A New Electronic Orbital Order Identified in Parent Compound of Fe-Based High-Temperature Superconductors

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Predictive Capability for Strongly Correlated Systems

Summary: The newly discovered Fe-based superconductors [1] have revived the decades-long intensive investigation of high-temperature superconductivity. In particular, similar to the still unsolved Cu-based cuprates, the parent compounds of this new class of materials demonstrate long-range magnetic order in close proximity to the superconducting region, guiding strongly the research attention toward the role of magnetic fluctuation in pairing the electrons in the superconducting state. Recently, the CMSN PCSCS collaborative research team has made important identification of a new electronic orbital order in the parent compounds. The orbital order is slightly stronger than the magnetic order, and couples intensively with the latter. This discovery introduces an additional key physics into consideration and is expected to spawn a new thread of theories beyond the scope of cuprates.

Interestingly, the parent compounds of Fe-based superconductors demonstrate a peculiar C-type magnetic structure in the Fe-layer[2]: aligning in the same direction (ferromagnetic) in one direction but staggered (anti-ferromagnetic) in another, in great contrast to the G-type magnetic structure (staggered in both directions) of the cuprates. Earlier theories proposed two possible explanations. In the momentum space, a “spin density wave” (SDW) scenario[3] was proposed in which the low-energy propagating electrons couple spontaneously to their partner via the momentum of the SDW enhanced by the nested shape of the Fermi surface. Alternatively, in the real space, local spins were proposed to couple strongly with their second nearest neighbors in addition to their immediate neighbors[4], such that the C-type structure has lower energy than the G-type. However, both proposals encounter serious difficulty when the recent inelastic neutron scattering found a strongly anisotropic coupling (large difference in the strength of coupling in the x- and y-directions) via measurement of the magnetic excitations[5].

To resolve the realistic electronic structure and the governing physical effects at low energy, the CMSN PCSCS collaborative research team has conducted a first-principles theoretical study of the representative parent compound, LaOFeAs, using the density functional theory[6]. To facilitate the analysis, a set of symmetry-respecting Wannier functions[7,8] was constructed that capture the relevant Hilbert space of low-energy (and thus the spin dynamics). These are shown in Fig. 1.

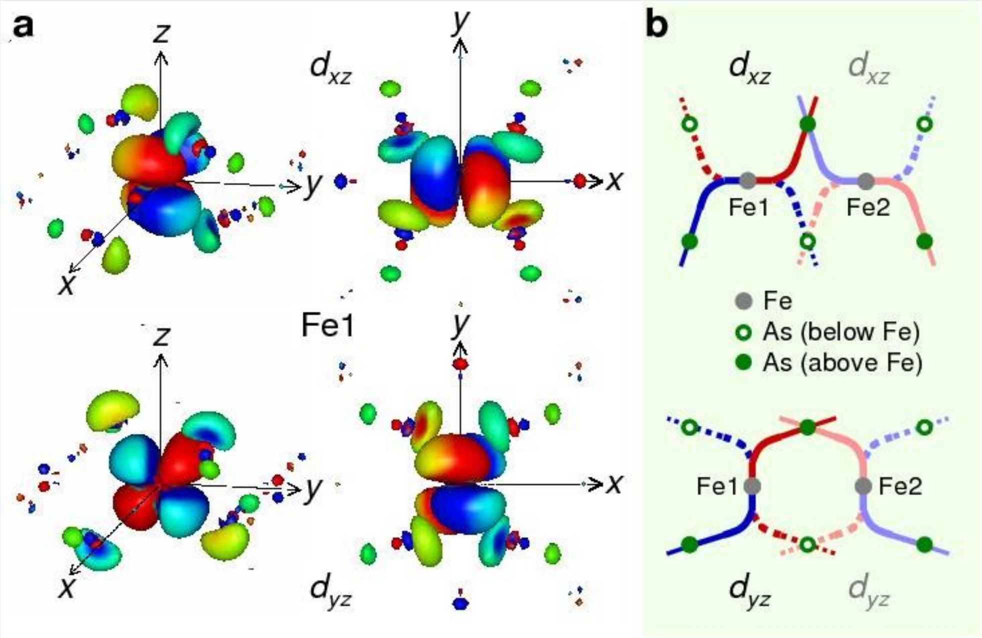

Fig. 1: Low-energy Wannier orbitals of LaOFeAs. **a.** *Side view and top view of the Wannier orbital with* d_{xz} *(upper panel) and* d_{yz} *(lower panel) symmetry. The center structure resembles the standard d-orbitals of Fe, while the tail growing in perpendicular directions results from mixing with p-orbitals of As.* **b.** *Cartoon illustration of overlap of Wannier orbitals at neighboring sites.*

These Wannier functions reveal an unusual property that seems anti-intuitive from the first sight. As can be observed in Fig. 1, while the center of the function resembles closely the well known structure of Fe *d*-orbitals, the tails of the functions show large mixing with As *p*-orbitals in a direction *perpendicular* to the center structure. This strange growth of the tails has a significant consequence in the efficient direction of movement of electrons between the Fe atoms and how the spin couples across sites.

With the help of the Wannier functions, the electronic band structure of the system can be analyzed. Figure 2 compares the non-magnetic and C-type anti-magnetic solutions of the density functional theory. Surprisingly, one finds that only the d_{yz} orbital couples strongly to the magnetic order parameter and opens up a large gap across the Fermi level (zero energy in the plot), while the other orbital remains at the Fermi level maintaining the metallic character of the material. It is thus clear that the magnetic order is driven by only one of the two orbitals and that the degeneracy of these two orbitals is spontaneously lifted (a effect named orbital polarization in analogy of spin polarization). Such orbital polarization is significant, as it implies breaking of rotational symmetry around the Fe atom, and anisotropic coupling to its neighboring sites.

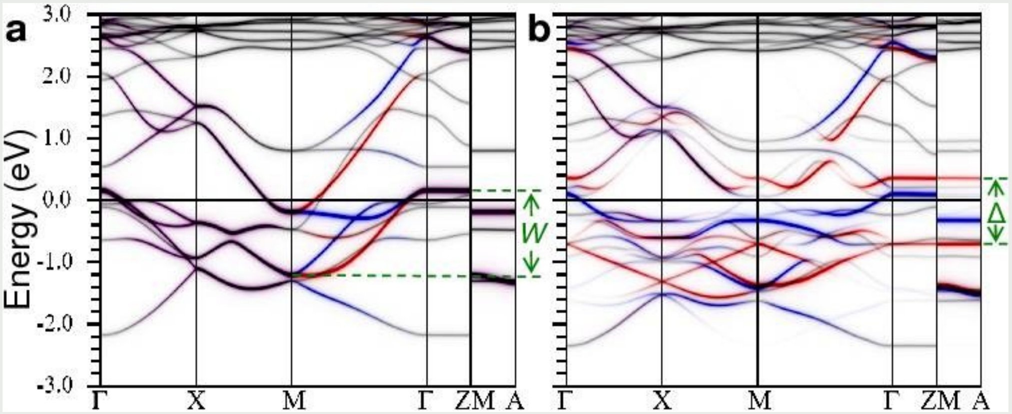

Fig. 2. Electronic structure of non-magnetic (left panel) and C-type anti-ferromagnetic (right panel) solution of the calculation. Blue/red color denotes the Wannier orbital character with d_{xz} and d_{yz} symmetry. The magnetic solution is “unfolded” to the non-magnetic k-zone with proper spectral weight to facilitate direct comparison. This representation contains band splitting, gap opening and development of shadow bands, all of which reflects the strength of the bands’ coupling to the magnetic order parameter.

Even more significantly, the numerical solution also reveals an alignment of the orbital polarization across Fe atoms. Similar to the alignment of spin with particular patterns, this spontaneous orbital alignment is termed “ferro-orbital order”, a very rare phenomenon. It turns out that the energy scale of this long-range order is as strong as the magnetic order, and is in fact the microscopic mechanism that drives the observed structure transition. Further theoretical analysis shows that the ferro-orbital order is almost entirely driven by the electronic degrees of freedom and does not benefit from electron-lattice interaction, in great contrast with standard orbital ordered systems like the $LaMnO_3$ families.

Given the long-range ferro-orbital order, the puzzle of strong anisotropic magnetic order can now be resolved. As shown in Fig.3, the perpendicular development of the Wannier orbital dictates strong anti-ferromagnetic couplings of each orbital (via the so-called “super exchange” process) *only along one direction*. With only one orbital aligned across sites and being active magnetically, the system would automatically order magnetically in the experimentally observed C-type anti-ferromagnetic pattern, as illustrated in Fig. 3.

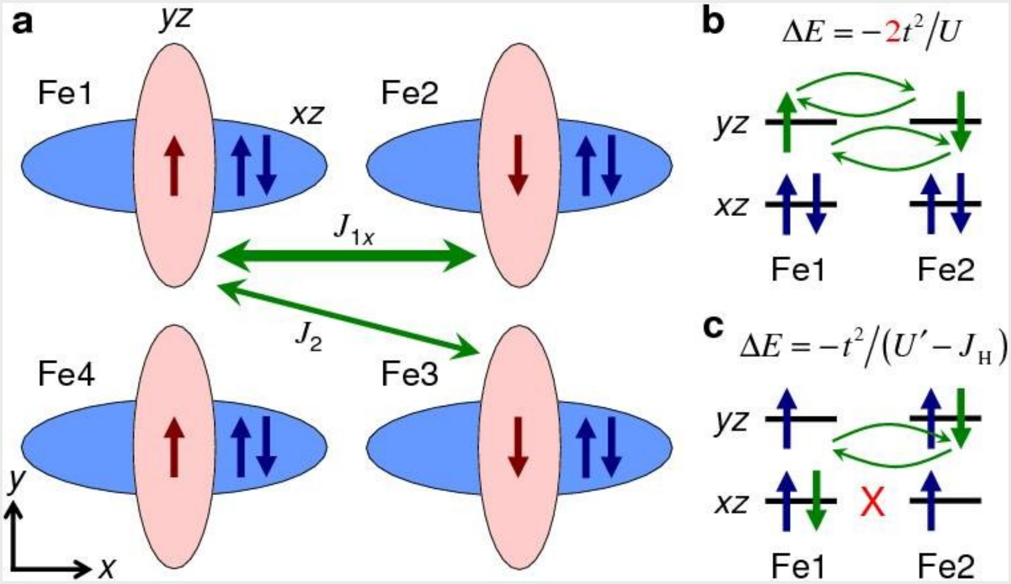

Fig. 3. Illustration of ferro-orbital order and the formation of C-type anti-ferromagnetic order. Each magnetic active orbital couples only anti-ferromagnetically to their neighbors along the x-directions, producing the C-type anti-ferromagnetic pattern. Panel b and c compare the microscopic super-exchange process of ferro-orbital order of LaOFeAs and more typical staggered order in $LaMnO_3$.

This novel picture of orbital order driven magnetism is distinct from existing explanations of the magnetism of LaOFeAs, and provides a unification of lattice and magnetic phase transition observed experimentally. It also leads to a simple microscopic origin of the puzzling strong anisotropy recently observed that has not been satisfactorily explained theoretically. Furthermore, it presents a clear indication of the fundamental difference between Fe-based superconductors and the Cu-based high-temperature superconductors.

This team effort of theoretical study, within the DOE Computational Materials Science Network, has resolved a timely issue of proper understanding of the electronic structure of the parent compounds of Fe-based superconductor. In particular, the introduction of another stronger ordering into the picture exemplifies the richness of the physics of Fe-based superconductors, and opens the door to novel considerations of electronic pairing via orbital fluctuations in addition to the standard spin fluctuation. The theoretical and experimental exploration of the interplay of these different 'channels' of strong correlation is likely to lead to exciting new developments in condensed matter physics and material sciences.

References

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