Crystal Symmetry and Magnetic Order in Iron Pnictides:
a Tight Binding Wannier Function Analysis

Z. P. Yin and W. E. Pickett
Department of Physics, University of California Davis, Davis, CA 95616
(Dated: July 20, 2010)

To perform a local orbital analysis of electronic and magnetic interactions, we construct the Wannier functions (WFs) of the Fe 3d orbitals in the parent compound of the recently discovered iron pnictide superconductors, LaFeAsO, and a comparison material LaFePO. Comparing the WFs for the stripe antiferromagnetic order with those for no magnetic order, the difference is a significant spreading ("delocalization") of specifically the $d_{xy}$ and $d_{xz}$ (but not $d_{yz}$) WFs, where parallel Fe spins lie along the $x$ direction. The WF basis gives a tight-binding representation of the first principles, density functional based Fe-derived bands. Comparing hopping parameters, it is found that changes due to stripe antiferromagnetism, even if it is weak, enables more isotropic hopping involving spin-majority electrons in the Fe 3$d_{xz}$ (but not the 3$d_{yz}$) orbital. This change, counterintuitively, actually reinforces electronic anisotropy. Further insight is gained by comparing the WFs of LaFeAsO and LaFePO, identifying how the difference in WFs is related to the difference in hopping integrals and showing how the pnictide atom is influential in forming the stripe antiferromagnetism. Kinetic energy considerations suggest that orbital fluctuation, in addition to spin fluctuation, may contribute to the decrease in observed ordered moment compared to the calculated values.

I. BACKGROUND AND MOTIVATION

Since the first report from Hosono’s group of superconductivity at $T_c=26$ K in F-doped LaFeAsO, hundreds of experimental and theoretical papers on these iron-pnictide compounds have appeared, aimed at elucidating various properties, including synthesizing new compounds to achieve higher $T_c$, measuring basic quantities (e.g. magnetic susceptibility, NMR, ARPES), and modeling and simulating to obtain explanations and predictions. Thanks to these efforts, there are now several families of these iron pnictide superconductors, including the 1111-family (e.g. LaFeAsO, CaFeAsF), 122 family (e.g. BaFe$_2$As$_2$), 111-family (e.g. LiFeAs) and a more complicated 22426-family (e.g. Fe$_2$As$_2$Sr$_2$Sc$_2$O$_8$), with $T_c$ up to 56 K. Several aspects have been clarified: the superconductivity lies in primarily iron 3$d$ bands and is not phonon-mediated, the ground state in most classes is a stripe antiferromagnetic phase with a significantly reduced Fe magnetic moment compared to theoretically calculated values, it is a moderately correlated system where a Coulomb interaction $U \approx 3$ eV might be appropriate. There is discussion that the superconducting order parameter may have a new $s_\pm$ character.

Despite a great deal of progress in understanding the electronic structure and magnetic interactions, some basic questions remain unresolved. One of them is: what is the underlying mechanism of the structural transition from tetragonal to orthorhombic in the parent compounds of iron-based superconductors? This question is especially challenging in the 1111-compounds (e.g. LaFeAsO), where the structural transition is observed (as the temperature is lowered) to occur before the magnetic transition (from nonmagnetic to stripe antiferromagnetic order which we denote as $Q_M$ AFM). It would have been natural to think that the stripe antiferromagnetic ordering of Fe provides the driving force for the structural transition because it introduces electronic anisotropy. (Table III in reference provides a summary of the structural transition temperature $T_S$ and stripe antiferromagnetic transition temperature $T_N$ of several iron pnictide compounds.)

Noting that the structural transition and magnetic transition occurs simultaneously in the 122 compounds (e.g. BaFe$_2$As$_2$), a possible argument is that the magnetism is in fact present, in the form of medium-range order, antiphase boundaries, etc., near the structural transition but its detection is greatly suppressed by strong spatial or temporal fluctuation. The suggestion by Mazin and Johannes that magnetic antiphase boundaries may be the dominant excitation has already stimulated numerical estimations by the present authors. With a time resolution of $10^{-15}$ s, photoemission experiments by Bondino et al. implied a dynamic magnetic moment of Fe with magnitude of 1 $\mu_B$ in the nonmagnetic phase of CeFeAsO$_{0.85}$F$_{0.15}$, which is comparable to the ordered magnetic moment of Fe in the undoped antiferromagnetic CeFeAsO.
compound. The fluctuation strength should be much stronger in 1111-compounds than 122 compounds based on the fact that the measured Fe ordered magnetic moment in 1111-compounds ($\sim 0.4 \mu_B$) is much less than in 122 compounds ($\sim 0.9 \mu_B$) and they are much smaller than DFT predicted value ($\sim 2 \mu_B$). One factor is that interlayer coupling of FeAs layers is stronger in 122 compounds than 1111-compounds because the interlayer distance in 122 compounds ($\sim 6 \text{ Å}$) is significantly smaller than 1111-compounds ($\sim 8-9 \text{ Å}$). Interlayer interaction should help to stabilize the ordered Fe magnetic moment by reducing fluctuations (reducing two dimensionality).

In this paper we address the effect of magnetic order, and of the pnictide atom, on the strength, character, and spin-dependence of Fe-Fe hopping processes by using a Wannier function representation based on all five Fe 3d orbitals, and only these orbitals. Several previous studies of the electronic structure have pointed out some aspects of the influence of the pnictide, or chalcogenide, atoms (due to size or chemical identities) and also of their positions. We provide one example of the effect of the pnictogen atom (comparing LaFeAsO with LaFePO) in this paper, where the effect of the pnictogen is included precisely but indirectly through the Wannierization process. This allows us to present results in an Fe-centric picture. This local orbital representation provides insight into both electronic and magnetic behavior even when the fundamental behavior is primarily itinerant.

II. CALCULATIONAL METHODS

We begin with first principle calculations using the full-potential local-orbital code (FPLO8) with local density approximation (LDA) exchange-correlation (XC) functional (PW92) and the experimental lattice constants and internal atomic coordinates for the compounds LaFeAsO and LaFePO, as given in our previous work. To obtain a consistent local orbital representation and the resulting hopping amplitudes, we then construct real-space Wannier functions (WFs) derived from Fe 3d orbitals in both NM and Q_M AFM phases. The WFs used in this paper, as implemented in the FPLO8 code, are constructed by projecting the Bloch functions from a specified energy range onto chosen atomic orbitals, roughly following the method of Ku et al. The resulting Wannier orbitals retain a symmetry that is common to both the atomic orbital and the point group symmetry of the site. These WFs provide an explicit basis set of local orbitals that give a tight binding representation, complete with on-site energies and hopping amplitudes to neighbors as distant as necessary to represent the chosen bands. In this paper we project onto the conventional real Fe 3d orbitals, with the energy range corresponding to the region with strong Fe 3d character in the bands.

![Graph](image-url)
III. DIFFERENCES IN BAND STRUCTURES

The differences in electronic structure that we will emphasize result from the changes due to stripe magnetic order, and the differences between LaFeAsO with larger ordered moment, and LaFePO, with smaller calculated moment (experimentally nonmagnetic). The necessary band structures are shown in Fig. 1 for LaFeAsO and 2 for LaFePO, where in each case the Fe $3d_{yz}$ and $3d_{xz}$ characters are highlighted. The total energy of LaFePO, which is experimentally found to be nonmagnetic, is only slightly lower (2 meV/Fe) in the $Q_M$ AFM phase than the nonmagnetic phase \cite{3}, so the incorrect prediction for LaFePO is actually a fine detail, and suggests it is nearly antiferromagnetic. The calculated Fe magnetic moment of LaFePO in the $Q_M$ AFM phase is 0.52 $\mu_B$. In LaFeAsO, the calculated moment is near 1.9$\mu_B$, substantially larger than the measured value of 0.36 $\mu_B$ as has been widely discussed (see, for example, Refs. \cite{3,11}).

For our calculations and discussion we have chosen the $x$-axis along the direction of aligned Fe spins, as shown in Fig. 3 the corresponding zone boundaries are denoted X and Y in the band plots. The nonmagnetic band structures of the two compounds are very similar, differing only in some fine details that do not arise in our analysis. However, the band structures in the $Q_M$ AFM phase of the two compounds differ substantially, which is due to the difference in the Fe magnetic moment (1.9 vs. 0.5 $\mu_B$)\cite{6,11}. The similarities and differences provide a way to study the effect of magnetic order in these compounds, and specifically to show that even small magnetic order has substantial consequences. Since the AFM and NM phases in LaFePO are nearly degenerate, our results have relevance to the effect of (longitudinal) magnetic fluctuations of the Fe atom.

The panels in Fig. 1 illustrate that the magnetic order substantially simplifies the band structure very near the Fermi level, which is all near $\Gamma$ in this doubled (magnetic) cell. The other difference to notice is the great difference in band structure along $\Gamma$-X and $\Gamma$-Y directions. Figure 2 shows the influence of a weak stripe antiferromagnetism (0.5 $\mu_B$) on the nonmagnetic band structure. The overall band structure remains the same except for some bands near the Fermi energy, where the main change is the separating of the Fe $3d_{xz}$ bands away from the Fermi level, which causes disappearance and change of topology of certain pieces of the Fermi surface of the Fe $3d_{xz}$ bands. Note that the Fe $3d_{yz}$ bands change insignificantly, leaving the bands near the Fermi level dominated by Fe $3d_{yz}$ character. This difference indicates that even a weak stripe antiferromagnetism has a very strong symmetry breaking effect on the $3d_{xz}$ and $3d_{yz}$ bands, which are equivalent in the nonmagnetic state. As a result, even a weak stripe antiferromagnetism induces a large anisotropy, let alone the much stronger (calculated) antiferromagnetism in FeAs-based compounds. (The much bigger anisotropy in the stripe AFM phase in LaFeAsO is evident by comparing Fig. 1 and 2.)
arrows for spin down electrons, where black arrows for \( y \) directions, up arrows for spin up electrons and down symbols for Fe 3d orbitals as in LaFePO, the orbital distinction and repopulation of the Fe 3d\(_{xz}\) and 3d\(_{yz}\) electrons suggests various means of analysis. The strong intra-atomic anisotropy discussed above is sometimes referred to as orbital ordering, but with the orbital occupations far from integers, the anisotropy also has a substantial itinerant (collective) component. Here we consider briefly the alternative, local viewpoint.

IV. 3d\(_{xz}\) AND 3d\(_{yz}\) ORBITAL REPOPULATION

Due to the strong influence of stripe antiferromagnetism on the band structure (even when weak as in LaFePO), the orbital distinction and repopulation of the Fe 3d\(_{xz}\) and 3d\(_{yz}\) electrons suggests various means of analysis. The strong intra-atomic anisotropy discussed above is sometimes referred to as orbital ordering, but with the orbital occupations far from integers, the anisotropy also has a substantial itinerant (collective) component. Here we consider briefly the alternative, local viewpoint.

Figure 3 shows two underlying (idealized) orbital populations, both of which are consistent with the Q\(_M\) AFM symmetry. (This orbital differentiation is often called “orbital ordering,” but based on the calculated populations, discussed below, this is more properly thought of as an itinerant cousin of orbital ordering.) \( t_{xy} \) denotes the hopping parameter of the \( d_{xz} - d_{yz} \) hopping in the \( y \) direction, and \( t_{yx} \) the \( d_{yz} - d_{xy} \) hopping in the \( x \) direction. In the nonmagnetic case, by symmetry

\[
t_{xy} = t_{yx} = t, \tag{1}
\]

whereas they differ in the Q\(_M\) AFM state. \( t_{xx} \) will denote \( d_{xz} - d_{xz} \) hopping in the \( x \) direction, and similarly \( t_{yy} \) denotes \( d_{yz} - d_{yz} \) hopping in the \( y \) direction (see Fig. 3).

Let \( U \) and \( U' \) denote the intra-orbital and inter-orbital Coulomb repulsion, and \( J_H \) the inter-orbital Hund’s exchange constants. Our purpose is to estimate the difference in kinetic energy gain of the two configurations shown in Fig. 3. At the level of second-order perturbation theory, the kinetic energy gain from the \( d_{yz} - d_{yz} \) hopping in the \( x \) direction (Fig. 3a) is

\[
\Delta E \text{(a)} = \Delta E_{xy} + \Delta E_{yx} = -2t^2/(U' - J_H), \tag{4}
\]

while it is

\[
\Delta E \text{(b)} = -2t^2/U \tag{5}
\]

for Fig. 3b. Because \( U \) is larger than \( U' - J_H \), the orbital ordering in Fig. 3a is favored over Fig. 3b by kinetic fluctuations. This result is a more transparent form of an analysis presented by Lee et al.\(^{29}\).

V. TIGHT BINDING HOPPING PARAMETERS AND WANNIER FUNCTIONS

Figure 4 shows the Wannier functions (WFs) of all five Fe 3d orbitals in both NM and Q\(_M\) AFM (majority spin) phases of LaFeAsO, using the same value of isosurface in all cases. In the NM (spin-degenerate, tetragonal) phase, all five WFs for Fe
3d orbitals have their density strongly concentrated on the Fe site. All Fe minority spin 3d WFs in the Q\textsubscript{M} AFM phase remain almost the same as in the NM phase, so they are not shown. The majority spin WFs for 3d\textsubscript{yz}, 3d\textsubscript{zx} and 3d\textsubscript{xyz} orbitals remain very similar to the corresponding Wannier functions in the NM phase, as can be seen in Fig. 1. The significant change is that the majority spin WFs for 3d\textsubscript{xy}, 3d\textsubscript{yz}, and 3d\textsubscript{zx} in LaFeAsO, become more delocalized in the Q\textsubscript{M} phase, with significant density at the nearest neighbor As sites, the effect being especially large for the d\textsubscript{xy} orbital. This difference reveals that the majority spin Fe 3d\textsubscript{xy} and 3d\textsubscript{yz} orbitals mix much more strongly with nearest-neighbor As 4p orbitals in the Q\textsubscript{M} phase than in the NM phase. The AFM order involves a highly anisotropic magnetization, and resulting difference in majority and minority potentials, that produces this strongly orbital-dependent effect.

Using these WFs as the basis gives a tight binding representation, for which the hopping parameters are obtained from matrix elements of the Wannier Hamiltonian using the FPLO code. The corresponding band structures of LaFeAsO and LaFePO are already shown in Fig. 1 and Fig. 2 and the resulting tight binding bands (not shown) fit very well the corresponding DFT-LSDA Fe-derived bands in both NM and stripe AFM phases.

Table I presents the hopping parameters of the Fe1 3d\textsubscript{yz}, 3d\textsubscript{zx}, and 3d\textsubscript{xy} orbitals to all the five 3d orbitals of its nearest neighbor Fe2 and Fe4 atoms and next nearest neighbor Fe3 atom in LaFeAsO. The highlighted (italicized and boldface) entries are discussed in the text.

| Fe1 | yz | xz | xy |
|-----|----|----|----|
| Fe2 | 3d \textsubscript{yz} | -0.12 | -0.16 | -0.08 |
|     | 3d \textsubscript{zx} | 0.34 | 0.42 | 0.28 |
|     | 3d \textsubscript{xy} | -0.33 | -0.42 | -0.29 |
|     | 3d \textsubscript{yz} | 0 | 0 | 0 |
|     | 3d \textsubscript{zx} | -0.06 | -0.29 | 0.09 |
|     | 3d \textsubscript{xy} | -0.22 | -0.21 | -0.20 |
| Fe4 | 3d \textsubscript{yz} | 0 | 0 | 0 |
|     | 3d \textsubscript{zx} | -0.06 | -0.09 | -0.09 |
|     | 3d \textsubscript{xy} | -0.34 | -0.39 | -0.34 |
|     | 3d \textsubscript{yz} | 0 | 0 | 0 |
|     | 3d \textsubscript{zx} | -0.33 | -0.35 | -0.35 |
|     | 3d \textsubscript{xy} | -0.18 | -0.33 | -0.07 |

The on-site energies (in eV) of all the five 3d orbitals in the NM phase and Q\textsubscript{M} AFM phase in both LaFeAsO and LaFePO are shown in Table II. The hopping parameters reported here are similar to the corresponding hopping parameters reported by Lee \textit{et al}.\textsuperscript{29} and Haule \textit{et al}.\textsuperscript{30} (The differences between our results and those of Lee \textit{et al}.\textsuperscript{29} reflect the fact that, although the original bands are the same and the Wannier transformation is formally the same, the Wannier transformation is not unique and depends somewhat on some details in the implementation.) Our hopping amplitudes are not directly comparable to those reported by Cao \textit{et al}.\textsuperscript{24} who focused on the hopping parameters from As 4p orbitals to Fe 3d orbitals and to its nearest neighbor As 4p orbitals. As shown in Table II in the NM phase, $t_{xy} = t_{yz} >> t_{zx} = t_{yy}$, which indicates...
FIG. 4: LaFeAsO Wannier functions of Fe 3d orbitals in the NM phase (top panel), and those for the majority spin in the QM AFM phase (bottom panel). The Wannier functions of Fe 3d orbitals for the minority spin in the QM AFM phase remain almost the same as in the NM phase. The important difference to be observed is that in the QM AFM phase, the (majority spin) Wannier functions of 3d$_{xz}$ and 3d$_{xy}$ orbitals (and only these) are more extended, with much increased density at neighboring As sites. The isosurface has the same value (density) in each panel.

The magnitude of the changes of the hopping parameters (both spin up and spin down) are either the same or very close to the NM value, except for two cases. These differences are intimately related to the changes in the corresponding WFs, as we now explain. The first one is the $d_{zz} - d_{xz}$ hopping between parallel spin Fe neighbors ($x$ direction) of a majority spin electron, whose absolute value increases significantly from the NM case (from -0.06 to -0.29 eV, see the highlighted numbers in Table II). This opens an extra hopping channel in addition to the original $d_{xz} - d_{zz}$ hopping in the $y$ direction. In the NM state, the electrons in the $d_{xz}$ or $d_{yz}$ orbitals separately only hop in one direction (in the sense that the hopping parameters in other directions are relatively small). The dramatic change of the 3d$_{xz}$ bands near Fermi level from NM to QM AFM, noted in several previous studies, can be traced to this difference.

The other case is for $d_{xy} - d_{xy}$ hopping, again between parallel spin atoms ($x$ direction). In the NM phase, the $d_{xy} - d_{xy}$ hoppings in $x$ and $y$ directions are the same by symmetry, with an amplitude of 0.18 eV. In the QM AFM phase, this hopping in the $y$ direction for both spins is slightly enhanced to 0.23 eV. However, the $d_{xy} - d_{xy}$ hopping in the $x$ direction is significantly enhanced to 0.33 for the majority spin and suppressed to 0.07 for the minority spin. These differences shows that the broken symmetry has a strong effect on the $d_{xy}$ orbital’s environment.

The important difference to be observed is that in the QM AFM phase, the corresponding hopping parameters (both spin up and spin down) are either the same or very close to the NM value, except for two cases. These differences are intimately related to the changes in the corresponding WFs, as we now explain. The first one is the $d_{zz} - d_{xz}$ hopping between parallel spin Fe neighbors ($x$ direction) of a majority spin electron, whose absolute value increases significantly from the NM case (from -0.06 to -0.29 eV, see the highlighted numbers in Table II). This opens an extra hopping channel in addition to the original $d_{xz} - d_{zz}$ hopping in the $y$ direction. In the NM state, the electrons in the $d_{xz}$ or $d_{yz}$ orbitals separately only hop in one direction (in the sense that the hopping parameters in other directions are relatively small). The dramatic change of the 3d$_{xz}$ bands near Fermi level from NM to QM AFM, noted in several previous studies, can be traced to this difference.

The other case is for $d_{xy} - d_{xy}$ hopping, again between parallel spin atoms ($x$ direction). In the NM phase, the $d_{xy} - d_{xy}$ hoppings in $x$ and $y$ directions are the same by symmetry, with an amplitude of 0.18 eV. In the QM AFM phase, this hopping in the $y$ direction for both spins is slightly enhanced to 0.23 eV. However, the $d_{xy} - d_{xy}$ hopping in the $x$ direction is significantly enhanced to 0.33 for the majority spin and suppressed to 0.07 for the minority spin. These differences shows that the broken symmetry has a strong effect on the $d_{xy}$ orbital’s environment.

The magnitude of the changes of the hopping parameters in the two special cases mentioned above, and thus the magnetic order induced changes in WFs, is directly related to the magnitude of the ordered Fe magnetic moment in the QM AFM state, which is evident by comparing the case of LaFeAsO and LaFePO (see Table II and III). The iron atom in the QM AFM state in the former compound has

### Table II: The on-site energies (in eV) of the $d_{x^2-y^2}$, $d_{yz}$, $d_{xz}$, and $d_{xy}$ Fe orbitals in the NM and QM AFM phases in LaFeAsO and LaFePO.

|          | LaFeAsO | LaFePO |
|----------|---------|--------|
|          | NM QM   | NM QM  |
| $d_{x^2-y^2}$ | -0.11 -0.95 0.18 | -0.17 -0.35 -0.04 |
| $x^2-y^2$ | -0.27 -1.14 0.07 | -0.27 -0.44 -0.14 |
| $yz$     | 0.02 -0.67 0.23 | 0.04 -0.19 0.07 |
| $xz$     | 0.02 -0.70 0.21 | -0.04 -0.21 0.07 |
| $xy$     | 0.18 -0.50 0.40 | 0.23 0.13 0.30 |
TABLE III: The hopping parameters (in eV) of the Fe1 3d$_{yz}$, 3d$_{xz}$, and 3d$_{xy}$ orbitals to all the five 3d orbitals of its nearest neighbor Fe2 and Fe4 atoms and next-nearest neighbor Fe3 atom in the nonmagnetic and Q$_M$ AFM phases of LaFePO.

| Fe1  | 3d$_{yz}$ | 3d$_{xz}$ | 3d$_{xy}$ |
|------|----------|----------|----------|
|      | up       | dn       | up       | dn       | up       | dn       |
| Fe2  |          |          |          |          |          |          |
|      | NM       | Q$_M$    | NM       | Q$_M$    | NM       | Q$_M$    |
| z$^2$ | -0.06   | -0.07   | -0.05   | 0        | 0        | 0        |
| x$^2$ - y$^2$ | 0.44 | 0.44   | 0.41   | 0        | 0        | 0        |
| yz    | -0.37   | -0.37   | -0.34   | 0        | 0        | 0        |
| zz    | 0       | 0       | -0.09   | -0.15   | -0.03   | -0.23   |
| xy    | 0       | 0       | -0.23   | -0.23   | -0.23   | -0.22   |
| Fe4  |          |          |          |          |          |          |
|      | NM       | Q$_M$    | NM       | Q$_M$    | NM       | Q$_M$    |
| z$^2$ | 0       | 0       | 0       | 0       | 0       | 0       |
| x$^2$ - y$^2$ | 0     | 0       | 0       | 0       | 0       | 0       |
| yz    | -0.09   | -0.09   | -0.09   | 0        | 0        | 0        |
| zz    | 0       | 0       | -0.36   | -0.36   | -0.36   | 0        |
| xy    | -0.23   | -0.22   | -0.24   | 0        | 0        | 0.27    |
| Fe3  |          |          |          |          |          |          |
|      | NM       | Q$_M$    | NM       | Q$_M$    | NM       | Q$_M$    |
| z$^2$ | -0.09   | -0.08   | -0.08   | -0.09   | -0.09   | -0.08   |
| x$^2$ - y$^2$ | -0.13 | -0.13   | -0.13   | -0.13   | -0.12   | -0.13   |
| yz    | 0.25    | 0.25    | 0.25    | 0.09    | 0.10    | 0.09    |
| zz    | 0.09    | 0.08    | 0.10    | 0.25    | 0.25    | 0.25    |
| xy    | -0.04   | -0.05   | -0.04   | -0.04   | -0.05   | -0.04   |

A large ordered magnetic moment of 1.9 $\mu_B$ while in the latter compound it is very weak, only 0.5 $\mu_B$, in DFT-LSDA calculations. The difference in the ordered Fe magnetic moment is consistent with the change of hopping parameters of $d_{xz} - d_{zz}$ and $d_{xy} - d_{xz}$ in the $x$ direction of the spin majority electron from the NM to the Q$_M$ AFM state, as shown in Table IV and Table III.

The difference in the changes of the hopping parameters of each Fe 3d orbital from NM phase to Q$_M$ AFM phase is related to the spin polarization of each orbital in the Q$_M$ AFM phase, as shown in Table IV. The 3d$_{zx}$ orbital has the largest moment (0.51 $\mu_B$ in LaFeAsO), followed by the 3d$_{xy}$ orbital (0.48 $\mu_B$ in LaFeAsO). The other three orbitals have significantly smaller moments (less than 0.41 $\mu_B$ in LaFeAsO). It is clear that the orbital with larger orbital spin magnetic moment has bigger changes in the relevant hopping parameters. The difference of the relevant hopping parameters between LaFeAsO and LaFePO can also be traced to the difference in the orbital spin magnetic moment.

The transition to the Q$_M$ AFM state is accompanied, in a local picture and to second order, by an extra kinetic energy gain of

$$\Delta E_{xx} = -t_{xx}^2/(U' - J_{HH})$$  \hspace{1cm} (6)

from the hopping process of $d_{xx} - d_{xx}$ hopping in the $x$ direction, which is comparable with $\Delta E_{xy}$. (Note that $\Delta E_{xx}$ is negligible in the NM state.) A substantial extra kinetic energy gain can also be obtained from the $d_{xy} - d_{xy}$ hopping in the $x$ direction. The anisotropy arises because the majority-spin electron in the 3d$_{xx}$ orbital can hop in both directions (i.e. to both parallel and antiparallel spin neighbors), while others in the 3d$_{xz}$ and 3d$_{yz}$ orbitals can basically only hop in one direction. This anisotropy is reflected in a large symmetry lowering of the 3d$_{xy}$ orbital in the AFM phase. The anisotropy leads to a large spin polarization (orbital spin magnetic moment) in the 3d$_{xx}$ and 3d$_{xy}$ orbital, which may also be related to the tetragonal to orthorhombic structural transition such that the lattice constant along the aligned-spin direction ($x$ direction in this paper) becomes shorter than the other direction ($y$ direction in this paper, thus $a < b$).

The additional 3d$_{xx} - 3d_{xx}$ hopping and the enhancement of the 3d$_{xy} - 3d_{xy}$ hoppings, both in the $x$ direction of the spin majority electron, promote kinetic energy gain. However, as pictured in Fig. 3, the 3d$_{xx}$ spin up electron of Fe1 atom cannot hop in the $x$ direction due to the Pauli principle. In order to take advantage of this extra kinetic energy gain of $\Delta E_{xx}$, the spin up occupation number of the 3d$_{xx}$ orbital should not be unity but instead must fluctuate. The same situation happens to the 3d$_{xy}$ orbital. The competition between the kinetic energy gain and Pauli principle results in a reduced magnetic moment and is possibly one mechanism of orbital fluctuation.
TABLE IV: Occupation numbers and spin polarizations in 3d orbitals in the NM and QM AFM phases of LaFeAsO and LaFePO compounds. $\delta n$ is the difference of the total occupation number in each orbital between the QM AFM phase and the NM phase. m is the spin magnetic moment in each orbital in the QM AFM phase.

|          | LaFeAsO | | | LaFePO | | |
|----------|---------|----------|----------|----------|----------|
|          | NM up | $\delta n$ | m | | NM up | $\delta n$ | m | |
| $z^2$    | 0.71  | 0.89  | 0.48  | -0.05  | 0.41  | 0.69  | 0.75  | 0.64  | 0.01  | 0.11  |
| $x^2 - y^2$ | 0.57  | 0.80  | 0.45  | 0.10  | 0.34  | 0.54  | 0.59  | 0.50  | 0.01  | 0.09  |
| $yz$     | 0.65  | 0.85  | 0.57  | 0.11  | 0.28  | 0.67  | 0.72  | 0.64  | 0.01  | 0.08  |
| $xz$     | 0.65  | 0.86  | 0.35  | -0.10 | 0.51  | 0.67  | 0.75  | 0.56  | -0.03 | 0.19  |
| $xy$     | 0.68  | 0.88  | 0.39  | -0.11 | 0.48  | 0.67  | 0.71  | 0.62  | -0.00 | 0.09  |

VI. SUMMARY

In this paper, we have compared the electronic structures of LaFeAsO and LaFePO, in both NM and QM AFM phases, and find that the stripe antiferromagnetism affects very differently the various Fe 3d orbital characters, even when the stripe antiferromagnetism is weak. By comparing LaFeAsO to LaFePO (and looking at similar results for other 1111 and 112 compounds\cite{footnote1}), we find that the pnictide atom and the structure are influential in the formation of QM AFM phase, consistent with several earlier reports that did not provide any detailed analysis. This information was obtained from a tight-binding representation for Fe 3d electrons based on first principles Wannier functions.

In the nonmagnetic phase the electrons in Fe 3d$_{xz}$ and 3d$_{yz}$ orbitals have very different amplitudes to hop in the $x$ and $y$ directions, resulting from the positions and chemical character of the pnictide atoms. Anti-intuitively, this “anisotropy” is almost gone for majority spin electrons in the AFM phase, when the 3d$_{xz}$ (or 3d$_{yz}$) electron can hop equally to parallel and antiparallel neighbors (both $x$ and $y$ directions). This change is accompanied by a lowering of symmetry, and extension in space, in the 3d$_{xy}$ Wannier function. The (large) changes in the near neighbor hopping parameters of the 3d$_{xz}$ and 3d$_{xy}$ orbitals in the $x$ direction is directly connected to the much larger orbital spin magnetic moments of these two orbitals than the other three orbitals.

The anisotropy in hopping in the Fe 3d$_{yz}$, 3d$_{xz}$, and 3d$_{xy}$ orbitals also favors orbital fluctuation by providing extra kinetic processes, which are partly compensated by the Pauli principle which inhibits the hopping processes, and which we expect to enhance fluctuations in the corresponding orbital occupation numbers (orbital fluctuation). Such fluctuations would reduce the ordered Fe magnetic moment in the QM phase, bringing them closer to the observed ordered moments. On the other hand, interlayer hoppings of the Fe 3d electrons in the $z$ direction may help to stabilize the Fe magnetic moment in the QM AFM phase.\cite{footnote2}

VII. ACKNOWLEDGMENTS

The authors thank Q. Yin and E. R. Ylvisaker for helpful discussions, and K. Koepernik for implementing the calculations of Wannier functions in FPLO code. This work was supported by DOE grant DE-FG02-04ER46111.

---

* Present address: Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854.

1 Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Amer. Chem. Soc. 130, 3296 (2008).

2 C. Wang, L. J. Li, S. Chi, Z. W. Zhu, Z. Ren, Y. K. Li, Y. T. Wang, X. Lin, Y. K. Luo, S. Jiang, X. F. Xu, G. H. Cao, and Z. A. Xu, Europhysics Letters 83, 67006 (2008).

3 R. H. Liu, T. Wu, G. Wu, H. Chen, X. F. Wang, Y. L. Xie, J. J. Yin, Y. J. Yan, Q. J. Li, B. C. Shi, W. S. Chu, Z. Y. Wu, and X. H. Chen Nature 459, 64 (2009).

4 L. Boeri, O. V. Dolgov, and A. A. Golubov Phys. Rev. Lett. 101, 026403 (2008).

5 C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff, J. L. Zaretsky, H. A. Mook, C. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, Nature 453, 899 (2008).

6 Z. P. Yin, S. Lebègue, M. J. Han, B. P. Neal, S. Y. Savrasov, and W. E. Pickett, Phys. Rev. Lett. 101, 047001 (2008).
7 M. Aichhorn, L. Pourovskii, V. Vildosola, M. Ferrero, O. Parcollet, T. Miyake, A. Georges, and S. Biermann, Phys. Rev. B 80, 085101 (2009).
8 I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
9 Y. Nagai, N. Hayashi, N. Nakai, H. Nakamura, M. Okumura, and M. Machida, New J. Phys. 10, 103026 (2008).
10 D. J. Singh and M.-H. Du, Phys. Rev. Lett. 100, 237003 (2008).
11 S. Lebègue, Z. P. Yin, and W. E. Pickett, New J. Phys. 11, 025004 (2009).
12 I. I. Mazin, M. D. Johannes, L. Boeri, K. Köpfernik, and D. J. Singh, Phys. Rev. B 78, 085104 (2008).
13 A. N. Yaresko, G.-Q. Liu, V. N. Antonov, and O. K. Andersen, Phys. Rev. B 79, 144421 (2009).
14 M. J. Han, Q. Yin, W. E. Pickett, and S. Y. Savrasov, Phys. Rev. Lett. 102, 107003 (2009).
15 M. D. Johannes and I. I. Mazin, Phys. Rev. B 79, 220510(R) (2009).
16 M. A. McGuire, A. D. Christianson, A. S. Sefat, B. C. Sales, M. D. Lumsden, R. Jin, E. A. Payzant, D. Mandrus, Y. Luan, V. Keppens, V. Varadarajan, J. W. Brill, R. P. Hermann, M. T. Sougrati, F. Grandjean, and G. J. Long, Phys. Rev. B 78, 094517 (2008).
17 K. Ishida, Y. Nakai, H. Hosono, J. Phys. Soc. Jpn. 78, 062001 (2009).
18 I. I. Mazin and M. D. Johannes, Nature Physics 5, 141 (2009).
19 Z. P. Yin and W. E. Pickett, Phys. Rev. B 80, 144522 (2009).
20 F. Bondino, E. Magnano, M. Malvestuto, F. Parmigiani, M. A. McGuire, A. S. Sefat, B. C. Sales, R. Jin, D. Mandrus, E. W. Plummer, D. J. Singh, and N. Mannella, Phys. Rev. Lett. 101, 267001 (2008).
21 V. Vildosola, L. Pourovskii, R. Arita, S. Biermann, and A. Georges, Phys. Rev. B 78, 064518 (2008).
22 K. D. Belashchenko and V. P. Antropov, Phys. Rev. B 78, 212505 (2008).
23 T. Yildirim, Phys. Rev. Lett. 102, 037003 (2009).
24 M. Berciu, I. Elfimov, and G. A. Sawatzky, Phys. Rev. B 79, 214507 (2009).
25 K. Köpfernik and H. Eschrig Phys. Rev. B 59, 1743 (1999).
26 J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
27 W. Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. 89, 167204 (2002).
28 W. Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar J. Solid State Chem. 171, 329 (2003).
29 C.-C. Lee, W.-G. Yin, and W. Ku, Phys. Rev. Lett. 103, 267001 (2009).
30 K. Haule and G. Kotliar, New J. Phys. 11, 025021 (2009).
31 C. Cao, P. J. Hirschfeld, and H.-P. Cheng, Phys. Rev. B 77, 220506(R) (2008).
32 Z. P. Yin, Microscopic Mechanisms of Magnetism and Superconductivity Studied from First Principle Calculations, Ph.D dissertation, University of California Davis (2009).
33 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
Supplementary Material to Crystal Symmetry and Magnetic Order in Iron Pnictides: a Tight Binding Wannier Function Analysis

Z. P. Yin and W. E. Pickett
Department of Physics, University of California Davis, Davis, CA 95616

VIII. CALCULATIONAL METHODS

We perform first principle calculations using the full-potential local-orbital code (FPLO) with local density approximation (LDA) exchange-correlation (XC) functional (PW92). In the calculations, we use experimental lattice constants and internal atomic coordinates for the compounds LaFeAsO, LaFePO, CaFeAsF, SrFeAsF, BaFe$_2$As$_2$, SrFe$_2$As$_2$, and CaFe$_2$As$_2$, as used in our previous work. For the other two hypothetical compounds LaFeNO and LaFeSbO, the lattice constants and internal atomic coordinates are taken from the optimized equilibrium values of first principle calculations done in the Q$_M$ AFM phase using GGA (PBE) XC functional, since such calculations were proven to predict the correct equilibrium lattice constants and internal atomic coordinates compared to the experimental values in all the known iron pnictide compounds.

IX. FURTHER OBSERVATIONS

Similar hopping parameters compared to LaFeAsO have been obtained for the CaFeAsF, SrFeAsF, and MFe$_2$As$_2$ (M=Ba, Sr, Ca) compounds, (which have similar FeAs layers), as shown in Table V. However, replacing As in LaFeAsO with other pnictides (N, P and Sb) results in similar $t_{xy}$, $t_{yx}$ to $t_{x}$ but different $t_{xx}$ and $t_{yy}$ but different $t_{xx}$ and $t_{yy}$. Compared to LaFeAsO, the $t_{xx}$ for the majority spin electron in the Q$_M$ AFM phase is reduced for LaFeNO and LaFePO, but enhanced in LaFeSbO. The importance of the pnictide for the formation of the Q$_M$ AFM phase is evident.

Another important factor is the interlayer hoppings. The interlayer distance of FeAs layers in 1111-compounds is in the range of 8.2 -9.0 Å and it is much smaller in 122-compounds, ranging from 5.9 Å to 6.5 Å. The interlayer hopping parameters of Fe 3$d$ electrons in the z direction are negligible in 1111-compounds but become substantial for certain hoppings in 122-compounds, especially in CaFe$_2$As$_2$, whose interlayer distance of FeAs layers is only 5.9 Å. Certain interlayer hopping parameters are as large as 0.15 eV for 3$d_{xy}$ and 3$d_{xz}$ orbitals, and 0.07 eV for 3$d_{yz}$, 3$d_{xz}$, and 3$d_{z^2}$ orbitals, calculated in the Q$_M$ AFM phase for CaFe$_2$As$_2$, which has the smallest interlayer distance.

The large interlayer hopping parameters for the Fe 3$d_{xy}$ orbital, which at first sight seems very surprising, becomes clear by noting that the 3$d_{xy}$ Wannier orbital is strongly distorted from its symmetric atomic shape to its nearest neighbor As atoms above and below the Fe plane, as shown in Fig.4 in the original paper. This extension in the z direction will favor interlayer hoppings, especially when the interlayer distance is small, as in the case of CaFe$_2$As$_2$. For comparison, the interlayer hopping parameters (if not zero) are less than 0.01 eV in FeAsO. The increasing hopping of Fe 3$d$ electrons in the z direction increases the interlayer coupling, and may inhibit fluctuations and thereby help to stabilize the ordered Fe magnetic moment in the Q$_M$ AFM phase.

The $k_z$ dispersion correlates with the experimental observations that the measured Fe magnetic moments in the Q$_M$ AFM phase are significantly larger in 122-compounds (~ 0.9 $\mu_B$) than 1111-compounds (~ 0.4 $\mu_B$).

| compound | $t_{xy}$ | $t_{yx}$ | $t_{xx}$ | $t_{yy}$ |
|----------|----------|----------|----------|----------|
| LaFeAsO  | 1.86 $\mu_B$ | -0.30 -0.33 -0.27 | -0.30 -0.31 -0.31 |
| LaFePO   | 0.52 $\mu_B$ | -0.37 -0.37 -0.34 | -0.36 -0.36 -0.36 |
| LaFeSbO  | 2.45 $\mu_B$ | -0.26 -0.26 -0.27 | -0.26 -0.28 -0.27 |
| CaFeAsF  | 1.75 $\mu_B$ | -0.36 -0.34 -0.34 | -0.36 -0.37 -0.37 |
| SrFeAsF  | 1.96 $\mu_B$ | -0.35 -0.33 -0.31 | -0.35 -0.37 -0.37 |
| SrFe$_2$As$_2$ | (1.88 $\mu_B$) | -0.32 -0.40 -0.29 | -0.32 -0.34 -0.34 |
| CaFe$_2$As$_2$ | (1.67 $\mu_B$) | -0.33 -0.38 -0.32 | -0.33 -0.35 -0.35 |