation suggests that photo-emission spectroscopy should be able to see this drop in the local DOS at low energies in systems where nematicity plays a major role, for example, in the de-twinned sample of FeSe.<sup>12,15,35</sup> It suggests that if the superconductivity is modified by enhanced nematicity, it does not result from a purely Fermi surface nesting driven mechanism. Within a purely BCS picture such a dip in  $\rho(E_F)$  would produce exponentially weak suppression of superconducting  $T_c$ . Even while nematicity reduces  $\rho(E_F)$ , it has the opposite effect on  $T_c$ . As

we will show in the following discussion,  $T_c$  increases as a consequence of the change in two-particle vertex which promotes the superconducting pairing glue.

### Orbitally resolved Magnetic susceptibilities

Before moving on to the discussion of superconductivity, we analyze our computed spin susceptibilities  $\chi(q, \omega)$ , particularly in an attempt to understand its orbital-structure. We show in Fig. 3 (a) that the irreducible vertex computed using CTQMC+DMFT is strongly orbital-dependent. It is crucially important that CTQMC+DMFT is site-local but not point-local. One of the primary successes of DMFT is its ability to pick up orbital dependent structures in self-energy and higher-

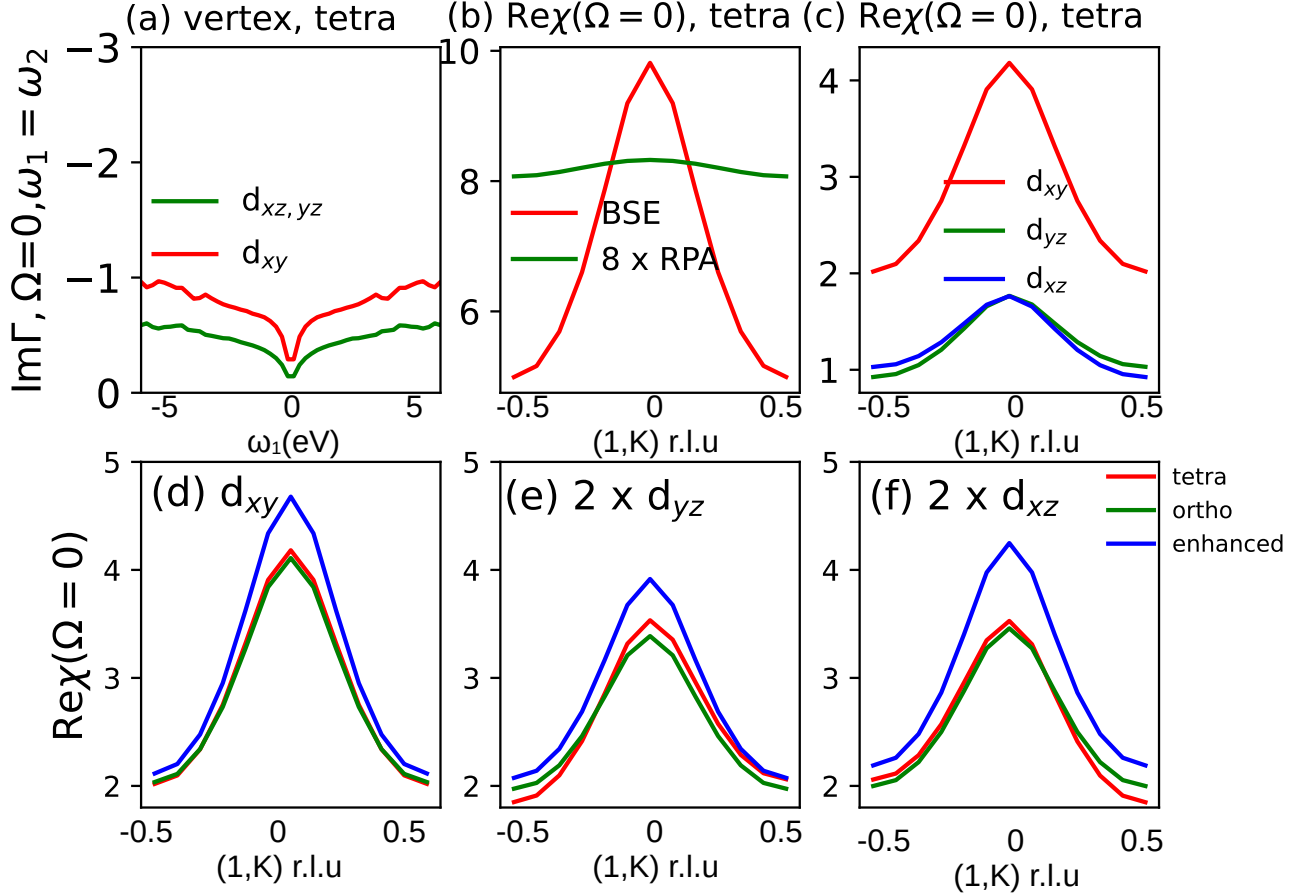


FIG. 3. (a) Magnetic vertex and its orbital structure. For all energies,  $\Gamma_{xy} > \Gamma_{xz,yz}$ . (b) The BSE approximation is shown to strongly modify the random-phase approximation (RPA) in the magnetic channel, in a momentum dependent way (note that  $\chi^{\text{RPA}}$  is scaled by a factor of 8). (c,d,e,f) Orbitally resolved static spin susceptibility,  $\text{Re}\chi(q)$  is plotted along  $\mathbf{Q}=(H,K,L=0)$ . The enhanced orthorhombic distortion increases the intensity of  $\text{Re}\chi(q)$  in all intra-orbital channels, however, the  $d_{xy}$  states remain dominant in all cases.  $\chi_{xz}$  and  $\chi_{yz}$  are scaled by a factor of two to improve visibility.

order vertex functions. This becomes even more crucial in Hund's metals since Hund's  $J$  generates strong orbital-differentiation. The local irreducible vertex computed in the magnetic channel depends on three frequencies (two Matsubara Fermionic frequency indices  $\omega_{1,2}$  and one Matsubara bosonic frequency index  $\Omega$ ). We show that for all energies (Matsubara Fermionic frequencies) the magnetic vertex  $\Gamma$  remains larger in the  $d_{xy}$  channel compared to the  $d_{xz,yz}$  channels, suggesting that magnetic scatterings are largest there.

The site-local vertex has a pronounced effect on the both the magnitude and momentum dependence of the nonlocal  $\chi$  (compare RPA to BSE in Fig. 3(b)), and it is the vertex that ensures that the antiferromagnetic instability suppresses magnetic instabilities at other  $q$ .  $\chi^{\text{RPA}}$  must be scaled by 8 or so to put on the same scale as  $\chi^{\text{BSE}}$ , which gives a rough measure of the Stoner enhancement. But it is important to stress once again that the orbital- and frequency- dependence of the vertex is crucial, and it cannot be adequately modeled by a con-

stant.

We resolve the computed static spin susceptibilities  $\chi(q)$  in different intra-orbital channels. Enhanced nematicity causes  $\chi(q)$  to increase in all intra-orbital channels; however, it remains smaller in the  $d_{xz}$  and  $d_{yz}$  channels than the  $d_{xy}$  channel (see Fig. 3 (c,d,e,f)). Orthorhombic distortion lifts the degeneracy between the  $d_{xz}$  and  $d_{yz}$  orbitals, that is observed in neutron measurements. In any case, the  $d_{xy}$  channel remains the dominant spin fluctuation channel, while the  $d_{xz}$  and  $d_{yz}$  channels each contribute nearly 40% of the  $d_{xy}$  spin fluctuations. This is crucial. Although this desired 'nematic' distortions that produce the agreements with experimentally observed  $\chi(q,\omega)$ , leads to moderate spectral weight redistribution between  $d_{xz}$  and  $d_{yz}$  one-particle channel,  $d_{xy}$  still remains the most correlated orbital that hosts the largest fraction of the magnetic collective fluctuations in the system.



### Computational details of superconducting instabilities

How particular orbitals govern spin fluctuations and thus control  $T_c$ , is key to understanding the superconducting mechanism in such a complex multi-band manifold. We probe the effect of such enhanced nematicity on the superconductivity. The superconducting pairing susceptibility  $\chi^{p-p}$  is computed by dressing the non-local pairing polarization bubble  $\chi^{0,p-p}(\mathbf{k}, i\nu)$  with the pairing vertex  $\Gamma^{irr,p-p}$  using the Bethe-Salpeter equation in the particle-particle channel.

$$\chi^{p-p} = \chi^{0,p-p} \cdot [\mathbf{1} + \Gamma^{irr,p-p} \cdot \chi^{0,p-p}]^{-1} \quad (3)$$

The particle-particle vertex in the singlet channel has odd-symmetry under exchange of two external spins,

$$\Gamma^{p-p,s} = \frac{1}{2} [\Gamma_{\uparrow\downarrow}^{p-p} - \Gamma_{\downarrow\uparrow}^{p-p}] \quad (4)$$

The irreducible particle-particle vertex function channel  $\Gamma^{p-p,irr}$  which provides the pairing glue to form Cooper pairs, consists of the fully irreducible vertex function  $\Gamma^{f,irr}$  and the reducible vertex functions computed in the particle-hole channels

$$\tilde{\Gamma}^{p-h} = \Gamma^{full,p-h} - \Gamma^{irr,p-h} \quad (5)$$

where  $\Gamma^{full}$  is,

$$\Gamma^{full} = \Gamma^{irr} - \Gamma^{irr} \chi \Gamma^{irr} \quad (6)$$

This results in  $\tilde{\Gamma}^{p-h}$ ,

$$\tilde{\Gamma}^{p-h} = \Gamma^{irr} \chi \Gamma^{irr} \quad (7)$$

This is one of the most crucial points of our implementation. Note that the  $\Gamma^{f,irr}$  is local within the single-site DMFT approximation and, hence, can not contribute to superconductivity. Nevertheless, the reducible magnetic/charge vertex  $\tilde{\Gamma}^{irr,p-h}$ , obtained from dressing  $\Gamma^{irr}$  with the full non-local and dynamic magnetic/charge susceptibilities, can have both momentum dependence and dynamics desired for superconductivity. The Parquet like equations that are solved to achieve this are presented below:

$$\tilde{\Gamma}_{\alpha_1, \alpha_3}^{p-h,m/d}(i\nu', i\nu)_{\mathbf{q}, i\omega} = \sum_{i\nu 1, i\nu 2} \sum_{\alpha'_2, \alpha'_4} \alpha'_2, \alpha'_4 \quad (8)$$

$$\Gamma_{loc}^{irr,p-h,m/d}{}_{\alpha_2, \alpha_4}{}_{\alpha_1, \alpha_1'}(i\nu, i\nu 1)_{i\omega} \chi_{\mathbf{q}}^{p-h,m/d}{}_{\alpha'_2, \alpha'_4}{}_{\alpha'_1, \alpha'_3}(i\nu 1, i\nu 2)_{i\omega} \quad (9)$$

$$\Gamma_{loc}^{irr,p-h,m/d}{}_{\alpha'_4, \alpha_4}{}_{\alpha_3, \alpha_3'}(i\nu 2, i\nu')_{i\omega}$$

The irreducible particle-particle vertex function  $\Gamma^{irr,p-p}$  is finally written in terms of the reducible magnetic/charge vertex  $\tilde{\Gamma}^{m/d}$  functions.

$$\Gamma_{\alpha_2 \uparrow, \alpha_4 \downarrow}^{irr,p-p}(\mathbf{k}, i\nu, \mathbf{k}', i\nu') = \Gamma_{\alpha_1 \uparrow, \alpha_3 \downarrow}^{f-irr}{}_{\alpha_1 \uparrow, \alpha_3 \downarrow}(i\nu, i\nu') - \frac{1}{2} [\tilde{\Gamma}^{p-h,(d)} - \tilde{\Gamma}^{p-h,(m)}]_{\alpha_2, \alpha_3}{}_{\alpha_1, \alpha_4}(\mathbf{k}' - \mathbf{k}, i\nu' - i\nu) + \tilde{\Gamma}_{\alpha_4, \alpha_3}^{p-h,(m)}{}_{\alpha_1, \alpha_2}(-\mathbf{k}' - \mathbf{k}, -i\nu' - i\nu) \quad (10)$$

$$\Gamma_{\alpha_2 \downarrow, \alpha_4 \uparrow}^{irr,p-p}(\mathbf{k}, i\nu, \mathbf{k}', i\nu') = \Gamma_{\alpha_2 \downarrow, \alpha_4 \uparrow}^{f-irr}{}_{\alpha_1 \downarrow, \alpha_3 \uparrow}(i\nu, i\nu') - \frac{1}{2} [\tilde{\Gamma}^{p-h,(d)} - \tilde{\Gamma}^{p-h,(m)}]_{\alpha_2, \alpha_3}{}_{\alpha_1, \alpha_2}(-\mathbf{k}' - \mathbf{k}, -i\nu' - i\nu) - \tilde{\Gamma}_{\alpha_2, \alpha_3}^{p-h,(m)}{}_{\alpha_1, \alpha_4}(\mathbf{k}' - \mathbf{k}, i\nu' - i\nu) \quad (11)$$

Finally, exploiting the Eqn. (6,7) and Eqn. (10,11) we obtain the  $\Gamma^{irr,p-p}$  in the singlet channel from the magnetic and density particle-hole reducible vertices,

$$\Gamma_{\alpha_2, \alpha_4}^{irr,p-p,s}(\mathbf{k}, i\nu, \mathbf{k}', i\nu') = \Gamma_{\alpha_2, \alpha_4}^{f-irr}{}_{\alpha_1, \alpha_3}(i\nu, i\nu') + \frac{1}{2} [\tilde{\Gamma}^{p-h,(m)} - \frac{1}{2} \tilde{\Gamma}^{p-h,(d)}]_{\alpha_2, \alpha_3}{}_{\alpha_1, \alpha_4}(i\nu, -i\nu')_{\mathbf{k}' - \mathbf{k}, i\nu' - i\nu} + \frac{1}{2} [\tilde{\Gamma}^{p-h,(m)} - \frac{1}{2} \tilde{\Gamma}^{p-h,(d)}]_{\alpha_4, \alpha_3}{}_{\alpha_1, \alpha_2}(i\nu, i\nu')_{-\mathbf{k}' - \mathbf{k}, -i\nu' - i\nu} \quad (12)$$

With  $\Gamma^{irr,p-p}$  in hand we can solve the p-p BSE to compute the p-p susceptibility  $\chi^{p-p}$ .

$$\chi^{p-p} = \chi^{0,p-p} \cdot [\mathbf{1} + \Gamma^{irr,p-p} \cdot \chi^{0,p-p}]^{-1} \quad (13)$$

The critical temperature  $T_c$  is determined by the temperature where  $\chi^{p-p}$  diverges. For such divergence the sufficient condition is that at least one eigenvalue of the pairing matrix  $-\Gamma^{irr,p-p} \cdot \chi^{0,p-p}$  approaches unity. The corresponding eigenfunction represents the momentum structure of  $\chi^{p-p}$ . Hence  $T_c$ , eigenvalues  $\lambda$  and eigenfunctions  $\phi^\lambda$  associated with different superconducting gap symmetries (in the singlet channel) can all be computed by solving the eigenvalue equation,

$$\frac{T}{N_k} \sum_{k', i\nu'} \sum_{\alpha_2, \alpha_4} \sum_{\alpha_5, \alpha_6} \Gamma_{\alpha_1, \alpha_3}^{irr,p-p,s}(k, i\nu, k', i\nu') \cdot \chi_{\alpha_5, \alpha_6}^{0,p-p}(k, i\nu') \phi_{\alpha_5 \alpha_6}^\lambda = \lambda \cdot \phi_{\alpha_5 \alpha_6}^\lambda \quad (14)$$

The gap function can be written in a symmetric and Hermitian form by

$$\frac{T}{N_k} \sum_{k', i\nu'} \sum_{\alpha_2, \alpha_4} \sum_{\alpha_6, \alpha_7, \alpha_8} (\chi_{\alpha_1, \alpha_3}^{0,p-p}(k, i\nu))^{1/2} \cdot \Gamma_{\alpha_5, \alpha_7}^{irr,p-p,s}(k, i\nu, k', i\nu') \cdot (\chi_{\alpha_6, \alpha_8}^{0,p-p}(k', i\nu'))^{1/2} \cdot \phi_{\alpha_6 \alpha_8}^\lambda(k', i\nu') = \lambda \cdot \phi_{\alpha_1 \alpha_3}^\lambda(k, i\nu) \quad (15)$$

It can be explicitly shown that the eigenvalues of the non-Hermitian gap equation are the same as eigenvalues of the Hermitian gap equation.

Finally,  $\chi^{p-p}$  can be represented in terms of eigenvalues  $\lambda$  and eigenfunctions  $\phi^\lambda$  of the Hermitian particle-particle pairing matrix.

$$\chi^{p-p}(k, i\nu, k', i\nu') = \sum_{\lambda} \frac{1}{1-\lambda} \cdot (\sqrt{\chi^{0,p-p}(k, i\nu)} \cdot \phi^\lambda(k, i\nu)) \cdot (\sqrt{\chi^{0,p-p}(k', i\nu')} \cdot \phi^\lambda(k', i\nu')) \quad (16)$$

To solve this eigenvalue equation, the most important approximation we make is to take the static limit of  $\Gamma^{irr,p-p}$  in the bosonic frequency  $i\omega=0$  (real frequency axis). The explicit dependence on the fermion frequencies are kept, as are all the orbital and momentum indices.

As is apparent from Equation (12) at what wave vector spin and charge fluctuations are strong is of central importance to the kind of superconducting pairing symmetry they can form. The entire momentum, orbital and frequency dependence of the vertex functions are computed explicitly and the BSE equations are solved with them. Since the vertex structure has no predefined form-factor, the emergent superconducting gap symmetry is calculated in an unbiased manner. This provides an unbiased insight into the superconducting gap symmetries, the strength of the leading eigenvalues in different systems and, most importantly, allows for a fair comparison of the relative strength of the leading superconducting instabilities in bulk tetragonal, orthorhombic and enhanced-ortho FeSe. Thus, our ability to predict these properties is limited mostly by the fidelity of the Green's functions that determine the vertices and  $\chi$ . Further, the fact that the charge component to the superconducting vertex is finite, within our formulation, ensures that the magnetic (in this case antiferromagnetic) instability can not drive an order and suppress superconductivity, as it naturally happens with density functional and other mean field approaches. We show in Fig. 4(a) that the antiferromagnetic instability remains the sub-leading instability in FeSe making way for superconductivity to take place.

There is a practical limitation, however. Since we compute the vertex functions from CTQMC, which limits the temperatures down to which the vertex can be computed. We have observed in different materials that the leading eigenvalue  $\lambda$  does not have a simple, analytic dependence on temperature,<sup>36</sup> and hence  $\lambda$  can not be reliably extrapolated to very low temperatures. For that reason, we avoid estimating  $T_c$  (the temperature at which  $\lambda$  reaches 1) for different systems from our method, rather, we compare the strength of  $\lambda$  for a given temperature in different materials (Fig. 4), which is free from any ambiguities. We have explored the fidelity of this implementation in predicting the gap symmetries and leading instabilities in several previous works.<sup>33,36,37</sup>

## Leading and sub-leading superconducting instabilities

We observe that the leading eigenvalue  $\lambda$  (Fig. 4) of the superconducting gap equation corresponds to an extended s-wave gap structure,<sup>38</sup> with a form factor  $\Delta_1 \sim \cos(k_x) + \cos(k_y)$  (see Fig. 5) in all the phases. The lagging instability  $\Delta_2$  has a  $\cos(k_x) - \cos(k_y)$  structure. Moreover, this dominant instability exists in the  $d_{xy}$  orbital channel (Fig. 4) consistent with our observations of dominant spin fluctuations in the same channel. To see what controls the instability, it is simplest to consider what increases  $\Gamma^{p-p} \cdot \chi^0$ ; see Eq. 13. We find that the orthorhombic distortion weakly affects both  $\chi^0$  (seen from the change in DOS, Fig. 2(f)) and  $\Gamma^{p-p}$  (Fig. 4) relative to the tetragonal phase, and hence,  $\Gamma^{p-p} \cdot \chi^0$  hardly changes. However, in the ortho-enhanced case,  $\Gamma^{p-p}$  increases while  $\chi^0$  drops. The increment in  $\Gamma^{p-p}$  overcompensates the reduction in  $\chi^0$  so that  $\Gamma^{p-p} \cdot \chi^0$  is enhanced relative to the tetragonal phase. We stress that the modest enhancement to  $T_c$  occurs for reasons completely different from approaches to superconductivity that rely on the BCS approximation or its extension. Within BCS any changes to the superconducting  $T_c$  is primarily discussed with arguments based on density of states. This is natural since the replacement of the density  $\rho$  by  $\rho(E_F)$  in BCS gap integrals is strictly possible only within the BCS approximation  $E_F \gg \hbar\omega_D \gg \Delta_0$  (where  $\omega_D$  is the phonon-frequency and  $\Delta_0$  is the superconducting gap at  $T=0$ ). Based on BCS theory,<sup>39</sup> a small suppression in  $\rho(E_F)$  would cause exponentially small reduction in  $T_c$ . Further, in the limit of strong electron-electron interaction (attraction) for dilute mobile charges,  $T_c$  is given by the Bose-Einstein condensation (BEC) temperature,<sup>40–42</sup> and not by the BCS limit. In BEC  $T_c$  has a power-law dependence on  $\rho$  in contrast to the exponential dependence in BCS. The famous Uemura plot<sup>43</sup> as was established in the early days of cuprates, showed how unconventional superconductivity in cuprates was more akin to the BEC limit, instead of the BCS limit. Nevertheless, in FeSe the BEC formula would again lead to weak suppression of  $T_c$  due to nematicity. In stark contrast, within our implementation of this finite temperature instability approach to superconductivity, no such approximations are made, moreover, we keep full energy dynamics of the one-particle Green's functions and full energy-dynamics (dependence on two Matsubara fermionic frequency indices and one Matsubara bosonic frequency index) of the two-particle vertex functions  $\Gamma^{p-p}$ . The approximation we do make, namely put the bosonic frequency to zero while diagonalizing the gap equation, is a sensible one that assumes that superconductivity is a low-energy phenomena. As noted, the full theory also predicts nematicity slightly enhances  $T_c$ , because of changes to the vertex.

As we showed in our recent work,<sup>36</sup> it is extremely challenging to perform the calculations at a low enough temperature where  $\lambda$  can reach unity, owing to several



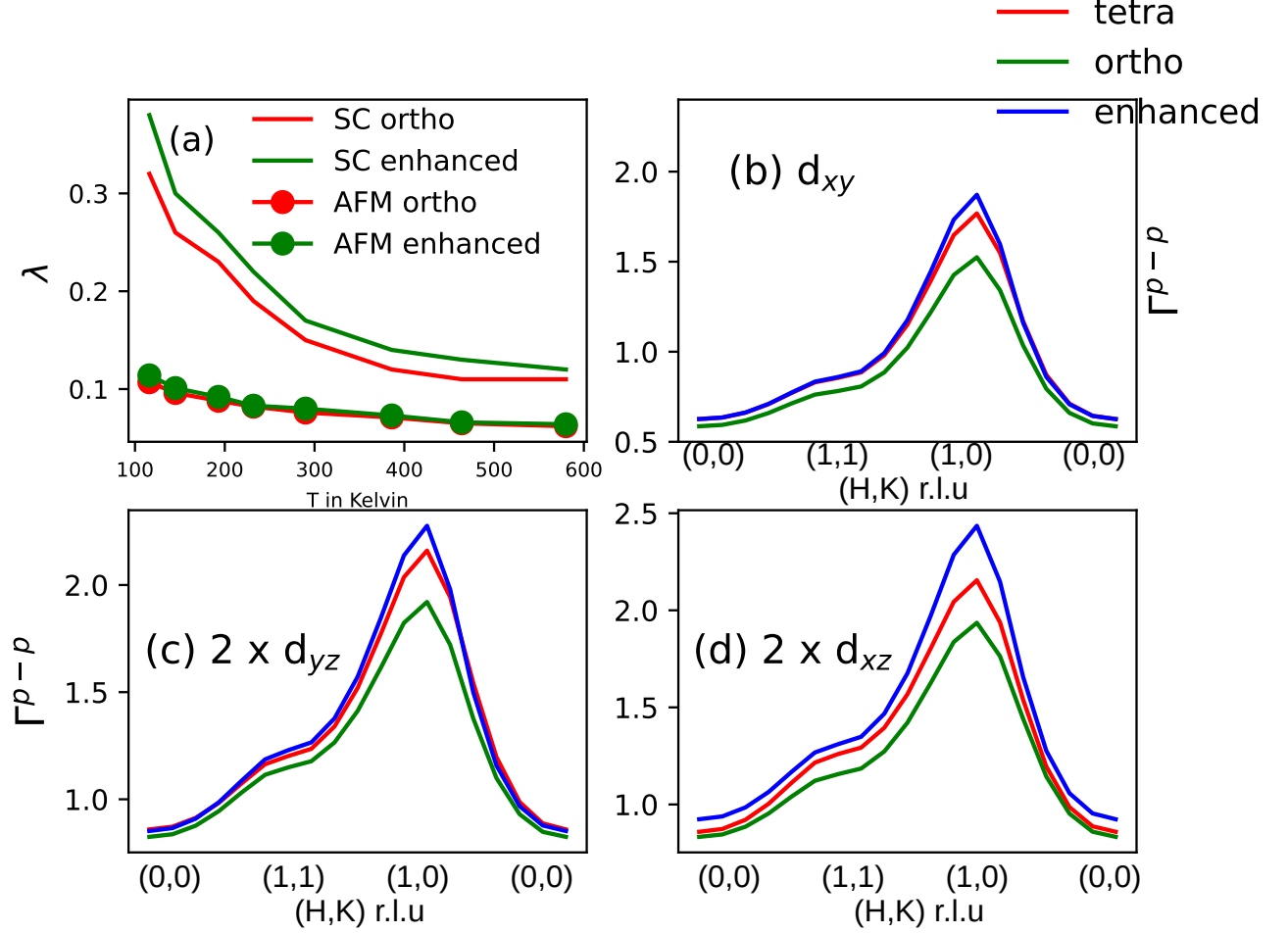


FIG. 4. (a) The leading instability in the superconducting channel is shown to dominate over the magnetic instability for all temperatures. In (b), (c), (d) the momentum structure of the particle-particle vertex is shown. The particle-particle instability remains at least twice larger in the  $d_{xy}$  channel in all phases of FeSe compared to the  $d_{yz}$  and  $d_{xz}$  channels.

technicalities primarily related to the stochastic nature of the CT-QMC solver. The lowest temperature where we could perform our calculations in these systems is 116 K, where  $\lambda$  remains less than unity. However, following the trend, it appears that the ortho-enhanced phase can at most realize a 10-15% enhancement in  $T_c$  in comparison to the bulk orthorhombic phase. Our calculations suggest that the tetragonal phase could also superconduct with a  $T_c$  not much different from the ortho-enhanced phase. This is consistent with the experimental observation that the  $\text{FeSe}_{1-x}\text{S}_x$  alloy realizes a superconducting  $T_c$  not significantly different from the bulk orthorhombic FeSe, even when sulfur doping suppresses the nematic phase completely.<sup>44–46</sup> The primary origin of this, as we show, is that in bulk FeSe, in all the phases, Fe-3d<sub>xy</sub> remains the most correlated orbital that sources the largest fraction of collective magnetic fluctuations and thus acts as the primary glue for the Cooper pair formation. However, as we explicitly show in Fig. 4 (b,c,d) that it is not only the magnetic susceptibilities, but the particle-particle vertex  $\Gamma^{p-p}$  that is a complicated combination of

both magnetic and charge vertex functions (see Eq. 12), remains most dominant in the  $d_{xy}$  channel in all phases of bulk FeSe. While nematic distortions drive spectral weight redistribution mediated by degeneracy lifting of  $d_{xz}$  and  $d_{yz}$  orbitals, they act as sub-leading channels for magnetism and superconductivity.

## CONCLUSIONS

To summarize, we perform *ab initio* calculations for bulk tetragonal and orthorhombic phases of FeSe and compute single and two-particle spectra and superconducting eigenvalues. We find that spin fluctuations are dominant in the Fe-3d<sub>xy</sub> channel in all cases and can potentially drive superconductivity in the bulk tetragonal FeSe. Nevertheless, a rigorous comparison against the observed spin susceptibilities in inelastic neutron scattering experiments in the orthorhombic phase reveals that our computed susceptibilities have the correct momentum structure at all energies, but not the intensity. We

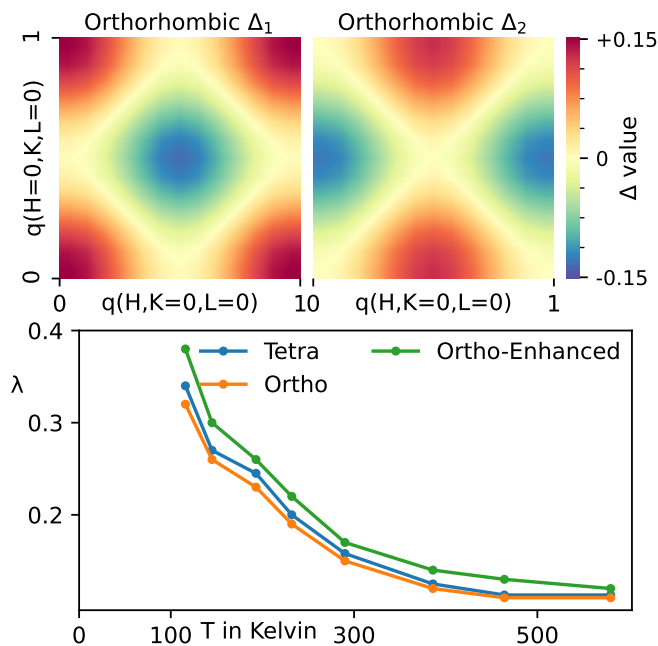


FIG. 5. The superconducting instabilities inside the orthorhombic phase are shown: instabilities correspond to the leading ( $\Delta_1$ ) and lagging ( $\Delta_2$ ) eigenvalues of the solutions to the BCS gap equation. The evolution of the leading eigenvalue as a function of temperature is shown for tetragonal, orthorhombic and ortho-enhanced phases in the bottom panel.

show that an artificially enhanced structural orthorhombic distortion simulates the missing spin fluctuation intensity and acts as the proxy for the desired nematicity, missing from our theory but present in the real world. This enhanced nematicity, **even while suppressing the one-particle density of states at the Fermi energy, nevertheless** leads to enhanced correlations **from** the particle-particle superconducting correlations, leading to an increment in  $T_c$  on the order of 10-15%.

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- \* [swagata.acharya@ru.nl](mailto:swagata.acharya@ru.nl)
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