The mechanism of anisotropic exchange interaction in superconducting iron arsenides

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Abstract

Using a combination of linear response theory and constrained orbital hybridization approach, we study the mechanism of magnetic exchange interaction of iron-based superconductor. We reproduce the observed highly anisotropic exchange interaction, and our constrain-orbital calculation unambiguously identifies that the anisotropic feature of exchange interaction is not sensitive to the unequal $d_{xz}/d_{yz}$ orbital population.

Keywords: First principle calculation, superconducting iron arsenides, magnetic exchange interaction

The discovery of high-temperature superconductivity in iron arsenides has attracted intense research interests\textsuperscript{1,2,3,4,5}. While the mediator of pairing in these systems remains officially unidentified, a large amount of circumstantial evidence points to magnetic spin fluctuations. Therefore, tremendous amount of efforts have been devoted to understand the magnetic properties\textsuperscript{5,6,7,8,9,10,11,12,13,14,15,16}.

However, despite vast efforts, the nature of magnetism in the iron-based superconductor is still a hotly debated topic\textsuperscript{4}. Early theoretical studies suggest that superconducting iron arsenides have an antiferromagnetic spin-density-wave (SDW) instability due to Fermi-surface nesting\textsuperscript{6,7}. Neutron scattering experiment\textsuperscript{8} confirms that LaFeAsO indeed exhibits the predicted

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stripe antiferromagnetic (S-AFM) long-range ordering followed by a small structural distortion. However, the observed magnetic moment is much smaller than the theoretical one. Moreover, although the general picture fits with a SDW model, there remain problems of matching to a purely itinerant scenario. In particular, the increased conductivity found in SDW state is not expected if a portion of the carriers become gapped. Alternatively, a Heisenberg magnetic exchange model had been proposed to explain the magnetic behavior. It had been suggested that nearest-neighbor and next-nearest-neighbor interactions between local Fe moments are both antiferromagnetic and of comparable strength, which results in a magnetic frustration. These frustrating effects have been used to explain the structural phase transition and small ordered moment. It was also suggested that the structural transition is actually a transition to a "nematic" ordered phase which will occur at a higher temperature than the SDW transition.

On the other hand, a short-range and highly anisotropic exchange interaction had been predicted theoretically and confirmed by the neutron scattering measurement subsequently. To understand this unexpected anisotropy is a hot topic. As a natural way to break the symmetry, orbital ordering (OO) had attracted intensive research attention, and there is increasing experimental evidence about the orbital physics. Band structure calculation proposes that the degeneracy between $d_{xz}$ and $d_{yz}$ orbitals had been lifted and there is a ferro-orbital ordering, which results in not only the strong anisotropic exchange but also structural transition. However, the electronegativity of As is much smaller than that of O, the crystal-field effect upon the $3d$ orbitals of Fe is much weaker than in transition metal oxides, consequently the orbital polarization is quite small. The OO had also been supported by the model calculation, but it is not clear whether the exchange anisotropy is related to OO or not. Therefore, a extensive study about the mechanism of exchange interaction is an important problem. In this work we address this issue using the linear response approximation as well as a recently developed constrained orbital hybridization approach. While our linear response approximation reproduce the known anisotropic exchange interaction, our constrained orbital calculation allows us to provide theoretically a conclusive insights to various contributions to magnetic exchange interactions.

We perform our electronic structure calculations based on the full-potential, all-electron linearized-muffin-tin-orbital (LMTO) method. Since for this system local spin density approximation (LSDA) can give reasonable re-
Figure 1: Definitions of $x$, $y$ axis, the nearest neighbor exchange interaction $J_{1x}$, $J_{1y}$ and the next nearest neighbor exchange interaction $J_2$.

...we therefore adopt it as the exchange-correlation potential. With the electronic structure information, we estimate the exchange interaction $J$ based on a magnetic force theorem that evaluates linear response due to rotation of magnetic moments. This technique has been used successfully for evaluating magnetic interactions in a series of compounds. The main results and conclusions are found to be the same for all iron arsenides, we therefore focus on LaFeAsO at the following.

The calculations are performed on the high-temperature tetragonal structure. The $x$ and $y$ axes are taken to be along the Fe-Fe bond direction, with the $x$ axis chosen along the AFM ordered direction of S-AFM as shown in Fig.1. Our calculated ground state properties, including the magnetic ordering configuration, density of state and band structure, are found to be in good agreement with previous theoretical results. Based on the electronic structure information, we evaluate the interatomic exchange constants as an integral over the q space using (8,8,8) reciprocal lattice grid. Our numerical results show that despite the metallic nature, the exchange interaction is a short range one with the magnetic coupling further than the second nearest neighbor to be almost equal to zero. The short-range feature of the exchange interaction may be caused by the small density of state at Fermi energy. We reproduce the experimental observed strong anisotropic near-neighbor exchange interaction. With the definition of positive $J$ meaning the anti-
ferromagnetic coupling, our numerical data of $J_{1x}$, $J_{1y}$ and $J_2$ are 47.9, -8.0 and 21.0 meV, respectively, which are in good agreement with the previous theoretical results\textsuperscript{14}.

Our LSDA calculation confirms that there is a small orbital polarization, and the difference between the occupation of $d_{xz}$ and $d_{yz}$ orbital is 0.135, which is very close to the previous theoretical work (0.141)\textsuperscript{30}. The magnetic moment at $d_{xz}$ and $d_{yz}$ orbital are 0.202 and 0.361 $\mu_B$ respectively, which is also consistent with the previous calculation (0.149 and 0.338 $\mu_B$)\textsuperscript{30}. After reproducing the orbital/spin polarization, we made a calculation of $J$’s with an artificial constrained external potential applied to the $d_{xz}$ orbital of Fe to adjust its energy consequently to control the orbital occupation, so that we can check the exact effect of unequal $d_{xz}/d_{yz}$ orbital population\textsuperscript{22}. As shown in Fig.2(a), $J_2$ almost does not depend on the shifting of $d_{xz}$ level and the associated orbital polarization, which is contrary to the suggestion of strong dependence in Ref.\textsuperscript{16}. Although the value of $J_{1x}$ and $J_{1y}$ do depend on the OO, but as shown in Fig.2(b) and Fig.2(c), even the $d_{xy}$ and $d_{xz}$ orbital has the same occupation (i.e., OO equal to zero), there is still strong anisotropy between them ($J_{1x}$ is almost twice larger than $J_{1y}$). Thus, we can conclude that the $d_{xz}$ and $d_{yz}$ orbital do have unequal population, but the anisotropic exchange is not related to it.

It is well known that the strength of hybridization between two orbitals strongly depends on their energy difference, therefore the exchange interaction will be sensitive to the shifting of special orbital if this orbital participate in the exchange process. We thus perform the constrained-hybridization approach\textsuperscript{22} to exactly analyze the possible virtual exchange mechanism directly. This technique has been used successfully in perovskite ruthenates and Europium Monochalcogenides\textsuperscript{22,28}. It turns out that a upshift of 5$d$ orbital of La or a downshift of 2$p$ orbital of O does not affect the exchange interaction. Therefore, the exchange process happens almost completely in the FeAs layer, and the inter-layer exchange interaction is negligible.

In additional to $d_{xz}$, we also shift other 3$d$ orbitals of Fe. Shifting the 3$d$ orbitals changes the orbital occupation, however only shifting $d_{xy}$ orbital has considerable effect on $J_2$. Since As anion is located above the center of the Fe plaquette, one can expect that the hybridization between Fe-$d_{xy}$ and As-$p_{x\pm y}$ is strong. Thus, our numerical results clearly show that $J_2$ is mainly contributed by the As-bridged antiferromagnetic superexchange. In contrast to $J_2$, all 3$d$ orbitals have large effect on $J_{1x}$ and $J_{1y}$, which indicates the importance of exchange interaction due to the direct hopping between
Figure 2: The relation between exchange interaction and orbital polarization. (a) is $J_2$; (b) is $J_{1x}$; (c) is $J_{1y}$. The x-axis is orbital ordering (i.e. the difference between the occupation of $d_{xz}$ and $d_{yz}$ orbital), y-axis is the strength of exchange interaction (in meV).
nearest-neighbor Fe 3d electron.

It is well known that the interatomic magnetic interaction basically is a band structure effect, and the spin ordering affects the covalency and details of the bonding topology. Therefore, it is not surprised that the exchange interaction depends on the magnetic configuration. For example, our additional calculation shows that even for NiO, which has well defined local moment, there is about 10% difference between the $J$ from AFM and FM configuration calculation. The magnetism in iron arsenides is much more itinerant, moreover, there is a competition between the As-Fe superexchange and Fe-Fe exchange interaction. The combination of these effects results in the highly anisotropic nearest neighbor exchange interaction.

To clarify the relation between the structural transition and magnetic property, we also perform calculation for low-temperature orthorhombic phase. Same with the high-temperature tetragonal structure, for orthorhombic phase the S-AFM configuration is also lower in energy comparing with other states. We reproduce that the ground state is the one with the magnetic moments at the iron sites aligning antiparallel along the longer $a$ axis. However, both the obtained magnetic moment (1.67 $\mu_B$) and the exchange interaction ($J_{1x}=48.2$, $J_{1y}=-10.1$, and $J_3=21.1$ meV) are almost the same as those in the high-temperature phase. Moreover, we optimize lattice parameter and the internal atomic coordinate for both stripe antiferromagnetic ordering (S-AFM) and checkboard antiferromagnetic ordering (C-AFM). Our numerical results confirm that the structure of Fe-pnictide is almost not depend on the magnetic configuration. Therefore, exchange-striction effect, which had been used to explain the uncentrosymmetric structural distortion and the associated multiferroics, cannot be used to explain the orthorhombic-tetragonal transition.

In summary, based on a combination of linear response theory and constrained orbital hybridization approach, we study the mechanism of magnetic exchange interaction of iron-based superconductor. Our results unambiguously identify that the magnetic exchange process happens in the FeAs layer, and the highly anisotropic feature of exchange interaction is not related to the orbital polarization. The magnetism is at least partially itinerant, which results in the anisotropic exchange interaction. While, the next nearest neighbor interaction $J_2$ is mainly contributed by the As-bridged superexchange, Fe-Fe exchange interaction has considerable effect on the nearest neighbor exchange interaction $J_{1x}$ and $J_{1y}$.

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