The electronic structures and magnetic properties of perovskite ruthenates from constrained orbital-hybridization calculations

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Abstract – We introduce a method to analyze the effect of hybridization by shifting the corresponding atomic levels using external potentials. Based on this approach, we study perovskite ruthenates, and unambiguously identify that the covalency between the A-site cation and the O ion modifies the Ru-O hybridization and change the density of state at the Fermi level, consequently affecting the magnetic properties significantly. We also study the effect of pressure and reveal that hydrostatic pressure has a small effect on the Ru-O-Ru bond angle of SrRuO₃, while it decreases the Ru-O length and increases the band width significantly. Therefore, the magnetic-ordering temperature will decrease monotonically with pressure.

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Due to their interesting electrical, structural and magnetic properties, perovskite ruthenates have attracted continual research attention [1–19]. SrRuO₃ crystallizes in an orthorhombic structure with space group Pbnm [2]. Similarly as SrRuO₃, CaRuO₃ also has a GdFeO₃-type perovskite structure [2], the only observable difference between their crystal structures is the Ru-O-Ru bond angle. However, their magnetic properties are completely different. SrRuO₃ is a ferromagnetic (FM) metal with a Curie temperature \( T_c = 160 \) K [4], while there is a debate about the ground state of CaRuO₃ [1,5,18,19]. It is believed that the leading factor to determine the magnetic properties of these 4d materials is the structural distortion and the associated Ru-O-Ru bond angle [20]. Comparing with Sr\(^{2+}\), Ca\(^{2+}\) has smaller radii, therefore CaRuO₃ has bigger structural distortion and smaller Ru-O-Ru bond angle, which lifts the band degeneracy and reduces the density of states at the Fermi energy \( N(E_F) \) [20]. Consequently the Stoner criterion for magnetism may not be satisfied for CaRuO₃. On the other hand, Ba\(^{2+}\) has a bigger radius, so the perovskite BaRuO₃ will have larger Ru-O-Ru bond angle, comparing with that of SrRuO₃. Thus it is very natural to expect that BaRuO₃ should have higher \( T_c \) than SrRuO₃.

Very recently, using high-pressure and high-temperature techniques, Jin et al. [21], synthesized the cubic perovskite BaRuO₃ successfully. The Ru-O-Ru bond angle of cubic BaRuO₃ is 180°, which is indeed larger than that of SrRuO₃. However, its \( T_c \) is only 80 K, which clearly indicates that in addition to the bond angle, there are other factors which also play important roles in the magnetic properties. Jin et al. [21] propose that the weaker Ba-O hybridization enhances the strength of the Ru-O bond, consequently reducing the \( T_c \). The importance of the A-site cation has also been emphasized by the density function calculations [22–24]. However in contrast to Jin [21], Zayak et al. [24] suggest that the magnetization in these compounds is anticorrelated with the degree of covalency between the A-site ion and the O ion.

In addition to the Ru-O-Ru bond angle and the A-site hybridization, the Ru-O bond length is another factor which also affects the band structure and the \( N(E_F) \), consequently changing the magnetic properties. Hydrostatic pressure may vary both the bond length and angle, and there are several publications which study the effect of pressure [25–28]. All experiments indicate that the \( T_c \) of SrRuO₃ decreases with pressure [25–28]. However, the reason why \( T_c \) decreases with pressure is not yet clear. X-ray diffraction [27] suggests the Ru-O-Ru bond angle decreases with pressure, which results in the decrease
of $T_c$. On the other hand, neutron powder diffraction [28] claims that the Ru-O bond length is sensitive to pressure while the bond angle remains almost constant. Therefore, to clarify the controversial issue about the influence of A-O covalence and pressure on the magnetic properties of perovskite ruthenates is an interesting problem which we address in the present work.

The local spin density approximation (LSDA) is well used for perovskite ruthenates [3,9,20,23,24,29]. The main aim of our study is to illustrate the effect of the A-O hybridization, we thus neglect the effect of Coulomb correlation, although there is a debate about whether the electronic correlation is important in perovskite ruthenates [4,19,29,30]. We perform the electronic band-structure calculation, although there is a debate about whether the electronic correlation is important.

The self-consistent calculations are considered to be converging when the difference in the total energy of the crystal does not exceed 0.25 meV per formula unit (f.u.) and the difference in the total electronic charge does not exceed 10$^{-3}$ electronic charge at consecutive steps.

Based on the experimental structure [21], we perform the calculation for the recently synthesized cubic BaRuO$_3$. We find that the FM metallic solution is the ground state, which agrees with experiment [21]. The energy difference $(E_{PM-FM})$ between total energy of its PM and FM solution is 25.6 meV/f.u. The magnetic moment at the Ru site $(M_{Ru})$ of BaRuO$_3$ is about 0.76 $\mu_B$, which is also close to the experimental value (about 0.80 $\mu_B$) [21]. Due to the strong hybridization with the Ru 4$d$ state, there is a considerable moment located at the O site. We also perform the calculation for SrRuO$_3$ and CaRuO$_3$ using their experimental structure [2]. Consistent with the experimental and previous theoretical work, our calculation also predicts that the ground state of SrRuO$_3$ is a FM metal. The obtained $E_{PM-FM}$ is 38.9 meV/f.u., which is slightly larger than that of BaRuO$_3$. The magnetic moment mainly locates at the Ru site (about 0.93 $\mu_B$), which is also in good agreement with the previous works [20]. On the other hand, for CaRuO$_3$, the FM state is unstable in energy, which is consistent with other theoretical work [20].

After reproducing the experimental results, we now try to explore the controversy about the effect of the A-O covalence. It is widely accepted that the alkali elements at the A-site of ABO$_3$ perovskites are highly ionic, the A-site only contributes to the distortion of the lattice structure and should not affect the Ru-O hybridization considerably. However, recently the effect of hybridization between the A-site cation and O and had been emphasized by several groups [21–24], although there is debate about its exact effect. Thus to gain a conclusive comment about the effect of the A-O hybridization is important.

It is well known that the strength of hybridization between two orbitals is strongly dependent on their energy difference. We thus introduce an external potential in the Kohn-Sham equation to shift the orbital level consequently controlling the hybridization:

$$(H_{KS} + |ilm\sigma|V_{ext}(ilm\sigma))\psi = E\psi,$$

where, $H_{KS}$ is the Kohn-Sham potential, the basis $|ilm\sigma|$ is the orbit which we try to shift ($i$ denotes the site, $n$ the main quantum number, $l$ the orbital quantum number and $\sigma$ the spin index), and $V_{ext}$ is the magnitude we shift. By this constrained calculation, we can directly study how various orbitals and hybridizations between them affect the physical properties of solids. Although similar in spirit, this constrained orbital-hybridization method is different with the constrained LSDA calculation where the external potential is applied to a particular orbital to constrain the orbital occupation.

For perovskite ruthenates, the bands near the Fermi energy $(E_f)$, which determine the magnetic properties, are mainly contributed by Ru 4$d$ and O 2$p$, on the other hand the d-bands of alkali elements are several eV above $E_f$. Thus when we upshift the empty band of the A-site atom by an external potential, the effective hybridization between this band and the O 2$p$-band will decrease, therefore we can study the effect of A-O hybridization directly by our constrained orbital-hybridization method.

Based on the experimental crystal structure [2,21], we perform the constrained orbital-hybridization calculation and the numerical results reveal that the position of the Sr 4$d$-band affects not only the magnetic moment but also the magnetization energy $E_{PM-FM}$. Upshifting the Sr 4$d$-band by 9 eV and 20 eV will reduce $M_{Ru}$ and $E_{PM-FM}$ to 1.10 $\mu_B$, 20.2 meV and 0.4 $\mu_B$, 7.5 meV, respectively. These results indicate that the strength of the Sr-O hybridization is correlated with the magnetization. Our constrained orbital-hybridization calculations also show that upshifting the Ba 5$d$-band has a similar effect as in SrRuO$_3$. The position of Ca 3$d$ will also affect the band structure of CaRuO$_3$, but shifting the Ca 3$d$-band cannot make the FM state stable.

To further understand the effect of the A-O hybridization on magnetic properties, we perform the constrained orbital-hybridization calculation for a PM state and show the density of states (DOS) of BaRuO$_3$ in fig. 1. It is found that the energy position of the Ba 5$d$-band has an important effect on its electronic band structure. Conventional LSDA calculation predicts that the $e_g$ band of Ru mainly locates at $-7.6$ to $-5.0$ eV and $-0.2$ to $5.1$ eV, while the $t_{2g}$ band has two sharp peaks centered at $-0.1$ and $-5.2$ eV, respectively, as shown in fig. 1(a). Upshifting the Ba 5$d$-band depresses the hybridization between Ba and O and consequently varies the band structure around $E_f$ considerably. As shown in fig. 1(b), decreasing the Ba-O hybridization will widen the $e_g$ band of Ru slightly, while it will change the $t_{2g}$ band significantly, make the $t_{2g}$ to distribute in the whole range from $-7.0$ to $0.9$ eV, and decrease $N(E_f)$ considerably. It is well accepted that ARuO$_3$ has an itinerant magnetism, and a large $N(E_f)$ in
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Fig. 1: (Color online) Partial density of states (DOS) of the cubic BaRuO$_3$. Red and green curves denote the $t_{2g}$ and $e_g$ band, respectively. (a) Conventional LSDA results; (b) constrained orbital-hybridization calculations results with the 5$d$-band of Ba upshifted by 9 eV.

the PM calculation is crucial for the magnetization. Therefore, according to the Stoner theory, the A-O hybridization can affect the magnetic properties considerably. We also perform the constrained orbital-hybridization calculation for SrRuO$_3$ and CaRuO$_3$. A similar sensitivity of the electronic structure to the energy position of the $d$-band of the cation has also been found. So we can conclude that the A-O hybridization will change the Ru-O hybridization, consequently changing the magnetization of perovskite ruthenates.

To study the effect of pressure on the structure, we optimize the structure and relax all independent internal atomic coordinates until the corresponding forces are less than 1 mRy/a.u. Consistent with the recent experiment [28], we find that the Ru-O-Ru bond angle of SrRuO$_3$ is not sensitive to the external pressure, while the Ru-O bond length decreases monotonically with pressure, as shown in fig. 2. Our numerical results agree with the experimental value at low pressures, as shown in the inset of fig. 2, while the experimental bond length at high pressure is not available. Based on the optimized structure, we perform the band-structure calculation for a number of different volumes and fit the curves $E(V)$ of the calculated total energies vs. volume to the Birch-Murnaghan equation of state. The obtained equilibrium volume $V_0$, the bulk modulus at equilibrium $B_0$, its pressure derivative $B'_0$ for SrRuO$_3$, together with the available experimental and theoretical values are summarized in table 1. Our theoretical equilibrium volume is only about 1.7% smaller than the experimental values. Such a deviation exists normally in the LSDA calculations. Our full-potential calculations agree with the experiment very well, while the pseudo-potential calculation [30] slightly overestimates the bulk modulus.

Perovskite ruthenate belongs to itinerant magnets, therefore one cannot estimate the interatomic exchange interaction and $T_c$ accurately as in local magnets [32]. One important parameter relevant to $T_c$ is $E_{PM−FM}$.
The experimental hydrostatic pressure has a small effect on the Ru-O-Ru distance, consequently affecting the magnetic properties significantly. We also study the effect of pressure and find that the energy difference between PM and FM solution of SrRuO$_3$ decreases monotonically and rapidly. The experimental curve of $T_c$ vs. pressure in fig. 3 is interesting to notice that both numerical $E_{PM-FM}$ and experimental $T_c$ decrease monotonically at low pressures yields a crude approximation of 23 GPa, which is quite close to our numerical results.

In summary, we introduce a method to identify the effect of covalence for a particular material by applying an orbital dependent external potential. This approach allows us to control the hybridization between the orbitals directly. Our constrained orbital-hybridization calculation unambiguously identifies that the covalency between the A-site cation and the O-ion modifies the Ru-O hybridization, consequently affecting the magnetic properties significantly. We also study the effect of pressure and find that hydrostatic pressure has a small effect on the Ru-O-Ru bond angle of SrRuO$_3$, while it decreases the Ru-O length, increases the band width and results in the monotonic decrease of the magnetic-ordering temperature.

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