How correlated is the FeSe/SrTiO$_3$ system?

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Using a combination of density functional theory and dynamical mean field theory (DFT+DMFT), we investigate the effects of electron correlations and local fluctuating moments in paramagnetic FeSe monolayer on SrTiO$_3$ (STO) substrate in comparison with bulk FeSe. We find that going from the bulk phase to monolayer phases the overall electron correlations on Fe-3d orbitals decrease and the coherent energy scale increases with and without STO substrate. The coherent scales of Fe-3d electrons are strongly orbital selective. In bulk phase $d_{xz}$ is the most kinetically frustrated orbital, but in monolayer phase it gains substantial spectral weight and other Fe-3d orbitals remain strongly correlated. From the bulk phase to the monolayer phase the loss in Hund’s rule coupling and the corresponding increment of spectral weight come from increased hybridization due to increased Se-Fe-Se bond angle and shorter pnictogen height. In addition to Hund’s J, Hubbard U also plays an important role in FeSe/STO system. We also find oxygen vacancy can dope electrons from STO to FeSe to suppress the hole pocket at the zone center.

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In addition to the cuprates, the discovery of superconductivity in Fe-based compounds with superconducting critical temperature ($T_c$) in the range from 26 to 56 K has created a new class of unconventional superconductors [1-3]. Recent observations of $T_c$ reaching as high as 100K in FeSe monolayer grown on SrTiO$_3$ (STO) have further boosted interest to search for high $T_c$ superconductors in this family[4-10]. However there is still no predictive theory for superconductivity in these systems and hence they can be called as unconventional superconductors. Photoelectron spectroscopy measurements showed that, unlike other Fe-based superconductors, the Fermi surface of single-layer (one unit-cell) FeSe on STO consists only of electron pockets at the zone corners (X-point), without the hole pockets around the zone center (Γ-point) [11,13]. This leads to a different mechanism of gap opening other than the sign changing s-wave pairing state from spin fluctuation found in Fe-based superconductors in its bulk phase [14].

The effect of electron correlations on the topology of the Fermi surface and the renormalization of bands varies a lot across the pnictide family. While for some pnictide compounds, electron correlations has a profound effect on the topology of the Fermi surface, some compounds are not that sensitive to it [15,16]. Fermi surface obtained using density functional theory on FeSe grown on a regular 1×1 STO shows both hole pockets at Γ-point and electron pockets at X-point [17,18]. Comparing this with the ARPES measurement, electron doping was suggested a possible way to suppress the hole pocket at Γ-point [12,19,20]. Recent studies reveals that oxygen vacancies are one of the promising sources of electron doping in FeSe/STO system [19,21].

Understanding the strength of electron correlations and the role of Fermi surfaces are fundamental tasks to understand unconventional superconductors [22-24]. The strong orbital-selective behavior in the bulk Fe-superconductor family, is a signature of its strong electron correlations which can arise either due to on-site Hubbard-U interaction [10,25,26] or due to strong Hund’s coupling [15,27,28]. FeSe/STO system was suggested to be in close proximity to a Mott-insulating phase where a strong orbital-selective renormalization was found and similar to the cuprates, the correlations strength was found to be controlled by the Hubbard-U interaction [10,13]. On the other hand, local fluctuating moment due to Hund’s coupling was found to have a significant effect on the electron correlations in the bulk phase and for that reason Fe-superconductors are often labeled as Hund’s metal [15,27,29].

Using the DFT+DMFT method [30,31] we study four phases of FeSe and STO : (I) FeSe bulk, (II) free standing FeSe monolayer, (III) FeSe on SrTiO$_3$ substrate without oxygen vacancy (FeSe/STO) and (IV) FeSe on SrTiO$_3$ substrate with 50% oxygen vacancy (FeSe/STO-Ovac).

Here we attempt to unlock the origin of electron correlation effect in FeSe/STO systems and try to address the following questions: 1) How does the electron correlations change from the bulk phase to the monolayer phase? 2) What is the origin of electron correlations? Hubbard-U or Hund’s coupling-J or both? 3) Can electron correlations change the topology of the Fermi surface in the systems? 4) What is the role of oxygen vacancy in STO beyond electron doping to FeSe? 5) What are the effects of the fluctuating local moments?

The structures and the atom positions for the monolayer phase are obtained from DFT calculations. More details of our methods and structural information are described in S.I [32]. Computed bond angle of Se-Fe-Se in FeSe/STO is close to the experimental bond angle.
of 111.9°\[33\]. The penitide height and/or bond angle between X-Fe-X (X=pnictide) plays an important role in determining the strength of the correlations \[34, 35\] in the Iron-pnictide family\[15\].

From bulk to monolayer phase the Fe-Se bond length is decreased by 3.4%. Importantly the Fe-Se height or pnictogen height is decreased significantly the Fe-Se bond length equals to the scattering rate \(-\Gamma\). Every \(\text{Im}\Sigma(\omega_n)\) of four different structures locate at zero points \((\text{I})\) FeSe bulk, \((\text{II})\) FeSe monolayer, \((\text{III})\) FeSe/STO, and \((\text{IV})\) FeSe/STO-Ovac are shown.

After DFT optimization of the structures, we use the DFT+DMFT method to investigate the correlated electronic structure. In Fermi liquid theory, the inverse quasiparticle life equals to the scattering rate \(\Gamma=-Z\text{Im}\Sigma(\omega^+)|_{\omega=0^+}\), where \(Z\) is the spectral weight and \(\text{Im}\Sigma(\omega^+)|_{\omega=0^+}\) is the imaginary part of self-energy at zero frequency. At low temperature when \(\text{Im}\Sigma(\omega^+)|_{\omega=0^+}\to 0\), system is in the coherent phase with infinite quasiparticle lifetime. When temperature is above the coherent energy scale, \(\text{Im}\Sigma(\omega^+)\) and consequently the quasiparticle lifetime are both finite. Our DFT+DMFT calculations show the coherent scales of Fe-3d electrons are strongly orbital selective and also tuned by the structure of FeSe/STO systems. In Fig. 1(a-e), the imaginary part of quasiparticle self-energy \(\text{Im}\Sigma(\omega_n)\) of Fe-3d electrons at temperature 300 K are extrapolated to \(\omega^+\). Every \(\text{Im}\Sigma(\omega^+)\) of bulk FeSe (black dots and lines) is finite (Fig. 1(a-e)), which indicates the system is incoherent and the coherent scales of bulk FeSe are below 300 K. In contrast, although \(\text{Im}\Sigma(\omega^+)\) of FeSe monolayer are still finite, their absolute values are much closer to zero indicating enhanced coherent scales. \(\text{Im}\Sigma(\omega^+)\) of FeSe/STO approaches zero proving the system is in the coherent phase. \(\text{Im}\Sigma(\omega^+)\) of FeSe/STO-Ovac is also finite like that of FeSe monolayer but much closer to zero than that of FeSe bulk. The behavior of \(\text{Im}\Sigma(\omega^+)\) of these four systems indicates monolayer structure of FeSe and its growth on SrTiO\(_3\) substrate greatly enhance their corresponding coherent energy scales. We also computed the temperature dependence of \(\text{Im}\Sigma(\omega^+)\) of FeSe/STO-Ovac (Fig.1 in SI \[32\]) for four different temperatures. At 120 K, all \(\text{Im}\Sigma(\omega^+)\) locate at zero points proving FeSe/STO-Ovac is in the coherent states. As temperatures increase from 120 K to 1000 K, \(\text{Im}\Sigma(\omega^+)\) tremendously move away from zero to finite values, which signifies a temperature driven coherence-incoherence crossover in FeSe/STO-Ovac. At 120 K and 300 K, the splines of self-energy of FeSe/STO-Ovac almost overlap implying the coherent scales (or coherent temperatures) of FeSe/STO-Ovac are barely below 300 K.

The structural tuned coherent scales are directly related to the electron correlations. To examine degree of electron correlations in more detail, we compute orbital dependent spectral weight \(Z\) (inverse of mass-enhancement \(m^*/m_{\text{band}}\)) after analytic continuation of the self-energy by MaxEnt\[37\]. \(Z\) is unity in a non-correlated system, and goes to zero in the strongly correlated limit. We compute \(Z\) for all the Fe-3d orbitals of four different structures. First, bulk FeSe is the most correlated, then the correlations are suppressed in FeSe

![FIG. 1. (Color online) Structural dependent imaginary part of self-energy \(\text{Im}\Sigma(\omega_n)\) of Fe-3d orbitals (a) \(d_{\mathbf{z}^2}\), (b) \(d_{\mathbf{z}^2-\mathbf{y}^2}\), (c) \(d_{\mathbf{z}x}\), (d) \(d_{\mathbf{y}z}\), (e) \(d_{\mathbf{xy}}\) and spectral weight (f) \(Z\) at 300 K. In subfigure (a-e), the solid symbols are \(\text{Im}\Sigma(\omega_n)\) data from continuous time quantum Monte Carlo (CTQMC), and the solids lines are cubic spline of \(\text{Im}\Sigma(\omega_n)\) to \(\omega^+\). In subfigure (f), the spectral weight on different Fe-3d orbitals (left) and Se-Fe-Se angle (right) show a similar trend across four structures: (I) FeSe bulk, (II) FeSe monolayer, (III) FeSe/STO, and (IV) FeSe/STO-Ovac are shown.

- $\omega_n$ (eV)
- \(\text{Im}\Sigma (\omega_n)\)
- FeSe bulk
- FeSe monolayer
- FeSe/STO
- FeSe/STO-Ovac
- (a)  $d_{\mathbf{z}^2}$
- (b)  $d_{\mathbf{z}^2-\mathbf{y}^2}$
- (c)  $d_{\mathbf{z}x}$
- (d)  $d_{\mathbf{y}z}$
- (e)  $d_{\mathbf{xy}}$
- (f)  $Z$
- Angle (Deg)
monolayer; FeSe/STO is the most weakly correlated, and in FeSe/STO-Ovac the correlation effect is almost the same as in FeSe monolayer (Fig 1(f)). Interestingly, the Se-Fe-Se angle follows the same trend as $Z$ (Fig. 1f). Hybridization among the Fe-3d orbitals and other orbitals is enhanced from the bulk to the monolayer phase [Fig.2 in the SI [32]]. Hence it shows that the quenched correlations in the monolayer phase is directly related to the increase in the hybridization that comes due to shorter Fe-Se height/bond length and increased Se-Fe-Se angle in the monolayer phase. Suppressed electron correlations could enhance the superconducting temperature, as may be seen in the heavy fermion systems and in 122 iron pnictides with pressure[16, 38, 39]. We found that the structural tuning effect in $Z$ is strongly orbital dependent. In FeSe bulk $d_{xy}$ is the most correlated orbital, but in FeSe monolayer, FeSe/STO, and FeSe/STO-Ovac it becomes the most weakly correlated one. The $d_{xy}$ orbital spectral weight in FeSe bulk is about 0.5 of that in FeSe/STO, and about 0.56 that of FeSe monolayer and FeSe/STO-Ovac.

Now, we describe the electron correlation effect on the spectral function in Fig. 2(a-h). On the top panel of Fig. 2 (a-d) we show DFT+DMFT computed spectral function on same color scale together with the band structures computed within DFT (blue lines). A significant change in the sharpness of the DFT+DMFT spectral function is noticed while going from the bulk phase to the monolayer phase of FeSe. This directly shows that going from bulk to monolayer phases, the DMFT spectral function becomes more coherent – indicating the suppression of correlations in the monolayer phase. We find significant changes in the topology of the Fermi surface in the monolayer phase, similarly predicted by DFT calculations. Especially the hole pocket at $\Gamma$ point shrinks and almost vanished when O-vacancy is introduced while electron pockets are found to get bigger. This leads to electron doping mechanism similarly found in DFT calculations[19, 21].

To identify the orbital dependent nature of electron correlation effect, we compute DFT+DMFT orbital-dependent spectral functions for four systems and plot them together on the bottom panel in Fig 2(e-h), where $d_{xy}$ and $d_{x^2-y^2}$ are in blue, $d_{xz}$ and $d_{yz}$ are in green, $d_{xy}$ is red. Orbital character for electron and hole pockets are found to change when going from bulk to the monolayer phase. In the bulk, the electron pockets at $M$ are mainly due to $d_{xy}$ (red), $d_{x^2-y^2}$ orbitals (green). In the monolayer phase (FeSe-monolayer, FeSe/STO, FeSe/STO-Ovac), the electron pockets are made of $d_{x^2-y^2}$ (blue) and $d_{xz+yz}$ orbitals (green). The contribution from $d_{xy}$ orbital on the Fermi surface is found to decrease a lot in the monolayer phase of FeSe when compared to the bulk phase. Especially, for the hole pockets the contribution for $d_{xy}$ orbital decreases in the monolayer phase of FeSe (Fig. 3 in the SI [32] ). The color change from reddish to blueish indicates this trend in Fig 2(e-h). Overall, going from bulk phase to the monolayer phase, the topology of the hole pockets significantly changes while electron pockets get bigger in DFT+DMFT. With the introduction of O-vacancy in STO, the DMFT spectral function becomes more correlated for $d_{xz}$ and $d_{yz}$ orbitals.

Since the Fermi surface of FeSe/STO-Ovac is close to the ARPES, we examine the oxygen vacant STO/FeSe
In DMFT the correlated impurity states can be projected onto series of atomic basis, e.g. for iron atom with 5 correlated 3d orbitals the corresponding atomic basis spans a size $4^5=1024$ Hilbert space. Each atomic basis is indexed by quantum number including occupancy number $N \in \{0,1,...,10\}$ and total spin $S_z$ of all electrons. Hund’s rule coupling requires electron spins on different orbitals to align in the same direction to maximize the total spin, so the strength of Hund’s J is related to the distribution of probability histogram. The normalized probability histogram for bulk and FeSe/STO-Ovac are compared in Fig. 3. In a histogram the first and last few states of an interval of particular $N$ are the high spin states, whereas the middle of that interval are states with low spins. The probability sums up to unity.

| $T$(K) | $U$ (eV) | J(eV) | $d_{xz}$ | $d_{x^2-y^2}$ | $d_{yz}$ | $d_{xy}$ |
|-------|---------|-------|----------|---------------|----------|----------|
| 300   | 5.0     | 0.8   | 0.528    | 0.531        | 0.464    | 0.498    |
| 300   | 5.0     | 0.5   | 0.696    | 0.720        | 0.700    | 0.679    |
| 300   | 2.0     | 0.8   | 0.735    | 0.748        | 0.729    | 0.697    |
| 120   | 5.0     | 0.8   | 0.521    | 0.513        | 0.487    | 0.446    |
| 600   | 5.0     | 0.8   | 0.513    | 0.512        | 0.493    | 0.480    |
| 1000  | 5.0     | 0.8   | 0.489    | 0.491        | 0.484    | 0.478    |

TABLE I. Orbital dependent spectral weight for FeSe/STO-Ovac system at various $U$ and J and temperatures.

Next we discuss the effect of Hubbard $U$ and Hund’s $J$. Changing $J=0.8$ eV to $J=0.5$ eV at 300 K, we again notice that the correlations are suppressed, especially for the $xz$, $yz$, and $xy$ orbitals. For $U=5.0$ eV and $J=0.8$ eV, the temperature dependence is interesting. Except the $d_{xz}$ orbital, the spectral weight is found to increase till 300 K and then very slowly decreases with $T$ (Fig. 5 in SI [32]). This directly shows that a coherence to incoherence cross over happens below 300 K.

In DMFT the correlated impurity states can be projected onto series of atomic basis, e.g. for iron atom with 5 correlated 3d orbitals the corresponding atomic basis spans a size $4^5=1024$ Hilbert space. Each atomic basis is indexed by quantum number including occupancy number $N \in \{0,1,...,10\}$ and total spin $S_z$ of all electrons. Hund’s rule coupling requires electron spins on different orbitals to align in the same direction to maximize the total spin, so the strength of Hund’s $J$ is related to the distribution of probability histogram. The normalized probability histogram for bulk and FeSe/STO-Ovac are compared in Fig. 3. In a histogram the first and last few states of an interval of particular $N$ are the high spin states, whereas the middle of that interval are states with low spins. The probability sums up to unity.

While some studies claim superconductivity in FeSe/STO can be mediated by electron-phonon coupling [10,12], the strength of electron-phonon coupling in conventional DFT is found to be too low to explain the super high $T_c$ in FeSe/STO [11,13]. Electron correlations can enhance the electron-phonon coupling in FeSe [10,14]. Our results establish that FeSe/STO display universal...
orbital-selective electron correlations. Unlike in the bulk where $d_{xy}$ orbital was found to be most kinetically frustrated, we found the $d_{xy}$ gains spectral weight whereas $d_{yz}$ and $d_{xz}$ orbitals remain strongly correlated. Instead of orbital selective Mott transition found in the slave boson model, orbital selective coherence to incoherence transition could happen with different Fe orbitals having different crossover temperatures. The quenched correlations in the monolayer phase is directly related to the increased hybridization due to short Fe-Se distance in the monolayer phase. The bond length, Fe-Se distance or pnictogen height and Se-Fe-Se angle -all show a similar pattern as the spectral weight for different phases of FeSe. The loss in Hund’s rule coupling due to increased hybridization in the monolayer phase is found to be responsible for the increased spectral weight. In addition to Hund’s rule, we find Hubbard-U also plays an important role in the electron correlations in FeSe/STO-Ovac.

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[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
[2] I. I. Mazin, Nature 464, 183 (2010).
[3] X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature 453, 761 (2008).
[4] J.-F. Ge, Z.-L. Liu, C. Liu, C.-L. Gao, D. Qian, Q.-K. Xue, Y. Liu, and J.-J. Fai, Nat Mater 14, 285 (2015).
[5] W. Qing-Yan, L. Zhi, Z. Wen-Hao, Z. Zuo-Cheng, Z. Jin-Song, L. Wei, D. Hao, O. Yun-Bo, D. Peng, C. Kai, W. Jing, S. Can-Li, H. Ke, J. Jin-Feng, J. Shuai-Hua, W. Ya-Yu, W. Li-Li, C. Xi, M. Xu-Cun, and X. Qi-Kun, Chinese Physics Letters 29, 037402 (2012).
[6] Y. Lubsahesvsky, E. Lahoud, K. Chashka, D. Podolsky, and A. Kanigel, Nat Phys 8, 309 (2012).
[7] M. K. Wu, P. M. Wu, Y. C. Wen, M. J. Wang, P. H. Lin, W. C. Lee, T. K. Chen, and C. C. Chang, Journal of Physics D: Applied Physics 48, 323001 (2015).
[8] D. Huang, C.-L. Song, T. A. Webb, S. Fang, C.-Z. Chang, J. S. Moodera, E. Kaxiras, and J. E. Hoffman, Phys. Rev. Lett. 115, 017002 (2015).
[9] K. W. Kim, A. Pashkin, H. Schfer, M. Beyer, M. Porier, T. Wolf, C. Bernhard, J. Demsar, R. Huber, and A. Leitenstorfer, Nat. Mater. 11, 497 (2012).
[10] M. Yi, Z.-K. Liu, Y. Zhang, R. Yu, J. X. Zhu, J. J. Lee, R. G. Moore, F. T. Schmitt, W. Li, S. C. Riggs, J. H. Chu, B. Lv, J. Hu, M. Hashimoto, S. K. Mo, Z. Hussain, Z. Q. Mao, C. W. Chu, I. R. Fisher, Q. Si, Z. X. Shen, and D. H. Lu, Nat Commun 6 (2015).
[11] J. J. Lee, F. T. Schmitt, R. G. Moore, S. Johnston, Y. T. Cui, W. Li, M. Yi, Z. K. Liu, M. Hashimoto, Y. Zhang, D. H. Lu, T. P. Devereaux, D. H. Lee, and Z. X. Shen, Nature 515, 245 (2014).
[12] S. Tan, Y. Zhang, M. Xia, Z. Ye, F. Chen, X. Xie, R. Peng, D. Xu, Q. Fan, H. Xu, J. Jiang, T. Zhang, X. Lai, T. Xiang, J. Hu, B. Xie, and D. Feng, Nat Mater 12, 634 (2013).
[13] J. He, X. Liu, W. Zhang, L. Zhao, D. Liu, S. He, D. Mou, F. Li, C. Tang, Z. Li, L. Wang, Y. Peng, Y. Liu, C. Chen, L. Yu, G. Liu, X. Dong, J. Zhang, C. Chen, Z. Xu, X. Chen, X. Ma, Q. Xue, and X. J. Zhou, PNAS. 111, 18501 (2014).
[14] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
[15] Z. P. Yin, K. Haule, and G. Kotliar, Nat. Mater. 10, 932 (2011).
[16] J. Diehl, S. Backes, D. Guterding, H. O. Jeschke, and R. Valentí, Phys. Rev. B 90, 085110 (2014).
[17] H.-Y. Cao, S. Tan, H. Xiang, D. L. Feng, and X.-G. Gong, Phys. Rev. B 89, 014501 (2014).
[18] D. Cheng, B. T. Hu, R. Y. Chen, G. Xu, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. B 86, 134503 (2012).
[19] K. V. Shanavas and D. J. Singh, Phys. Rev. B 92, 035144 (2015).
[20] J. Bang, Z. Li, Y. Y. Sun, A. Samanta, Y. Y. Zhang, W. Zhang, L. Wang, X. Chen, X. Ma, Q.-K. Xue, and S. B. Zhang, Phys. Rev. B 87, 220504 (2013).
[21] K. Zou, S. Mandal, S. D. Albright, R. Peng, Y. Pu, D. Kumah, C. Lau, G. H. Simon, O. E. Dagdeviren, X. He, I. Božović, U. D. Schwarz, E. I. Altman, D. Feng, F. J. Walker, S. Ismail-Beigi, and C. H. Ahn, Phys. Rev. B 93, 180506 (2016).
[22] A. Damascelli, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. 75, 473 (2003).
[23] M. R. Norman, H. Ding, J. C. Campuzano, T. Takeuchi, M. Randeria, T. Yokoya, T. Takahashi, T. Morishita, and K. Kaduwad, Phys. Rev. Lett. 79, 5506 (1997).
[24] P. D. Johnson, T. Valla, A. V. Fedorov, Z. Yusof, B. O. Wells, Q. Li, A. R. Moodenbaugh, G. D. Gu, N. Koshizuka, C. Kendziora, S. Jian, and D. G. Hinks, Phys. Rev. Lett. 87, 177007 (2001).
[25] M. Yi, D. H. Lu, R. Yu, S. C. Riggs, J.-H. Chu, B. Lv, Z. K. Liu, M. Liu, Y.-T. Cui, M. Hashimoto, S.-K. Mo, Z. Hussain, C. W. Chu, I. R. Fisher, Q. Si, and Z.-X. Shen, Phys. Rev. Lett. 110, 067003 (2013).
[26] L. de’ Medici, G. Giovannetti, and M. Capone, Phys. Rev. Lett. 112, 177001 (2014).
[27] P. Hardy, A. E. Böhmer, D. Aoki, P. Burger, T. Wolf, P. Schweiss, R. Heid, P. Adelmann, Y. X. Yao, G. Kotliar, J. Schmalian, and C. Meingast, Phys. Rev. Lett. 111, 027002 (2013).
[28] Z. P. Yin, K. Haule, and G. Kotliar, Phys. Rev. B 86, 195141 (2012).
[29] S. Backes, H. O. Jeschke, and R. Valentí, Phys. Rev. B 92, 195128 (2015).
[30] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti, Rev. Mod. Phys. 78, 865 (2006).
[31] K. Haule, C.-H. Yee, and K. Kim, Phys. Rev. B 81, 195107 (2010).
charge density, impurity level, chemical potential, self-energy, lattice and impurity Green’s functions. The lattice is implemented fully self-consistent and all-electron \[15, 31\]. The computations are converged with respect to (DFT+DMFT) \[30, 31\] to capture the local moments physics in paramagnetic FeSe since this method can successfully describe fluctuating local moments and electron correlation \[49, 50\]. In the DFT+DMFT method, the self-energy, enhancement in bonding with smaller Se-Ti distance is also found in a recent study \[19\].

Compared to the O-vacancy, Se-Fe-Se plane is parallel to the z-axis. There are two kinds of Se-Fe-Se angles. In Table I we show the one that the Se-Ti distance and the Se-Fe-Se angle are found to be 3.11° when 50% O-vacancy is introduced on STO. The enhancement in bonding is found to increase from 0.073 to 0.60 eV per Ti-Se site. However the Se-Fe-Se angle remains almost unchanged with the introduction of Se-Fe-Se plane is parallel to the z-axis.

Structural details and Methods. To investigate the effect of the interface on the electronic structure of FeSe, we construct FeSe slab with and without STO substrate. While we include STO, we consider pure undoped STO as well as STO with oxygen vacancy. The in-plane lattice parameter of STO is fixed to the experimental value of 3.905 Å. In addition, a pristine isolated FeSe monolayer chopped from the FeSe/STO optimized structure is constructed to study free standing FeSe monolayer. This way the in-plane lattice remains constant to the STO since an epitaxial growth was found in the experiment \[21\].

The structures and the atom positions are obtained from DFT calculations performed within the generalized gradient approximation of Perdew-Burke-Ernzerhof \[47\] for exchange and correlation using the plane wave pseudopotential \[48\]. The plane wave kinetic approximation of Perdew-Burke-Ernzerhof \[47\] for exchange and correlation using the plane wave pseudopotential was found in the experiment \[4, 21\].

A uniform 6×6×6 mesh of k points per 1 interfacial unit cell. Structural optimizations of the structures considered in STO towards electron doping in FeSe \[21\]. For the bulk FeSe we use the experimental lattice constant and atom (Se) positions. The important structural parameters for all the systems are described in the Table I. There are two kinds of Se-Fe-Se angles. In Table I we show the one that the Se-Fe-Se plane is parallel to the z-axis.

The Se-Ti distance and the Se-Fe-Se angle are found to be 3.11 Å and 115.1° for FeSe/STO structure. Se-Ti distance decreases to 2.82 Å when 50% O-vacancy is introduced on STO. The enhancement in bonding is found to increase from 0.073 to 0.60 eV per Ti-Se site. However the Se-Fe-Se angle remains almost unchanged with the introduction of the O-vacancy. Computed bond angle in FeSe/STO is close to the experimental bond angle of 111.9° \[33\]. A similar enhancement in bonding with smaller Se-Ti distance is also found in a recent study \[19\].

Once the structures are obtained from DFT, we apply DFT in combination with dynamical mean field theory (DFT+DMFT) \[30, 31\] to capture the local moments physics in paramagnetic FeSe since this method can successfully describe fluctuating local moments and electron correlation \[49, 50\]. In the DFT+DMFT method, the self-energy, sampling all Feynman diagrams local to the Fe ion, is added to the DFT Kohn-Sham Hamiltonian \[30, 31\]. This implementation is fully self-consistent and all-electron \[15, 31\]. The computations are converged with respect to charge density, impurity level, chemical potential, self-energy, lattice and impurity Green’s functions. The lattice is

Supplemental Materials: How correlated is the FeSe/SrTiO\(_3\) system?
represented using the full potential linear augmented plane wave method, implemented in the Wien2k \[51\] package in its generalized gradient approximation (PBE-GGA). The continuous time quantum Monte Carlo method is used to solve the quantum impurity problem and to obtain the local self-energy due to the correlated Fe 3d orbitals. The self-energy is analytically continued from the imaginary to real axis using an auxiliary Green’s function. The Coulomb interaction $U$ and Hund’s coupling $J$ are fixed at 5.0 eV and 0.8 eV, respectively \[52\]. To study the effect of $U$ and $J$, $U=2$ eV and $J=0.5$ eV are also used. A fine k-point mesh of $10 \times 10 \times 10$ and total 80 million Monte Carlo steps for each iteration are used for the paramagnetic phase of the FeSe/STO at $T=300K$ and $T=120K$.

\textbf{Results.} In Fig 1 we show temperature dependent imaginary part of self-energy $\text{Im}\Sigma(i\omega_n)$ of 3d-electrons in FeSe/STO-Ovac for (a) $d_{z^2}$, (b) $d_{x^2-y^2}$, (c) $d_{xz}$, (d) $d_{yz}$, (e) $d_{xy}$ orbitals. In DMFT loop, the hybridization between the impurity and its mean-field bath is derived by $G_{0}^{-1}(i\omega) = i\omega + \mu + \Delta(i\omega)$, in which $\Delta(i\omega)$ is the hybridization function and $G_{0}^{-1}(i\omega)$ is the non-interacting Green’s function. The hybridization functions of Fe-3d orbitals in FeSe bulk and FeSe monolayer in both DFT level and DMFT level are shown in Fig. 2. These functions show that from the bulk phase to the monolayer phase the hybridization of Fe-3d electrons with other electrons in crystal is generally enhanced with/without self-energy corrections due to electron correlations. In Fig. 3 we present orbitally resolved band structures for FeSe/STO obtained with conventional DFT as implemented all-electron Wien2K (left) and DFT+DMFT methods(right). Our computed DFT+DMFT spectral function for FeSe/STO-Ovac with different $U$, $J$ and $T$ are shown in Fig. 4. For same system, corresponding temperature dependence spectral weight ($Z$) for different 3d orbitals are shown in Fig. 5. Finally in Fig. 6 we show computed probability histogram of atomic states in FeSe/STO (red line) and compared with that in FeSe/STO-Ovac (black line) at 300K.
| System              | Fe-Se height (Å) | Fe-Se bond length (Å) | Se-Fe-Se angle (°) |
|---------------------|------------------|-----------------------|--------------------|
| FeSe bulk           | 1.476            | 2.395                 | 104.014            |
| FeSe monolayer      | 1.241            | 2.313                 | 115.155            |
| FeSe/STO            | 1.238            | 2.312                 | 115.376            |
| FeSe/STO-Ovac       | 1.233            | 2.314                 | 115.070            |

**TABLE II. Structural parameter for four systems.**

**FIG. 4.** (Color online) Temperature dependent imaginary part of self-energy $\text{Im}\Sigma(i\omega_n)$ of 3d-electrons in FeSe/STO-Ovac for (a) $d_{z^2}$, (b) $d_{x^2-y^2}$, (c) $d_{xz}$, (d) $d_{yz}$, (e) $d_{xy}$ orbitals. The solid symbols are $\text{Im}\Sigma(i\omega_n)$ at Matsubara frequency and the solid lines are cubic spline of $\text{Im}\Sigma(i\omega_n)$ to $i0^+$. From 120 K to 1000 K, there are obvious coherence-incoherence crossovers in all 3d-orbitals.
FIG. 5. (Color online) The hybridization functions of Fe-3d electrons in FeSe bulk and FeSe monolayer in DFT level (left panels) and DMFT level (right panels). The DFT level hybridization functions are calculated by setting self-energy correction to zero, and the DMFT level hybridization functions are calculated using fully self-energy correction. These functions show the hybridization in the monolayer phase is generally enhanced relative to that in the bulk phase with/without including of electron correlation effects.
FIG. 6. (Color online) Orbitally resolved band structures for FeSe/STO obtained with conventional DFT as implemented all-electron Wien2K (left) and DFT+DMFT methods (right). Contribution of the orbitals are proportional to the size of the dots on left. On the right, high (low) DFT+DMFT orbital contributions on the spectral function are shown by the colors (black).
FIG. 7. (Color online). Left (a-d): Computed DFT+DMFT spectral function for FeSe/STO-Ovac with (a) $U=5.0, J=0.8$ eV, $T=300K$; (b) $U=5.0, J=0.5$ eV, $T=300K$; (c) $U=2.0, J=0.8$ eV, $T=300K$; (d) $U=5.0, J=0.8$ eV, $T=120K$. Corresponding spectral weights are tabulated in Table I in the main text.
FIG. 8. (Color online). Temperature dependence spectral weight ($Z$) for different 3d orbitals.

FIG. 9. (Color online). Probability histogram of atomic states in FeSe/STO (red line) is compared with that in FeSe/STO-Ovac (black line) at 300K; identical probability histogram shows no effect of increased Se-Ti binding energy with oxygen vacancy in FeSe/STO and indicates that the correlation from Hund’s coupling depends on Se-Fe-Se bond angle which is same for both systems.