Microscopic nature of correlations in multi-orbital $AFe_2As_2$ ($A=$K, Rb, Cs): Hund’s coupling versus Coulomb repulsion

Steffen Backes,[*] Harald O. Jeschke, and Roser Valentí
Institut für Theoretische Physik, Goethe-Universität Frankfurt,
Max-von-Laue-Str. 1, 60438 Frankfurt am Main, Germany
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We investigate via LDA+DMFT (local density approximation combined with dynamical mean field theory) the manifestation of correlation effects in a wide range of binding energies in the hole-doped family of Fe-pnictides $AFe_2As_2$ ($A=$ K, Rb, Cs) as well as the fictitious FrFe$_2As_2$ and $a$-axis stretched CsFe$_2As_2$. This choice of systems allows for a systematic analysis of the interplay of Hund’s coupling $J_H$ and on-site Coulomb repulsion $U$ in multi-orbital Fe-pnictides under negative pressure. With increasing ionic size of the alkali metal, we observe a non-trivial change in the iron 3$d$ hoppings, an increase of orbitally-selective correlations and the presence of incoherent weight at high-binding energies that do not show the typical lower Hubbard-band behavior but rather characteristic features of a Hund’s metal. This is especially prominent in $a$-stretched CsFe$_2As_2$. We also find that the coherent/incoherent electronic behavior of the systems is, apart from temperature, strongly dependent on $J_H$ and we provide estimates of the coherence scale $T^*$. We discuss these results in the framework of reported experimental observations.

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I. INTRODUCTION

The nature and degree of correlations in Fe-based superconductors has been a subject of intensive discussions since the discovery of the first high-$T_c$ iron pnictide superconductor in 2008.[1] A significant amount of work has concentrated on the description of experimentally observed effects of correlation like large effective masses or possible non-Fermi liquid behavior.[2] Due to the multi-orbital nature of Fe-based superconductors, the Hund’s coupling $J_H$ has been shown to play a key role in determining the behavior of these systems.[3,4,5] However, there is an ongoing debate regarding the role of $J_H$ versus the on-site Coulomb repulsion $U$ and the interpretation of the correlated nature of Fe-pnictides and Fe-chalcogenides.[6,7,8,9] An important feature observed in many of these studies is that, depending on the electronic filling, the Hund’s coupling $J_H$ on the one hand renders a moderately correlated system even more correlated and pushes it into a bad metal regime, while on the other hand it can also reestablish a metallic behavior, albeit orbital selective, in a strongly correlated system.[10,11] The main question for the Fe-based superconductors narrows down to which regime of parameters do they belong to and how do correlations manifest in a wide range of binding energies as a function of doping and/or pressure?

Of special interest are the hole-doped $AFe_2As_2$ ($A=$ K, Rb, Cs) end members of the 122 iron pnictide series. Compared to the parent compound BaFe$_2As_2$, the substitution of Ba by K accounts for a doping of one hole per formula unit and it is accompanied by a complete suppression of any structural or magnetic phase transition[12,13] and by the appearance of superconductivity at low temperatures. This behavior is common[14,15] to all hole-doped end members $AFe_2As_2$ and they all seem to have a nodal gap structure[16,17], which is different to the nodeless gap structure found in the parent BaFe$_2As_2$ system.[18] Further, experimentally Ba$_{1-x}$K$_x$Fe$_2As_2$ is thought to undergo a coherence-incoherence transition[19,20] as a function of temperature, that has been interpreted in terms of a strong increase in correlation.[21,22] Measurements of the Sommerfeld coefficient suggest that the hole-doped end systems are among the strongest correlated 122 iron-pnictide superconductors[23,24,25], which is also corroborated by theoretical investigations on KFe$_2As_2$.[26,27,28,29] The measured Sommerfeld coefficient increases from BaFe$_2As_2$ to KFe$_2As_2$ by more than an order of magnitude[27,28,29] and increases further as K is substituted by Rb and Cs.[30,31] In view of these observations, the hole doped end members $AFe_2As_2$ provide an ideal background for investigating correlation effects as function of negative pressure.

In the present work we analyze via a combination of density functional theory (DFT) in the local density approximation (LDA) with dynamical mean field theory (LDA+DMFT) the electronic structure of the series $AFe_2As_2$ ($A=$ K, Rb, Cs) as well as the fictitious FrFe$_2As_2$ and $a$-axis stretched CsFe$_2As_2$ in an extended range of binding energies. The combination of density functional theory with many body methods such as dynamical mean field theory has proven to be a very helpful tool to investigate electronic correlation effects[32,33] While a compression of the unit cell usually decreases correlation effects in the 122 iron pnictides[34,35] similarly, the opposite is to be expected when lattice parameters are expanded since the larger interatomic distances...
should reduce the hybridization of neighboring atomic orbitals and lead to stronger localization of the electronic states. We show in this study that these considerations are correct only at first sight; actually, the strong correlation effects in these systems are mostly governed by a subtle interplay of $J_H$ and $U$.

II. RESULTS AND DISCUSSION

We performed DFT(LDA) and LDA+DMFT calculations on experimental structures of KFe$_2$As$_2$, RbFe$_2$As$_2$ and CsFe$_2$As$_2$ in tetragonal symmetry. Additionally, we prepared a fictitious structure for FrFe$_2$As$_2$ with lattice parameters and As height obtained by extrapolating the experimental parameters for AFe$_2$As$_2$ (A = K, Rb, Cs) (see Appendix A). Furthermore, we considered an $a$-axis stretched CsFe$_2$As$_2$ structure by slightly expanding the lattice of CsFe$_2$As$_2$ in the $a$-$b$ plane to mimic an experimental biaxial stretching of the crystal. This may be achieved experimentally by epitaxial growth of CsFe$_2$As$_2$ on a substrate with slightly larger lattice parameter. The structural trends of this series are an expansion along $a$ and $c$ and a decrease of the As height. A detailed explanation of the structures and computational methods is given in Appendix A.

A. Momentum-resolved spectral function $A(k, \omega)$

In Fig. 1 we show the momentum-resolved spectral function for KFe$_2$As$_2$ and CsFe$_2$As$_2$ as obtained within LDA+DMFT (gray density plot) at a temperature $T = 145$ K and compare it to the DFT bandstructure (red). We estimate for both systems Fe 3$d$ effective masses $m^*/m_{\text{LDA}}$ between 2.2 and 4.1 (depending on the orbital) which lead to a renormalization of the DFT(LDA) band energies and overall reduction of bandwidth. The average effective mass increases slightly from 2.89 to 2.95, which indicates an increase in correlation along the AFe$_2$As$_2$ series due to enhanced localization of electrons on Fe. Already at the Fermi level we observe diffuse structures corresponding to incoherent quasiparticle excitations with finite lifetimes. At energies below $-0.5$ eV all coherent features are basically washed out due to correlation. This effect is present in all systems Fe 3$d$ contribution at $E_F$ along the series. At energies below $-2$ eV coherent features become visible again, which correspond to the As $p$ states that partially hybridize with Fe 3$d$ states. Even though the self-energy in DMFT has no momentum dependence, an effective momentum dependence is present in the results due to the momentum dependent orbital character of the original DFT bands. This leads to $k$-dependent broadening effects in LDA+DMFT.

B. Density of states at the Fermi level and orbital-resolved electronic filling

We first analyze the manifestation of correlation effects near the Fermi level. For that we compare in Fig. 2 LDA+DMFT (Fig. 2(a)) with DFT(LDA) (Fig. 2(b)) orbital-resolved density of states at the Fermi level $N(E_F)$ for all studied systems. The LDA+DMFT calculations show an increasing and pronounced dominance of 3$d_{z^2}$ contribution at $E_F$ along the series. This is in contrast to the DFT results where the Fe 3$d_{z^2}$ contribution also increases, but is much lower and only significant for $a$-axis stretched CsFe$_2$As$_2$ with shortest As height. The nonmonotonous behaviour of the Fe 3$d_{xz/yz}$ contribution in DFT is a result of the special electronic structure of these systems at the M point. This feature is greatly suppressed by broadening effects in the LDA+DMFT calculation.
FIG. 2: (Color online) The density of states of the Fe 3d orbitals at the Fermi level as obtained from (a) LDA+DMFT and as comparison with (b) DFT. The electronic correlations induce a marked deviation from the DFT results: The contribution of the Fe 3d_{z^2} orbital is strongly enhanced, while a more pronounced decrease of the Fe 3d_{xy} orbital is found towards the end system of stretched CsFe₂As₂. Also, the trend in the Fe 3d_{xz/yz} orbital in DFT is completely evened out in LDA+DMFT.

Linked to these results is the behavior of the LDA+DMFT orbitally-resolved electronic filling (see Fig. 3). We observe that inclusion of correlation effects not only reduces the overall Fe 3d filling due to the additional cost of the Coulomb interaction energy for doubly occupying a certain orbital, but also introduces orbital-dependent effects (see section II D). While the Fe 3d_{z^2} and 3d_{x^2-y^2} filling decreases along the series, it increases for 3d_{xz/yz} and 3d_{xy}.

C. Spectral function \( A(\omega) \)

In order to understand the origin of the changes in \( N(E_F) \) and orbital filling, we show in Fig. 4 the local density of states (spectral function \( A(\omega) \)) for Fe 3d_{z^2} and Fe 3d_{xy} in the energy range \([-2, 2]\) eV for the representatives KFe₂As₂, CsFe₂As₂ and \( a \)-axis stretched CsFe₂As₂. We chose these two orbitals since they are the most affected along the series: 3d_{z^2} because of the decrease in As height from KFe₂As₂ to CsFe₂As₂ and 3d_{xy} because of the increase in the orbital localization with increasing \( a \) lattice parameter. Fe 3d_{z^2} shows a shift of orbital weight to negative energies (high binding energies) and a narrowing of the quasiparticle-like peak structure at \( E_F \) from KFe₂As₂ to CsFe₂As₂. Since the electronic filling of the iron 3d orbitals is larger than half-filling in these systems, the quasiparticle-like peak is located close to but below the Fermi level. In Fe 3d_{xy} due to the reduction of the filling from 0.66 in KFe₂As₂ to 0.63 in stretched CsFe₂As₂ (see Fig. 3) caused by an increase of electronic correlations, the quasiparticle peak-like structure is shifted even closer towards the Fermi level along the series, which in turn leads to the observed increase of the density of states at the Fermi level (Fig. 2(a)). Such a shift of the quasiparticle peak-like structure in KFe₂As₂ was already noted in Ref. 33. For the 3d_{xy} orbital, the quasiparticle peak is much closer to the Fermi level since the filling is closer to half filling at \( n_{xy} \approx 0.59 \). This orbital shows a strong suppression of the quasiparticle peak (up to \( \approx 30\% \)) from KFe₂As₂ to the \( a \)-axis stretched CsFe₂As₂ which points to an important increase of decoherence along the series. This increase of decoherence will be studied in more detail in the next section. Reduction of the maximum of the quasiparticle peak combined with a slight change of its position results in the almost constant density of states at the Fermi level for the 3d_{xy} orbital observed in Fig. 2(a).

Additionally, a shoulder-like feature appears in the spectral function at 1 eV and \(-1\) eV in CsFe₂As₂ closely resembling the typical spectral function shape of a quasiparticle peak and a lower and upper Hubbard band.
These features do not correspond to any property found in the non-interacting DOS and are purely an effect of correlations and, at first sight, are similar to the emergence of Hubbard bands as a function of $U$ in strongly correlated systems. This is also in agreement with the $3d_{xy}$ orbital being the strongest correlated one, whereas these features are far less developed in the $3d_{z^2}$ and other orbitals (see Appendix D). However, as we will show in section III F, these peaks do not behave as expected for Hubbard bands in a one-band Hubbard model.

D. Effective masses and quasiparticle lifetimes

In order to quantify the change in correlation along the series $\text{AFE}_2\text{As}_2$ we plot in Fig. 5 the orbitally resolved quasiparticle lifetimes and effective masses $m^*_i/m^{*\text{LDA}}$. The effective masses for Fe $3d_{z^2}$ and $3d_{x^2}-y^2$ increase along the $\text{AFE}_2\text{As}_2$ series but remain constant or even slightly decrease for $3d_{x^2/z^2}$ and $3d_{xy}$. This last result cannot be explained solely by the behavior of the DFT-derived tight binding parameters (see Appendix B and C).

Information on the origin of this behavior can be obtained from the quasiparticle lifetimes which strongly decrease for all orbitals along the series (Fig. 3). This indicates that the coherent quasiparticle picture, being the basis for the calculation of the effective masses, becomes less appropriate along the $\text{AFE}_2\text{As}_2$ series, and accordingly, the effective masses obtained by this procedure are an underestimation of the true value. This result shows that already at the temperature of $T = 145$ K these systems are quite incoherent. With increasing lattice parameter incoherence significantly increases, albeit leading to an orbital dependent change in localization of the Fe $3d$ electrons. In particular, we find a pronounced decrease of the quasiparticle lifetime from $\text{KFe}_2\text{As}_2$ to $\text{RbFe}_2\text{As}_2$, which we attribute to the competing effects of decrease of Fe-Fe direct hopping and increase in Fe-Fe indirect hopping through As, which seem to have a crossover point between RbFe$_2$As$_2$ and CsFe$_2$As$_2$ (see Appendix B).

In Fig. 5 we show the temperature dependence of the quasiparticle scattering rates and effective masses of $\text{KFe}_2\text{As}_2$. We find a similar temperature dependence as also observed for multi-orbital $\text{SrRuO}_3$ and $\text{CaRuO}_3$ in Ref. 40. As the temperature is lowered in the calculation, the quasiparticle picture, which is suppressed at high temperatures, is partially restored, leading to an
benchmarking calculations with fully rotational Hund’s coupling and find that the coherence transition shifts to higher temperatures as found in other studies\cite{20,21}. In this sense the presented results can be considered as a lower bound to the experimental observations.

The increase of effective masses at lower temperatures in our calculation is precisely the effect of restoring the coherent quasiparticle picture, so that the effective masses at the lowest temperature (72 K) we investigated can be considered as the closest approximation to the true values, i.e. 6.1 (3dₓᵧ), 4.6 (3dₓz/yz), 3.4 (3d₂) and 2.5 (3dₓ²−y²).

Combining these observations along the series we conclude that alkali 122 systems show typical signs of strong correlations but, in the studied range of temperatures, are actually quite deep in the incoherent bad metal region with a well defined, albeit strongly suppressed, quasiparticle peak.

### E. Nature of the Fe 3d wavefunction

We proceed now with an analysis of the wave function in terms of the Fe atomic basis states, similar to what has been done for other pnictide systems\cite{22,23}. In Fig. 7 we show a sketch for a few typical orbital configurations in these systems with the orbital splittings obtained from the downfolded charge self-consistent LDA Hamiltonian. Since the nominal electronic filling for Fe 3d for these systems is 5.5 electrons per Fe, one would expect atomic Fe 3d states with 5 and 6 electrons to be the most likely states. However, as shown in Fig. 5, the actual average Fe 3d filling is slightly larger than 6 and this can be analyzed in the histogram of Fig. 7. For the interacting system there is a non-trivial competition between the energy contribution due to the crystal field splitting, which prefers to occupy the lowest states first, the on-site $U$ interaction, which tends to decrease the filling of the localized states and the Hund’s coupling $J_H$, which prefers orbital states with maximum total spin. When the Hund’s coupling $J_H$ is large compared to the total crystal field splitting, the high-spin states will have the highest probability and the
low-spin states will be suppressed. This is indeed true for the hole-doped 122 iron-pnictides.

In Fig. 8 we show for KFe$_2$As$_2$ the atomic histogram of the Fe 3$d$ shell, i.e. the projection of the wave function onto the Fe 3$d$ atomic basis states. The states are sorted by the number of electrons $N$, and inside the interval of constant filling the states are sorted by energy. Because of the Hund’s coupling, the leftmost states in such an interval correspond to the high-spin states, while the rightmost states correspond to low-spin states. The probability assigned to each state corresponds to the fraction of time the Fe 3$d$ orbital spin state $|S|$ spent in one of the 1024 possible states. Within the interval of constant electron number $N$ the states are sorted by increasing energy, i.e. the leftmost states within an interval correspond to high-spin states, while the rightmost states correspond to low-spin states.

![Graph of atomic histogram for KFe$_2$As$_2$](image)

FIG. 8: (Color online) The histogram of the Fe 3$d$ atomic state for KFe$_2$As$_2$ at $T = 145$ K. The probability corresponds to the fraction of time the Fe 3$d$ orbitals spend in one of the $2^{10} = 1024$ possible states. Within the interval of constant electron number $N$ the states are sorted by increasing energy, i.e. the leftmost states within an interval correspond to high-spin states, while the rightmost states correspond to low-spin states.

Generally, the systems can reduce their energy by assigning a higher probability to high-spin states due to the Hund’s coupling $J_H$. This leads to a significant increase of localization caused by the orbital blocking mechanism. Since $J_H$ enforces a high-spin state, or-

![Graph of orbital probability](image)

FIG. 9: (Color online) (a) Probabilities of the most likely atomic states of the Fe 3$d$ atomic orbitals for the AFe$_2$As$_2$ series. The probability corresponds to the fraction of time the atom in the DMFT calculation spends in a specific state. (b) The summed probability of all atomic states with a given total spin $S$. High-spin states become more likely for increasing lattice parameter $a$, while the probability of low-spin states is reduced.

all systems, six out of the seven most likely atomic states are solely composed of the maximal high-spin states with $S = 2.5$ and $S = 2$. For the earth alkali (undoped) 122 iron-pnictides like BaFe$_2$As$_2$ the atomic ground state of the Fe atom with a valence charge of 6 has a maximum possible spin of $S = 2$. Since for the systems studied here one electron per formula unit has been removed by hole doping, the probability for the fully polarized half-filled $S = 2.5$ state with 5 electrons in the Fe 3$d$ orbitals is among the most likely states with a comparably high probability of 1.4% (or 2.8% when accounting for spin degeneracy) in KFe$_2$As$_2$, that increases up to 1.8% (or 3.6%) in the stretched CsFe$_2$As$_2$ system. Along the series the low-spin states become suppressed while the high-spin states increase in probability, as can be seen in Fig. 9(b).

This behavior becomes even more pronounced when we perform this analysis along the AFe$_2$As$_2$ series. In Fig. 9(a) we analyze the most likely atomic states from the histogram of the Fe 3$d$ orbitals for AFe$_2$As$_2$. For all systems, six out of the seven most likely atomic states are solely composed of the maximal high-spin states with $S = 2.5$ and $S = 2$. For the earth alkali (undoped) 122 iron-pnictides like BaFe$_2$As$_2$ the atomic ground state of the Fe atom with a valence charge of 6 has a maximum possible spin of $S = 2$. Since for the systems studied here one electron per formula unit has been removed by hole doping, the probability for the fully polarized half-filled $S = 2.5$ state with 5 electrons in the Fe 3$d$ orbitals is among the most likely states with a comparably high probability of 1.4% (or 2.8% when accounting for spin degeneracy) in KFe$_2$As$_2$, that increases up to 1.8% (or 3.6%) in the stretched CsFe$_2$As$_2$ system. Along the series the low-spin states become suppressed while the high-spin states increase in probability, as can be seen in Fig. 9(b).

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![Graph of orbital probability](image)
bital mixing is greatly suppressed compared to a vanishing Hund’s coupling where high- and low-spin states would have equal energies and, therefore, probabilities. This is the typical behavior of a so-called Hund’s metal, in which the electronic correlations are much more sensitive to the value of $J_H$ than to the on-site Coulomb term $U$. Therefore, in the hole-doped end systems like CsFe$_2$As$_2$ and especially the $a$-axis stretched CsFe$_2$As$_2$ the Hund’s coupling becomes the most important interaction that governs the physical properties of these systems.

F. Dependence on $U$ and $J_H$

In order to investigate the effects of $U$ and $J_H$ more explicitly and to determine the nature of the peak/shoulder at $[-1.5, -1]$ eV we performed calculations for different interaction parameters for the most correlated case, the $a$-axis stretched CsFe$_2$As$_2$ system. For computational efficiency these calculations were done at higher temperature $\beta = 40$ eV$^{-1}$. While the height of the quasiparticle peak is reduced at higher temperatures, the behavior of the spectral function at $[-2, -1]$ eV is quite robust. We considered on-site Coulomb values $U = 4, 5$ and 6 eV and Hund’s couplings of $J_H = 0.8, 1.0$ and 1.2 eV. In Fig. 10 and 11 we show the spectral function $A(\omega)$ for Fe 3$d_{x^2-y^2}$ and 3$d_{2z^2}$. An increase of $U$ from 4 eV to 6 eV at a fixed $J_H$ implies only moderate changes in the spectral function in general for all Fe 3d orbitals. The Hubbard-like shoulder at $-1.2$ eV becomes more pronounced for larger $U$ values and its maximum moves only very slightly to negative energies ($-1.4$ eV). Due to particle-hole asymmetry, we obtain a quasiparticle like peak slightly shifted away from the Fermi level. On the other hand, an increase in the Hund’s coupling $J_H$ for fixed $U$ immediately renders the system very incoherent, with a strong increase in the scattering rate and a reduction of the quasiparticle lifetime, leading to a strong suppression of DOS at the Fermi level and a significant shift of spectral weight to lower energies, forming a broad lower Hubbard band located between $-4$ and $-5$ eV. Finally, the combined effect of $U$ and $J_H$ yields an even more well defined lower Hubbard-like band at around $-4.5$ eV. While this characteristic dependence on $U$ and $J_H$ is very similar for all Fe 3d orbitals, we still find a strong orbital selection regarding the remaining spectral weight at the Fermi level. Especially the Fe 3$d_{xy}$ orbital is almost gapped at the Fermi level for the largest interaction values considered (see Fig. 11), while the least correlated Fe 3$d_{x^2-y^2}$ orbital experiences basically no suppression of the DOS at the Fermi level regardless of the interaction parameters and instead retains a well defined quasiparticle peak for higher values of $U$ and $J_H$ (see Appendix D). We also checked the case of negligible Hund’s coupling by setting $J_H = 0$, which recovered the coherence properties even at $T = 300$ K, with low effective masses around 1.4 and a spectral function that resembled quite well the DFT density of states.

Our results confirm the general picture of the iron pnictides being “Hund’s metals” with strong orbital separation, especially for the strongly correlated hole-doped end systems considered in this study. In this case, a slight increase of $J_H$ renders the system much more incoherent and “bad metal”, like for the same value of $U$, while the spectral weight at the Fermi level differs strongly between the orbitals but remains finite even for larger values of $U$.

III. CONCLUSIONS

From our analysis of the electronic properties within LDA+DMFT in a wide range of binding energies, we conclude that along the isoelectronic doping series AF$\text{Fe}_2\text{As}_2$ ($A = \text{K}, \text{Rb}, \text{Cs}$) as well as the fictitious Fr$\text{Fe}_2\text{As}_2$ and $a$-axis stretched CsFe$_2$As$_2$, which shows a monotonous increase of the $a$-lattice parameters and a decrease of the As $z$-height, correlation and incoherence of the Fe 3d orbitals increase, albeit orbitally selective, and the systems show clear features of a Hund’s metal. In this case the Hund’s coupling plays the major role and renders these materials much more incoherent than expected from the value of the Coulomb repulsion $U$ alone. While the most correlated orbitals ($d_{xy}$) show features that resemble those of being close to an orbital selective Mott transition, specially for $a$-stretched CsFe$_2$As$_2$, the system is quite deep in the incoherent bad metal regime with a finite spectral weight at the Fermi level even for $U = 6$ eV and $J_H = 1.2$ eV. Experimentally, we predict that an increase of the Fe-Fe distance in CsFe$_2$As$_2$ by stretching will induce an orbital dependent increase in correlations and incoherence of the Fe 3$d$ orbitals, where the Fe 3$d_{x^2}$ and Fe 3$d_{2z}^2$ orbitals are strongly but not fully localized and the other Fe 3$d$ orbitals retain a bad metallic behaviour. From our results we estimate the coherence temperature to be located around 50 K in KFe$_2$As$_2$ and even lower for RbFe$_2$As$_2$ and CsFe$_2$As$_2$ in qualitative agreement with the experimental observations. These features make the hole doped end systems of the 122 iron pnictides, namely KFe$_2$As$_2$, RbFe$_2$As$_2$ and especially CsFe$_2$As$_2$ and $a$-axis stretched CsFe$_2$As$_2$ a valuable test bed to study the behavior of strongly correlated Hund’s metals and orbital-selective bad metallicity and its interplay with superconductivity.

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Appendix A: METHODS

For our fully charge self-consistent LDA+DMFT calculations (see Ref. 33 for detailed explanation) we use the structural parameters from Ref. 45 for the tetragonal structures of KFe$_2$As$_2$, RbFe$_2$As$_2$ and CsFe$_2$As$_2$ at room temperature. Due to the almost perfect linear dependence of the lattice parameters as a function of atomic radius, we further use linear extrapolation to obtain structural parameters for fictitious FeFe$_2$As$_2$, avoiding possible ambiguities from DFT-based relaxation methods which do not work satisfactorily for these systems. Additionally, we prepare a structure for CsFe$_2$As$_2$ that is extended along the $a/b$-axis by 3% and has a reduced relative As $z$ height of 2% to mimic a small expansion of the lattice. The expansion is performed in both the $x$- and $y$-direction so that tetragonal symmetry is preserved. The lattice parameters and As $z$ position are shown in Fig. 12.

For the DFT calculations we used the WIEN2k implementation of the full-potential linear augmented plane wave (FLAPW) method in the local density approximation. The Kohn-Sham equations were solved on 726 $k$-points in the irreducible Brillouin zone, resulting in a $21 \times 21 \times 21$ $k$ mesh in the conventional Brillouin zone. A local orbital basis was obtained by a projection of the Bloch wave functions to the localized Fe 3d orbitals, using our implementation of the method described in Refs. 9, 51. Please note that a coordinate system which is rotated by 45° around the $z$-axis with respect to the conventional $I4/mmm$ unit cell is used. Thus, the $x$- and $y$-axis point towards neighboring Fe atoms. The energy window for the bands to be considered for projection was chosen to be $[-6, 13]$ eV, with the lower boundary lying...

FIG. 10: (Color online) The density of states for the Fe 3$d_{z^2}$ orbital of the stretched CsFe$_2$As$_2$ compound as a function of the on-site Coulomb repulsion $U$ and Hund’s coupling $J_H$. (a) An increase only in $U$ leads to an increase in renormalization, i.e. effective masses and a pronounced Hubbard-like peak at $-1.5$ eV but no other qualitative changes are observed. (b) The Hund’s coupling $J_H$ greatly increases the decoherence of the electronic states at the Fermi level and leads to a significant shift of spectral weight down to lower energies. (c) The combined effect of $U$ and $J_H$ is qualitatively very similar to an increase in $J_H$ alone.

FIG. 11: (Color online) The density of states for the Fe 3$d_{xy}$ orbital of the stretched CsFe$_2$As$_2$ compound as a function of the on-site Coulomb repulsion $U$ and Hund’s coupling $J_H$. Similar to the Fe 3$d_{z^2}$ orbital, we see that the shift of spectral weight to lower energies is almost exclusively dependent on the Hund’s coupling $J_H$. Being the most correlated orbital, the DOS of the Fe 3$d_{xy}$ orbital at the Fermi level is almost gapped for $U = 6$ eV and $J_H = 1.2$ eV.
in a gap in the density of states (DOS). Consequently, 35 bands on average were taken into account for the projection, resulting in a representation of the $k$-dependent and local non-interacting spectral function for each orbital that is indistinguishable from the DFT result in the chosen energy window.

The DMFT impurity problem was solved with the continuous-time quantum Monte Carlo method in the hybridization expansion\cite{[22]} as implemented in the ALPS\cite{[53],[54]} project. In the calculations we used an inverse temperature of $\beta = 80$ eV$^{-1}$, corresponding to the temperature of 145 K, unless stated differently. A total number of at least $50 \times 10^6$ Monte-Carlo sweeps were performed for each solution of the impurity model and up to $90 \times 10^6$ sweeps for the larger interaction parameters. For the double counting correction we used the nominal double counting\cite{[61]} which has been shown to yield significantly better agreement with photoemission experiments\cite{[62]} especially for low and high binding energies, while other methods like the FL1\cite{[63]} double counting scheme overestimate the valence charge and underestimate a possible Mott gap\cite{[65]}. The interaction parameters were used in the definition of the Slater integral\cite{[66]} $F^k$ with $U = F^0$ and $J_H = (F^2 + F^4)/14$. For the on-site Coulomb interaction we considered a value of $U = 4$ eV and for Hund’s rule coupling $J_H = 0.8$ eV, unless stated differently. We calculate the effective masses directly from the impurity self-energy via

$$\frac{m^*}{m_{\text{LDA}}} = 1 - \frac{\partial \text{Im} \Sigma(i\omega)}{\partial \omega} \bigg|_{\omega=\epsilon_0^+},$$  \hspace{1cm} (A1)

with the quasiparticle weight being defined as the inverse of the effective mass $Z = \left[ \frac{m^*}{m_{\text{LDA}}} \right]^{-1}$. The continuation of the Monte Carlo data to the real axis was done by stochastic analytic continuation\cite{[67]}.

For obtaining the hopping matrix elements we obtained a tight-binding Hamiltonian from projective Wannier functions\cite{[68]} from DFT, generated by the all-electron full-potential local orbital (FPLO\cite{[69]} code, using a 10 (16) orbital model, including the Fe 3d only (10-orbital model\cite{[70]}) or Fe 3d and As 4p orbitals (16-orbital model).

Appendix B: 10-band tight binding model

In order to quantify at the level of DFT the effects of negative pressure introduced by isovalent doping in $\text{AFe}_2\text{As}_2$ ($\text{A} = \text{K, Rb, Cs, Fr}$), we calculated the Fe-Fe hopping matrix elements via projective Wannier functions. The absolute values of the hopping parameters are plotted in Fig. 13. There are two main contributions that affect the values of the Fe-Fe hopping parameters: First, the increase of the interatomic distances due to increasing atomic radii of the alkali ions implies a decrease of correlation in the Fe 3$d$ orbitals along the series $\text{KFe}_2\text{As}_2$, $\text{RbFe}_2\text{As}_2$, $\text{CsFe}_2\text{As}_2$ and $\text{FrFe}_2\text{As}_2$.
FIG. 14: (Color online) The first six largest hopping parameters $t_i$ for the Fe-Fe hopping obtained from a 16-band tight binding fit. Fe$^i$ denotes the $i$-th atom out of the two equivalent iron atoms in the irreducible Brillouin zone.

When the interatomic distance that leads to a reduced overlap of Fe 3d orbitals. As noted in the main text, the indirect hopping through the As 4p orbitals has an important effect on the effective hopping parameters. Taking only the direct Fe-Fe hopping into account, we observe the expected decrease of the hopping parameters which resembles the reduced hybridization as the lattice parameters are increased. In combination with the indirect hopping via the As atom, this leads to a nontrivial behaviour of the effective hopping parameters.

**Appendix C: 16-band tight binding model**

In Fig. 14 we show the six largest Fe-Fe hopping parameters obtained from a 16-band tight binding fit, encompassing the Fe 3d and As 4p orbitals. The overall monotonous decrease resembles the increase of the interatomic distance that leads to a reduced overlap of the neighboring Fe 3d orbitals. As noted in the main text, the indirect hopping through the As 4p orbitals has an important effect on the effective hopping parameters. Taking only the direct Fe-Fe hopping into account, we observe the expected decrease of the hopping parameters which resembles the reduced hybridization as the lattice parameters are increased. In combination with the indirect hopping via the As atom, this leads to a nontrivial behaviour of the effective hopping parameters.

**Appendix D: DOS for other orbitals**

In Fig. 15 we show the local spectral function of the Fe 3d$_{xz/yz}$ and 3d$_{x^2-y^2}$ orbital for KFe$_2$As$_2$, CsFe$_2$As$_2$ and $a$-axis stretched CsFe$_2$As$_2$. Compared to the other Fe 3d orbitals they are less affected by an increase of the lattice parameter $a$. Similar to the 3d$_z$ and 3d$_{xy}$ orbital a small Hubbard-like peak becomes more pronounced in the 3d$_{xz/yz}$ orbital, while the 3d$_{x^2-y^2}$ orbital shows the opposite trend, increasing its spectral function at the Fermi level at the cost of decreasing it at negative energies.

In Fig. 15 we show the dependence of the Fe 3d$_{xz/yz}$ and 3d$_{x^2-y^2}$ orbital spectral function on $U$ and $J_H$. The results are very similar to the other orbitals, with the effect of increasing $U$ being much less extreme than that of $J_H$. While at higher $U$ the spectral functions still mimics the LDA result, an increase in $J_H$ results in a large shift of spectral weight to negative energies. The 3d$_{x^2-y^2}$ orbital shows the smallest degree of correlations and is the only orbital that retains a well defined quasiparticle peak at the Fermi level even for larger interaction parameters.

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* Electronic address: backes@itp.uni-frankfurt.de

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FIG. 16: (Color online) The density of states for the Fe 3d$_{x^2-y^2}$ and 3d$_{x^2-y^2}$ orbital of the stretched CsFe$_2$As$_2$ compound as a function of the on-site Coulomb repulsion $U$ and Hund’s coupling $J_H$. (a)+(d) An increase only in $U$ leads to a slightly better pronounced lower Hubbard band-like feature but otherwise no qualitative changes to the high energy features. (b)+(e) The $U$ and $J_H$ is qualitatively very similar to an increase in $J_H$ alone.
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