Doping effects on electronic states in electron-doped FeSe: Impact of self-energy and vertex corrections

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The pairing glue of high-\(T_c\) superconductivity in heavily electron-doped (e-doped) FeSe, in which hole-pockets are absent, has been an important unsolved problem. Here, we focus on a heavily e-doped bulk superconductor Li\(_{1-x}\)Fe\(_{2}\)O\(_x\)FeSe (\(T_c \sim 40\) K). We construct a first-principles model beyond the rigid band approximation and analyze the spin and orbital fluctuations by taking both vertex corrections (VCs) and self-energy into consideration. Without e-doping (\(x = 0\)), the ferro-orbital order without magnetism in FeSe is reproduced by the VCs. The orbital order quickly disappears when the hole-pocket vanishes at \(x \sim 0.05\). With increasing \(x\) further, the spin fluctuations remain small, whereas orbital fluctuations gradually increase with \(x\) due to the VCs. The negative feedback due to the self-energy is crucial to explain experimental phase diagram. Thanks to both vertex and self-energy corrections, the orbital-fluctuation-mediated \(s_{++}\)-wave state appears for a wide doping range, consistent with experiments.

The high-\(T_c\) superconducting (SC) state in heavily electron-doped (e-doped) FeSe systems attracts great attention, but its pairing mechanism is still open question. One of the characteristics of e-doped FeSe is the lack of magnetic order. Bulk FeSe exhibits spontaneous orbital polarization \(n_{zz} \neq n_{yy}\) at \(T_S = 90\) K, whereas no magnetic order occurs down to the SC transition temperature \(T_c = 9\) K. The orbital order is suppressed by only a few-percent e-doping, and instead, a high-\(T_c\) SC phase with \(T_c \geq 40\) K appears for a wide doping range in various e-doped FeSe compounds, such as an ultra-thin FeSe layer on SrTiO\(_3\) (\(T_c = 40 - 100\) K), K-dosed FeSe (\(T_c \sim 40\) K)\(^{33,34}\), and intercalated superconductors (\(T_c \sim 40\) K)\(^{35,36}\). Angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM) measurements have revealed that the SC gaps on the electron Fermi surfaces (FSs) are fully gapped\(^{33,34}\).

In conventional Fe-based superconductors with electron-FSs (e-FSs) and hole-FSs (h-FSs), strong spin orbital fluctuations coexist in many compounds. This fact means that two kinds of \(s\)-wave SC states, the \(s_{+}\)-wave state with sign reversal and the \(s_{++}\)-wave state without sign reversal, can be mediated by spin and orbital fluctuations, respectively\(^{14-20}\). Up to now, lots of experimental efforts have been devoted to detect the presence or absence of sign reversal\(^{21-26}\). The recently reported impurity-induced \(s_{\pm} \rightarrow s_{++}\) crossover in Ba(Fe,Rh)\(_2\)As\(_2\)\(^{25}\) has clarified the coexistence of sizable repulsive and attractive pairing gluers in Fe-based compounds.

In e-doped FeSe compounds, in contrast, the top of the h-FSs completely sinks below the Fermi level\(^{37,38}\). In spite of its high \(T_c\), nuclear magnetic resonance (NMR) measurements have revealed that the spin fluctuations at \(T_c\) in e-doped FeSe are considerably weaker than those in undoped FeSe\(^{22}\). It is still a big mystery that the high-\(T_c\) state (\(T_c > 40\)K) realizes in e-doped FeSe in spite of its weak spin fluctuation. Therefore, the pairing glue for the high-\(T_c\) state in e-doped FeSe is still controversial. Up to now, (nodeless) \(d\)-wave state\(^{39,40}\) andincipient \(s_{+}\)-wave state\(^{30,33,34}\) have been proposed based on the spin fluctuation theory, while \(T_c\) will not be high. In FeSe/SrTiO\(_3\), it is expected that strong interfacial electron-phonon coupling increases \(T_c\) up to \(\sim 60\) K\(^{32,33,36}\). However, \(T_c \sim 40\) K is realized in Li\(_{1-x}\)Fe\(_{2}\)OHFeSe even in the absence of strong interfacial electron-phonon interaction\(^{10}\), indicating that the main pairing glue originates from the electron correlation.

The present authors investigated the pairing mechanism in e-doped FeSe by focusing on the impact of vertex corrections (VCs), which are higher-order many-body effects beyond the mean-field theories\(^{22}\). It was found that orbital-fluctuation-mediated \(s_{++}\)-wave SC can appear even in the absence of h-FSs. This result is consistent with the recent quasiparticle interference (QPI) measurement reported in Ref. \(^{4}\), while another QPI study indicates sign reversal between inner- and outer- electron FSs\(^{41}\). However, it was not explained why a high-\(T_c\) state is realized in various e-doped FeSe families for a very wide doping range (\(x = 0.05 - 0.20\))\(^{42}\). Therefore, we have to make further progress on the theory of pairing mechanism.

In this paper, we discuss the mechanism of high-\(T_c\) superconductivity in heavily e-doped FeSe by focusing on the bulk superconductor Li\(_{1-x}\)Fe\(_{2}\)OHFeSe (\(T_c \sim 40\)K). We construct a first-principles model using the virtual crystal approximation (VCA), and analyze the spin and orbital fluctuations using the self-consistent-vertex correction (SC-VC) method with self-energy developed in Ref. \(^{38}\). The latter correction was dropped in our previous study\(^{22}\). At \(x = 0\), the ferro-orbital order without magnetism in FeSe is reproduced. With increasing \(x\), the orbital order quickly disappears, and spin fluctuations remain small for 0.05 < \(x\) < 0.20. Interestingly, orbital fluctuations gradually increase with \(x\) due to the VCs. Therefore, the orbital-fluctuation-mediated \(s_{++}\)-wave state appears for a wide doping range, consistent with experiments. The negative feedback due to the self-energy is crucial to explain appropriate e-doping phase diagram of FeSe compounds.
First, we construct the eight-orbital $d$-$p$ tight-binding model for Li$_x$-$y$Fe$_2$OFeSe by using WIEN2k and Wannier90 packages, and the doping effect is incorporated using the VCA. To reproduce the experimental Fermi surfaces, we modify the tight-binding parameters in a similar manner to that of Ref. [1]; please see Appendix A.

Figure (a) shows the band dispersions for $x = 0.15$ with $\lambda_{\text{SOI}} = 50 \text{ meV}$. The green, red, and blue lines correspond to the $xz$, $yz$, and $xy$ orbitals, respectively. The dotted lines represent the band dispersions in the RB model. Fermi surfaces for (b) $x = 0$ and (c) 0.15. e-FS$_1$ and e-FS$_2$ are inner and outer e-FS$_S$, respectively. (d) $x$ dependence of d-orbital DOS. The h-FS around $\Gamma$ disappears at $x_c \sim 0.03$.

The $d$-orbital density of states (DOS) is shown in Fig. (d). With increasing $x$ from 0, the total DOS and $xz$ orbital DOS decrease toward $x = x_c$. For $x > x_c$, the $xy$-orbital DOS is dominant and increases gradually with doping. Therefore, in e-doped FeSe, we can expect some fluctuations related to the $xy$ orbital.

Next, we study the eight-orbital $d$-$p$ Hubbard model: $H = \hat{H}_0^d + r\hat{H}_U$, where $\hat{H}_0^d$ is the tight-binding model for each doping level $x$, and $\hat{H}_U$ is the first-principles screened Coulomb interaction for $d$ orbitals in FeSe. The doping effect is incorporated similarly to the previous study on K-dosed FeSe.

We calculate the spin susceptibilities using the fluctuation exchange (FLEX) approximation. The self-energy $\Sigma(k)$ is given by

$$\Sigma(k) = \frac{T}{N} \sum_{k^'} \left[ \frac{3}{2} \hat{V}^s(k - k^') + \frac{1}{2} \hat{V}^c(k - k^') \right] \hat{G}(k'),$$

where $k = (k, \imath \epsilon_n)$ and $\epsilon_n = (2n + 1)\pi T$ represents the fermion Matsubara frequencies. The Green’s function is expressed as $\hat{G}(k) = [(\hat{G}^0(k))^{-1} - \Sigma(k)]^{-1}$, where $\hat{G}^0(k) = [(\imath \epsilon_n - \mu)\mathbb{1} - \hat{H}_U(k)]^{-1}$ is the bare Green’s function and $\mu$ is the chemical potential. $\hat{V}^s = \hat{U}^s \hat{\chi}^s \hat{U}^s$ is the spin (charge) part interaction, where $\hat{\chi}^s$ is the susceptibility and $\hat{U}^s$ is the matrix form of the Coulomb interaction. The self-energy represents the negative feedback effect by fluctuations and gives the renormalization of the Green’s function.

Figures (a) and (b) show the momentum dependence of the spin susceptibility $\chi^s(q)$ for $x = 0$ and 0.2, respectively. At $x = 0$, $\chi^s(q)$ has commensurate peaks at $q = (\pi, 0)$ and $(0, \pi)$ due to the e-h FS nesting. In addition, the peak at $q = (\pi, \pi)$ originates from the e-e FS nesting. With increasing doping, the former disappears and the latter becomes dominant, and its position moves as shown in Fig. (b). The broad peak obtained at $q \sim (\pi, \pi/2)$ is consistent with the experiments.

Figure (c) shows the $x$ dependence of the spin Stoner factor $\alpha_s$. The relation $\alpha_s = 1$ is satisfied at a spin order. It is apparent that the spin fluctuations are relatively unenhanced even in the heavily e-doped regime. This result is consistent with the NMR results. A similar result is also obtained by the random-phase approximation (RPA), for which the self-energy is ignored.

Figure (d) shows the $x$ dependence of the mass-enhancement factor $Z = m^*/m$ for $xz$ and $xy$ orbitals. $Z_{xz}$ is approximately 3–4, being larger than $Z_{xy}$: this is similar to the previous DFT+DMFT study. Next, we study the orbital fluctuations considering both the Aslamazov-Larkin (AL) VC, $X_{AL}$, and self-energy $\Sigma_{\text{AR}}$. Here, the Maki-Thompson (MT) term is dropped for simplicity, because it is less important than the other terms. The diagrammatic expressions for $X_{AL}$ are shown in Fig. (a). Following the “SC-VC with $\Sigma^*$” method developed in Ref. [28], the $X_{AL}$ in Fig. 3(a) is composed of $\chi^s_{\alpha''}$ given by the FLEX approximation and three-point vertex $\hat{G}^0(q, p) \equiv \sum_k \hat{G}^0(k + q)\hat{G}^0(k)\hat{G}^0(k - p)$ given by the bare Green’s functions. The orbital susceptibilities obtained via this method are qualitatively similar to the results of the “DW equation with self-energy” method developed in Ref. [48], which satisfies the criteria of the conserving approximation; therefore, they are reliable. Note that, in Appendix B, we present application of the DW equation with self-energy to the $d$-$p$ Hubbard model for LaFeAsO. The obtained
doping, and following the theoretical procedure reported in Refs. \[37\]. The linearized gap equation is given by:

$$\lambda Z_\alpha(k, \epsilon_n) \Delta_\alpha(k, \epsilon_n) = -\frac{\pi T}{(2\pi)^2} \sum_{\beta} \int \frac{dp}{v_\beta(p)} V^{SC}_{\alpha,\beta}(k, \epsilon_n; p, \epsilon_m) \frac{\Delta_{\beta}(p, \epsilon_n)}{|\epsilon_m|}$$

where $\lambda$ is the eigenvalue, which is roughly proportional to $T_c$, and the relation $\lambda = 1$ is satisfied at $T = T_c$. Further, $\Delta_\alpha(k)$ is the gap function, $v_\beta(p) = \frac{\partial \epsilon_\beta(p)}{\partial k}$ is the Fermi velocity, and $Z_\alpha(k)$ is the mass-enhancement factor on FS $\alpha$.

Here, we consider the many-body effects beyond the Migdal-Eliashberg (ME) approximation. In that approximation, the pairing interaction is given by $\tilde{V}^{SC}_{ME} = \frac{\Delta}{2} V^s - \frac{i}{2} V^c$. However, we have found two important effects beyond ME: $U$-$VC$ and $V^{cross}$, where $U$-$VC$ represents the VCs for the electron-boson coupling \[37,53,55\] and $V^{cross}$ is the AL-type crossing-fluctuation-exchange term.\[55\] The diagrammatic expression of $U$-VC is shown in Fig. 4(a). With $U$-$VC$, $\tilde{V}^\nu$ in $\tilde{V}^{SC}_{ME}$ is replaced with $\hat{\Lambda}^{U$-$VC,\nu}$, where $\nu = s, c$. In strongly correlated electron systems, we found that the relations $|\hat{\Lambda}^{U$-$VC,\nu}| \gg 1$ is realized in various models. Such a large charge-channel $U$-VC originates from the spin susceptibilities in AL-VCs shown in Fig. 4(a). In contrast to that, the opposite relation $|\hat{\Lambda}^{U$-$VC,\nu}| \ll 1$ is hold. Therefore, $U$-$VC$ enlarges orbital-fluctuation-mediated attractive interactions and suppresses spin-fluctuation-mediated repulsive interactions \[37,53,55\]. In addition, we consider $V^{cross}$ for the pairing interaction according to Ref. \[37\]. This double-boson exchange process gives the attractive intra- FS and repulsive intra- FS interactions in the e-doped FeSe model, as revealed in Ref. \[37\].

Figure 2(b) shows the doping dependence of $\lambda$. The fully gapped $s_{++}$-wave state has the largest eigenvalue
Throughout the entire doping region, the obtained $\lambda$ for the $s_{++}$-wave state is enhanced due to the synergy between $U$-VC and $V_{\text{cross}}$. The obtained fully gapped phase for a wide doping range. Therefore, the orbital-fluctuation-mediated $s_{++}$-wave state appears for $0.05 < x < 0.2$, consistent with experiments. The negative feedback due to the self-energy is crucial for explaining the appropriate $e$-doping phase diagram. In contrast, the obtained $d$-wave $T_c$ is small. The orbital fluctuations will be the main pairing glue in both $e$-doped FeSe and H-doped 1111 systems.

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Appendix A: VCA tight-binding model

In this appendix, we explain how we constructed the VCA tight-binding. First, we perform the bands calculation of $\text{Li}_{1-x}\text{Fe}_x\text{OHFeSe}$ using WIEN2k. Here, we employ the crystal structure of $\text{Li}_{0.8}\text{Fe}_{0.2}\text{OHFeSe}$ and the doping effect is incorporated using the VCA with $\Sigma$ method developed in Ref. [38]. At $x = 0$, the ferro-orbital order without magnetism in FeSe is reproduced. With increasing $x$, the orbital order quickly disappears, and the spin fluctuations remain weak for $0 < x < 0.2$. Interestingly, small spin fluctuations cause large orbital fluctuations due to the $\text{AL-VC}$ $X_{\text{AL}}$ for a wide doping range. In either case, SOI works as a repulsive effect for $d$-wave state. Finally, we focus on the similarities between $e$-doped FeSe and heavily $e$-doped ReFeAsO, both of which exhibit high-$T_c$ phases but their spin fluctuations are rather weak. These high-$T_c$ compounds have very similar FSs: large e-FSs and tiny or absent h-FSs. (The FSs in heavily $e$-doped ReFeAsO are shown in Fig. 1(c) in Ref. [38]). As discussed in Ref. [38], the $xy$-orbital DOS is dominant, and weak spin fluctuations on $xy$-orbital efficiently induce strong orbital fluctuation on $xy$-orbital, $\chi_{xyy'}$, thanks to the AL-VCs. The present analysis indicates that similar pairing mechanism is realized in these compounds.

In summary, we discussed the pairing mechanism in the $e$ and $d$-e-doped bulk compound $\text{Li}_{1-x}\text{Fe}_x\text{OHFeSe}$. We constructed a first-principles model using the VCA and analyzed the electronic states using the SC-VC with $\Sigma$ method developed in Ref. [38]. At $x = 0$, the ferro-orbital order without magnetism in FeSe is reproduced. With increasing $x$, the orbital order quickly disappears, and the spin fluctuations remain weak for $0 < x < 0.2$. Interestingly, small spin fluctuations cause large orbital fluctuations due to the $\text{AL-VC}$ $X_{\text{AL}}$ for a wide doping range. In contrast, the obtained $d$-wave $T_c$ is small. The orbital fluctuations will be the main pairing glue in both $e$-doped FeSe and H-doped 1111 systems.

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0, 0, 0, +0.3] in unit eV, by introducing the additional inter-orbital hopping integrals for \( l = xz, yz, \) and \( xy \). In addition, we enlarge the hopping parameters between \( d_{xy} \) and \( p_z \) by 1.25 times to maintain the absence of an e-FS at the \( \Gamma \) point.

### Appendix B: DW equation in conserving approximation

Here, we discuss the charge (orbital) order based on the \( \mathbf{q} = \mathbf{0} \) DW equation\(^{57,58}\), where the form factor \( \tilde{f}(k) \) is taken into account. In order to satisfy the conserving rules\(^{49}\), we introduce the self-energy by using the FLEX approximation\(^{44}\). The FLEX self-energy \( \Sigma \) is given by \( \Sigma = \sum_q \tilde{V}^\Sigma(q)G(k-q) \), where \( G(k) = (\epsilon_n - \mu)\mathbf{1} - \tilde{h}^0(k) - \tilde{\Sigma}(k) \)^{-1} is the Green’s function with the self-energy, and \( \tilde{V}^\Sigma \) is the interaction matrix for the self-energy. \( \Sigma \) is as follows

\[
\tilde{V}^\Sigma = \frac{3}{2} \tilde{\Gamma}_s \tilde{\chi}^s(q)\tilde{\Gamma}_s + \frac{1}{2} \tilde{\Gamma}_c \tilde{\chi}^c(q)\tilde{\Gamma}_c - \frac{1}{4} \left[ \tilde{\Gamma}_c \tilde{\chi}^c(0)\tilde{\Gamma}_c + \tilde{\Gamma}_s \tilde{\chi}^0(0)\tilde{\Gamma}_s + (\tilde{\Gamma}_s + \tilde{\Gamma}_c)\tilde{\chi}^0(q)(\tilde{\Gamma}_s + \tilde{\Gamma}_c) \right].
\]

We solve \( \tilde{\Sigma}, \tilde{G}, \) and \( \tilde{\chi}^s, \tilde{\chi}^c \) self-consistently. By introducing these obtained functions, we solve the following DW equation in the framework of the conserving approximation (CA).

The DW equation is given as

\[
\lambda^{DW} f_{l,l'}(k) = \frac{T}{N} \sum_{k',m,m'} K_{l,l';m,m'}(k,k')f_{m,m'}(k')(B2)
\]

where \( K \) denotes the kernel function. \( l, m \) are orbital indices and we denote the 3d orbitals \( d_{xz} \rightarrow -d_{xz}, \) \( d_{yz}, \) \( d_{xy} \), \( d_{x'y'} = -d_{y'x'} \), \( p_x, p_y, p_z \) of Se as 7, 8, 9. The kernel function \( K(k,k') \) is given by

\[
K_{l,l';m,m'}(k,k') = \sum_{m_1,m_2} I_{l,l';m_1,m_2}(k,k')g_{m_1,m_2,m,m'}(k'),
\]

where \( g_{l,l';m,m'}(k) \equiv G_{l,m}(k + q)G_{m',l'}(k) \). \( \tilde{I}^q(k,k') \) is a four-point vertex given as

\[
\tilde{I}^q_{l,l';m,m'}(k,k') = \sum_{b=s,c} \left[ \tilde{a}_b \right] \tilde{V}^b_{l,m,l',m'}(k-k') - \frac{T}{N} \sum_{p,l_1,l_2,m_1,m_2} \left[ \tilde{a}_b \right] \tilde{V}^b_{l_1,l_2,m_1,m_2}(p+q) \tilde{V}^b_{m_2,m_1,l',m_1}(p)
\]

\[
\times G_{l_1,m_1}(k+p)G_{l_2,m_2}(k'+p)
\]

\[
\times G_{l_1,m_1}(k-p)G_{l_2,m_2}(k'-p),
\]

\[
\tilde{G}(k) = (\epsilon_n - \mu)\mathbf{1} - \tilde{h}^0(k) - \tilde{\Sigma}(k) \]

\[
\lambda^{DW} f_{l,l'}(k) = \frac{T}{N} \sum_{k',m,m'} K_{l,l';m,m'}(k,k')f_{m,m'}(k')(B2)
\]

We employ the \( d-p \) LaFeAsO model derived via the first-principles calculations\(^{38}\). Figure[5] shows the T dependence of \( \lambda^{DW} \) in the CA. We note that \( \lambda^{DW} \) reaches 1 at \( T = 10 \text{meV} \), indicating that the ferro-orbital transition is realized in the realistic CA. In Fig.[5](b), we show the T dependence of \( 1/(1 - \alpha_s(\pi,0)) \) for \( \mathbf{q} = (\pi,0) \). The strength of the spin fluctuations \( 1/(1 - \alpha_s(\pi,0)) \) follows the Curie-Weiss law. Figures[5](c), (d), and (e) are the obtained \( B_{1g} \) form factors \( f_{33}(k), f_{44}(k), \) and \( \text{Im} f_{34}(k) \), respectively. \( f_{33}(k_x, k_y) = -f_{22}(-k_x, k_x) \) corresponds to the orbital order \( n_{xz} \neq n_{yz} \). The orbital order originates from the large spin susceptibilities \( \chi_{yz} \) for orbital 3 in Fig.[5](f): these are induced by the good nesting between the h-FSs around the \( \Gamma \) point and the e-FSs around the X point. On the other hand, \( f_{44}(k) \propto \cos k_x - \cos k_y \) corresponds to the \( B_{1g} \) bond order, where the nearest-neighbor correlation hoppings are modulated.
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