The electronic structure of NaIrO$_3$, Mott insulator or band insulator?

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Abstract – Motivated by the unveiled complexity of nonmagnetic insulating behavior in the pentavalent post-perovskite NaIrO$_3$, we have studied its electronic structure and phase diagram in the plane of Coulomb repulsive interaction and spin-orbit coupling by using the newly developed local density approximation plus Gutzwiller method. Our theoretical study proposes that the metal-insulator transition can be generated by two different physical pictures: renormalized band insulator or Mott insulator regime. For the realistic material parameters in NaIrO$_3$, Coulomb interaction $U = 2.0$ eV ($J = U/4$) and spin-orbit coupling strength $\eta = 0.33$ eV, it tends to favor the renormalized band insulator picture as revealed by our study.

Recently there have been increasing research activities on the spin-orbit coupling (SOC) driven metal-insulator transition (MIT) in 5$d$ transition metal compounds [1–6]. Compared with 3$d$ and 4$d$ orbitals, the 5$d$ ones are spatially more extended, leading to smaller on-site Coulomb repulsive interaction. However, since the effect of Coulomb interaction is compatible with SOC, the interplay between these two can lead to unexpected interesting phenomena in these materials [7–17]. The first well-studied material of this type is Sr$_2$IrO$_4$ [1], where $t_{2g}$ and $e_g$ orbitals are separated by large crystal field with the lower $t_{2g}$ orbitals filled with five electrons. Due to strong SOC in the system, the $t_{2g}$ orbitals are split into nearly full-filled fourfold $j_{\text{eff}} = 3/2$ states and half-filled twofold $j_{\text{eff}} = 1/2$ states. As a result, the system can be simplified to an effective one-band half-filled system with reduced bandwidth, which has Mott insulator ground state with antiferromagnetic long-range order. Further theoretical studies show that both SOC and on-site Coulomb interaction are essential to explain the Mott insulator behavior in this material, which has also been supported by recent experimental studies including angle-resolved photoemission spectroscopy, optical conductivity, X-ray absorption [1] and resonant X-ray scattering [2] measurements. Other well-studied 5$d$ compounds with non-trivial magnetic and transport properties including Na$_2$IrO$_3$, with complicated magnetic structure may be described by the Kitaev-Heisenberg model, [18,19] Na$_4$Ir$_3$O$_8$ with possible spin liquid ground state [7,11,20] and A$_2$Ir$_2$O$_7$ with Weyl points around the Fermi level [14].

Recently, another novel post-perovskite compound NaIrO$_3$ with pentavalent iridium Ir$^{5+}$ ions was synthesized by Cava’s group in Princeton [21]. The transport and susceptibility measurements show that NaIrO$_3$ is an insulator without magnetic order. However, electronic structure calculations based on density functional theory (DFT) with local density approximation (LDA) found significant density of states (DOS) at the Fermi level, indicating that the material is metallic, which is in strong contrast with the experimental observations. The failure of DFT-type calculation on predicting the basic electronic structure implies that the strong correlation effect may play an important role here, which is poorly treated by LDA alone. The DFT calculation shows that in NaIrO$_3$ the energy bands near the Fermi level are mainly formed by the Ir $t_{2g}$ orbitals from its 5$d$ shell. The SOC splits the $t_{2g}$ bands into two groups of bands with effective total angular momentum $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$, respectively. Since for NaIrO$_3$ there are totally four electrons remaining in the $t_{2g}$ bands, large enough SOC will naturally lead to a

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band insulator phase with fully occupied $j_{\text{eff}} = 3/2$ bands and empty $j_{\text{eff}} = 1/2$ bands. While the LDA calculation predicts a metallic phase, simply because the spin-orbit splitting is still several times smaller than that of the $t_{2g}$ bandwidth and is not strong enough to generate a band insulator by SOC alone.

In this type of system, there are two possible ways for the correlation effect induced by local Coulomb interaction to generate insulating behavior. The first one is called “renormalized band insulator”, in which the correlation effect reduces the effective bandwidth and enhances the effect of SOC leading to a band insulator phase with “renormalized” band structure. The second possibility is the Mott insulator with completely vanishing of quasiparticles, which is caused by strong local Coulomb repulsive interaction. Unlike the Mott insulator phase in Sr2IrO4, which has five 5d electrons on each Ir ion leading to magnetically ordered phase at zero temperature, in NaIrO3 there are four electrons in the $t_{2g}$ orbitals, which leads to nonmagnetic atomic ground states with spin and orbital moments canceling each other even in the strong-coupling limit with very large Coulomb interaction and weak SOC. Since there is no symmetry difference between the above two possible insulator phases, these two “phases” should be adiabatically connected to each other and there will be no phase transition but crossover between them in the parameter space. While it is then interesting to ask that for this particular material, NaIrO3, is it closer to a “renormalized band insulator” or is it closer to “Mott insulator”?

In the present paper, we apply the newly developed LDA+Gutzwiller [22–29] method to study the interplay between SOC and local Coulomb interaction among 5d electrons in NaIrO3. We find that both the above two effects are important to explain the insulating behavior in this material and it can be better described by the picture of “renormalized band insulators” than that of Mott insulator.

Firstly, we carry out the electronic structure calculation by DFT with LDA using the experimentally determined post-perovskite crystal structure [21], which is shown in fig. 1. In such structure each Ir atom is surrounded by six oxygen to form an octahedron. These octahedrons are connected by sharing corner oxygens along the $c$-axis and by sharing edge oxygens along the $a$-axis, which forms IrO3 sheets stacking along the $b$-axis separated by Na ion layers. Our LDA calculation indicates that the coupling between neighboring IrO3 sheets is quite weak, being consistent with the two-dimensional electron transporting property found in transport experiments. To search for the possible magnetic ordering of Ir ions, four types of magnetic orderings, namely, ferromagnetic ordering in both $a$- and $c$-axis (noted as aFeC), ferromagnetic ordering along $a$- and anti-ferromagnetic ordering along $c$-axis (noted as aFeA), anti-ferromagnetic ordering along $a$- and ferromagnetic along $c$-axis (noted as aAcF), and anti-ferromagnetic ordering along both $a$- and $c$-axis (noted as aAcA), are studied. The first-principles calculations of these states are performed by using full potential all electron method implemented in the WIEN2k software package in order to get highly accurate total energies. The LDA calculations can get only nonmagnetic solution, and the density of states in fig. 1 shows that Ir 5d $t_{2g}$ and $e_g$ orbitals are well separated by about 3.5 eV under the octahedral crystal field.

The bandwidth of $t_{2g}$ orbitals is about 3.0 eV, which is quite large since the direct overlap of neighboring $t_{2g}$ orbitals is possible due to the edge-sharing connection along the $a$-axis. The main physics is dominated by

![Fig. 1: (Color online) The experimental crystal structure of NaIrO3 is shown in the left panel. The green (large) ball represents the Na atom. Red (small) and darkslategray (middle) balls represent O and Ir atoms, respectively. The total density of states and the projected one for Ir $d$ orbitals obtained from LDA calculation of NaIrO3 are shown in the right panel.](image-url)
Ir $t_{2g}$ orbitals around the Fermi level. Since both the correlation effect and the SOC are important in 5d transition metal compounds, we further apply the LDA+$U$+SOC to study the electronic structure of this material with $U$ varying from 1.0 to 7.0 eV. Our numerical results show that the LDA+$U$+SOC calculations always converge to nonmagnetic and metallic solution even when $U$ is as large as 7.0 eV. These results indicate the failure of the mean-field treatment of such a correlated system and the profound influence of SOC on the electronic structures. In order to well describe the observed insulating behavior in NaIrO$_3$, we have further performed LDA+Gutzwiller calculations combining the DFT with the Gutzwiller variational method, which can treat the correlation effects more precisely.

We firstly construct an accurate low-energy model Hamiltonian, which can well catch the crystal field splitting, the hopping parameters among active $t_{2g}$ orbitals and the SOC in real material. To do this, the projected atomic Wannier functions [30–32] (PAW) are constructed for the $t_{2g}$ orbitals of Ir ion by using the OpenMX software package [33] within the LDA calculation. This approach has been used to treat 3d transition metal $t_{2g}$ orbitals successfully [34]. In one unit cell, there are two non-equivalent Ir ions and the $t_{2g}$ orbitals are defined in each local coordinates. The obtained PAW orbitals are quite localized and the band structure obtained by first-principles calculations can be well reproduced by the tight-binding Hamiltonian using these basis. It is found that the $d_{xz}$-$d_{yz}$-like PAW is lower than the nearly degenerated $d_{x^2}$ and $d_{y^2}$-like PAWs by about 0.52 eV, which is known as tetragonal crystal field. The atomic SOC is added to the above tight-binding (TB) Hamiltonian and the effective SOC strength $\eta$ is found to be 0.33 eV by inspecting the SOC splitting in $t_{2g}$ bands at the $\Gamma$-point from the LDA+SOC calculations. As a result, the whole band structure from this TB plus atomic SOC calculation can well reproduce that from LDA+SOC calculation. The effect of SOC splits $j_{\text{eff}} = 1/2$ (higher in energy) and $j_{\text{eff}} = 3/2$ states by about $3\eta/2 \approx 0.5$ eV. Therefore, the splitting due to SOC and tetragonal crystal field are comparable and they compete against each other in considering of the orbital degeneracy. Implemented with the local Coulomb interaction terms among the $t_{2g}$ orbitals, the total Hamiltonian can be written as

$$H = H_t + H_u + H_\eta + H_\Delta.$$  

(1)

The first term describes the hopping process of electrons between local spin-orbitals “$a\sigma$” and “$b\sigma'$”,

$$H_t = \sum_{ij, \sigma} \sum_{a\sigma, b\sigma'} t_{a\sigma'b\sigma'} d_{i,a\sigma}^\dagger d_{j,b\sigma'},$$  

(2)

where $\sigma$ denotes electronic spin, and $a$ represents the three $t_{2g}$ orbitals with $a = 1, 2, 3$ corresponding to $d_{xz}, d_{yz}, d_{xy}$ orbitals, respectively. The remaining terms of the Hamiltonian are all local terms expressed by $H_u^i = H_u^\eta + H_u^\Delta$, which contains the Coulomb interaction $H_u^i$, the SOC $H_\eta^i$ and the tetragonal crystal field splitting $H_\Delta^i$ (in the following, the site index is suppressed for the sake of simplicity):

$$H_u = U \sum_a n_{a\uparrow} n_{a\downarrow} + U' \sum_{a<b, \sigma\sigma'} n_{a\sigma} n_{b\sigma'} - J \sum_{a<b, \sigma} \left( d_{a\sigma}^\dagger d_{b\sigma}^\dagger d_{b\sigma} d_{a\sigma} + \text{h.c.} \right),$$  

(3)

$$H_\eta = \sum_{a\sigma, b\sigma'} \eta(a\sigma|x_x + l_y s_y + l_z s_z|b\sigma') d_{a\sigma}^\dagger d_{b\sigma'},$$  

(4)

$$H_\Delta = \sum_{\alpha, \beta\sigma^r} \Delta_{\alpha\beta\sigma^r} d_{\alpha\sigma}^\dagger d_{\beta\sigma^r},$$  

(5)

where $U$ ($U'$) is the strength of intra-orbital (interorbital) Coulomb interaction and $J$ describes Hund’s rule coupling. $U$, $U'$ and $J$ satisfy Kanamori constraint $U = U' + 2J$. $l$ and $s$ represent the orbital and spin angular-momentum operators, respectively. $\eta$ represents the SOC strength and $\Delta$ describes the crystal field splitting between the three $t_{2g}$ orbitals. We emphasize that in the present study we treat Hund’s rule coupling terms in a full rotational invariant way [22,23,29], which is crucial to guarantee that the locking of spin and orbital spaces is purely due to SOC but not to $S_z$-$S_z$ Hund’s coupling term with artificially chosen $z$-direction. We also fix the ratio between Hund’s coupling $J$ and Hubbard interaction $U$ to be 1/4 throughout the entire paper.

Next, we briefly introduce the Gutzwiller wave function (GWF) used in this paper. The generalized GWF $|\Psi_G\rangle$ with rotational invariant local interaction terms can be constructed by acting a many-particle projection operator $P$ on the uncorrelated wave function $|\Psi_0\rangle$,

$$|\Psi_G\rangle = P|\Psi_0\rangle,$$  

(6)

with

$$P = \prod_{\mathbf{R}} P_{\mathbf{R}} = \prod_{\mathbf{R}} \prod_{\Gamma\Gamma'} \lambda(\mathbf{R})_{\Gamma\Gamma'}|\Gamma, \mathbf{R}\rangle \langle \Gamma', \mathbf{R}|,$$  

(7)

where $|\Psi_0\rangle$ is a normalized uncorrelated wave function in which Wick’s theorem holds, $|\Gamma, \mathbf{R}\rangle$ represents atomic eigenstates on site $\mathbf{R}$ and $\lambda(\mathbf{R})_{\Gamma\Gamma'}$ are Gutzwiller variational parameters to be determined by the variational principle. In our work, $|\Gamma, \mathbf{R}\rangle$ are eigenstates of the atomic Hamiltonian $H_{\text{loc}}$. The expectation value of the hopping terms $H_t$ in our Hamiltonian can be expressed as

$$\langle \Psi_G|H_t|\Psi_G\rangle = \sum_{ij} \sum_{\alpha\beta\gamma} t_{ij}^{\alpha\beta \gamma} R_{\alpha\gamma}^{\dagger} R_{\beta\gamma} \langle \Psi_0|d_{i\alpha}^\dagger d_{j\gamma}|\Psi_0\rangle,$$  

(8)

with $\alpha(\beta, \delta, \gamma)$ being the combined spin-orbital index and

$$R_{\alpha\gamma} = \frac{\text{Tr} (\phi_{i\alpha}^\dagger d_{j\gamma}^\dagger)}{\sqrt{n_0^\alpha (1 - n_0^\gamma)}},$$  

(9)

$$\phi_{i\alpha} = |\Gamma| |\Gamma'\rangle \sqrt{\langle \Psi_0|\Gamma'\rangle \langle \Gamma|\Psi_0\rangle},$$  

(10)
where $|I⟩$ stand for the many-body Fock states and $n^0_γ = ⟨Ψ_0|n_γ|Ψ_0⟩$ with $n_γ$ being the occupation number operator for the $γ$ state. The Gutzwiller variational parameters $\lambda(R)_{\Gamma\Gamma'}$ are determined by the minimizing the above total energy. The quasiparticle weights in the generalized Gutzwiller method are defined as the eigenvalues of the Hermite matrix $R^\dagger R$. The detail numerical procedure for the rotational invariant Gutzwiller method can be found in refs. [22–29]. The complete phase diagram in the parameter space spanned by SOC $\eta$ and Hubbard interaction $U$ with fixed $J/U = 1/4$ has been plotted in fig. 2. According to the strength of SOC, the whole phase diagram can be divided into two regions. In the left part of the phase diagram, the SOC is much weaker than the tetragonal crystal field, which splits the $t_{2g}$ orbitals into twofold (including spin) low-lying and fourfold high-lying energy levels, respectively. With the lower twofold bands being fully occupied, the rest of the system can be considered approximately as two-band system filled with two electrons. A typical Mott transition happens when the Hubbard interaction $U$ increases over the critical value, which is around 2.7 eV in the weak SOC limit. The quasiparticle weight $z$ as a function of $U$ for the weak SOC strength ($\eta = 0.1, 0.2$ eV) is plotted in fig. 3, which shows typical Mott transitions with strong first-order nature. The behavior of the quasiparticle weight, both the concave shape of the curve and the first-order nature for the Mott transition, agrees quite well with results obtained by studying the model Hamiltonians with semi-circle–like density of states [35]. The increment of SOC will further split the above two bands and transfer part of the electrons from one band to another, which will suppress the orbital correlation in the effective two-band system and raise the critical $U_c$ for the system. The same increment of $U_c$ as a function of energy level splitting in the two-band Hubbard model has been also reported and discussed in detail by Werner et al. [35] On the right part of the phase diagram, compared to the tetragonal crystal field, the SOC becomes more dominant and we find a completely deferent behavior as we increase the interaction strength $U$. The quasiparticle weight $z$ in the large SOC region ($\eta = 0.3, 0.4$ eV) is again plotted as a function of $U$ in fig. 3, which indicates that the quasiparticles with non-zero weight $z$ persists all the way up to above 4.0 eV. Detailed analysis of the corresponding band structure, which is plotted in fig. 4 for SOC strength $\eta = 0.33$ eV, indicates that there is a transition to band insulator around $U_c = 1.8$ eV, above which a clear band gap appears between the forth and fifth bands as illustrated in fig. 4. Unlike the Mott transition we discussed in the previous paragraph, the transition in the right part of our phase diagram is a typical Lifshitz transition characterized by the vanishing of the electron and hole Fermi surfaces right at the transition point. The reason for this transition is mostly due to the reduction of the $5d$ bandwidth caused by the local Hubbard interaction $U$, which eliminates the overlap between the valance and conduction bands as shown in fig. 4. Therefore for this

Fig. 2: (Color online) The phase diagram in the plane of Coulomb interaction and spin-orbit coupling (SOC). There exist three different regions: Mott insulator, band insulator and metal. The star located in the band insulating region denotes the realistic parameters of NaIrO$_3$: Coulomb repulsive interaction $U = 2.0$ eV and SOC strength $\eta = 0.33$ eV. Hund’s rule coupling $J$ is fixed as $U/4$. 

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particular material, with the different strength of SOC, the on-site Coulomb interaction can induce Mott transition for weak SOC and Lifshitz transition for strong SOC cases. The SOC strength of NaIrO$_3$ has been found to be around 0.33 eV from ab initio calculation. For the Hubbard $U$ parameter, since 5$d$ orbitals are much wider than 3$d$ ones, the reasonable value should be around 2.0–3.0 eV. Here we choose $U = 2.0$ eV, which is slightly above the metal-insulator transition as indicated in fig. 2 by a star. These two realistic parameters for NaIrO$_3$ result in an insulator with gap around 0.5 eV in fig. 4. This is quite consistent with the experimental data.

In conclusion, our LDA+Gutzwiller calculation confirms that NaIrO$_3$ is a band insulator with renormalized bandwidth induced by the correlation effect among the 5$d$ orbitals. As shown in fig. 3, the quasiparticle weight drops to about 0.65 at $U = 2.0$ eV, which completely eliminates the overlap between the conduction and valence band leading to a band insulator with renormalized bandwidth. The SOC in this material plays
a very important role, which leads to very different behavior for weak and strong SOC. In the former case, the on-site Coulomb interaction among the 5$d$ orbitals will generate a Mott transition, after which the system is well described by local moments. While in the latter case, when the strength of SOC overwhelms the tetragonal crystal field, the correlation effect will always generate band insulators with renormalized bandwidth. The correlation effect in these renormalized band insulator phase may also manifest itself in the dynamical properties, i.e., the unusual exciton behavior, which will be discussed in our further publications.

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