Interplay of Spin-Orbit Interaction and Electron Correlation on the Van Vleck Susceptibility in Transition Metal Compounds

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We have studied the effects of electron correlation on Van Vleck susceptibility ($\chi_{VV}$) in transition metal compounds. A typical crossover behavior is found for the correlation effect on $\chi_{VV}$ as sweeping spin-orbit interaction, $\lambda$. For a small $\lambda$, orbital fluctuation plays a dominant role in the correlation enhancement of $\chi_{VV}$; however, the enhancement rate is rather small. In contrast, for an intermediate $\lambda$, $\chi_{VV}$ shows a substantial increase, accompanied by the development of spin fluctuation. We will discuss the behavior of $\chi_{VV}$ in association with the results of Knight-shift experiments on Sr$_2$RuO$_4$ and an anomalously large magnetic susceptibility observed for 5d Ir compounds.

KEYWORDS: Van Vleck susceptibility, multi-orbital system, spin-orbit interaction, dynamical mean-field theory

Multi-orbital systems often show intriguing phenomena, such as unconventional superconductivity\(^1,2\) and colossal magneto-resistance.\(^3\) In most cases, orbitals do not just complicate a system by increasing the number of local degrees of freedom, but they lead to qualitatively new features, which are absent in single-orbital systems. Among the characteristic properties inherent in multi-orbital systems, the role of orbital angular momentum and the spin-orbit coupling deserves special attention, since they underlie many anomalous phenomena in transition metal and rare-earth materials.

Above all, these two factors give rise to “residual” paramagnetic susceptibility, called Van Vleck susceptibility ($\chi_{VV}$).\(^4,5\) It is well known that the Pauli susceptibility ($\chi_P$) is proportional to the density of states, and it vanishes, as soon as an energy gap opens at the Fermi level. Meanwhile, $\chi_{VV}$ has a residual nature, in the sense that it remains finite at zero temperature, even in the presence of an energy gap.

To be more specific, the residual nature of $\chi_{VV}$ can be attributed to the fact that the orbital angular momentum or spin-orbit interaction makes magnetization a non-conserved quantity. To illustrate this, suppose a system in which the magnetization is conserved. In this case, the Hamiltonian and magnetization operators are commutative, and thus a fixed magnetization quantum number can be assigned to each eigenstate of the Hamiltonian. Consequently, for the magnetic susceptibility to be finite at zero temperature, the ground state has to be replaced with one of the excited states with an infinitesimal magnetic field, which is obviously impossible in a gapped system. Meanwhile, for a system where the magnetization is not conserved, an infinitesimal magnetic field leads to magnetization by mixing the ground-state and excited-state wave functions, resulting in a finite susceptibility even in the presence of an energy gap.

In fact, the residual nature of $\chi_{VV}$ causes much confusion in gapped systems. A typical example can be found in a Knight-shift experiment to determine the parity of a superconducting order parameter. Below the superconducting transition temperature $T_c$, only $\chi_P$ decreases, responding to spin gap formation, while $\chi_{VV}$ remains invariant. This means that the invariant Knight shift at $T_c$ does not necessarily serve as evidence of spin-triplet superconductivity, but suggests another possibility that a very large $\chi_{VV}$ masks the decrease in $\chi_P$ to experimental accuracy. The most famous material that suffers from this difficulty may be UPt$_3$, for which a decrease in Knight shift has been observed; however, the decrease is only 1% of the total Knight shift.\(^6\) Similar difficulties have been reported for conventional vanadium-based superconductors.\(^7\) Recent Knight-shift experiments on Sr$_2$RuO$_4$ also led to the same question. Murakawa and coworkers found that the magnetic susceptibility shows no change at $T_c$, irrespective of the magnetic field direction.\(^8,9\) In order to provide a basis for discussing these interesting superconductors, it is desirable to clarify the Van Vleck susceptibility of multi-orbital systems.

5d Ir compounds provide another example in which Van Vleck susceptibility plays a crucial role. One of the confusing properties common in Ir compounds is their unusually large magnetic susceptibility and Wilson ratio. For example, for Eu$_2$Ir$_2$O$_7$, the magnetic susceptibility amounts to $\chi \sim 1.0 \times 10^{-2}$emu/mol-Ir, in contrast to the rather small specific heat coefficient $\gamma \sim 8.0$mJ/K$^2$ mol-Ir, leading to an anomalously large Wilson ratio, $R_W \sim 90$.\(^10\) A similar huge paramagnetic susceptibility has also been reported for the so-called “hyperkagome material” Na$_4$Ir$_3$O$_8$, where a large residual magnetic susceptibility, $\chi \sim 1.0 \times 10^{-3}$emu/mol-Ir was observed,\(^11\) despite that this compound is an insulator. To reconcile a large paramagnetic susceptibility with a small $\gamma$, substantial increase in $\chi_{VV}$ is necessary, since a large $\chi_P$ requires the existence of rich gapless spin excitations, which should also contribute to $\gamma$.

Actually, in rare-earth systems, correlation effects on Van Vleck susceptibility have been studied by several groups.\(^12-17\) Among them, Kontani and Yamada pointed
out the general tendency that the correlation enhancement of $\chi_{VV}$ is comparable to that of $\chi_p$. However, it has also been reported that the enhancement rate considerably depends on individual properties of a system, such as orbital degeneracy. Therefore, it is highly non-trivial how electron correlation affects $\chi_{VV}$ in transition metal compounds, which have quite different characters from rare-earth materials.

In this research, we will study the correlation effect on $\chi_{VV}$ in transition metal compounds. For this purpose, we adopt Sr$_2$RuO$_4$ as a model material, since its simple orbital structure is appropriate for establishing a general theory, and the $\chi_{VV}$ of Sr$_2$RuO$_4$ is interesting of its own right. Although the spin-orbit coupling of Sr$_2$RuO$_4$ is rather small, we also investigate the case with a large spin-orbit coupling, in order to gain insights into large $\chi_{VV}$ in 5$d$ transition metal compounds. Hereafter, we set $\hbar = k_B = \mu_B = 1$.

We start with a multi-orbital Hubbard model, which takes account of the three $t_{2g}$ orbitals of Sr$_2$RuO$_4$:

$$H = H_0 + H_I,$$

$$H_0 = \sum_{i} \sum_{\alpha, \beta} \epsilon_i c_{\alpha i, \beta}^\dagger c_{\beta i, \alpha},$$

$$\times \sum_{\alpha, \beta} \left[ (c_{1, \alpha}^\dagger \epsilon_1 \alpha - \lambda \alpha \left( -\epsilon_2 \beta \right) \left( -\epsilon_3 \alpha \right) \epsilon_3 \beta \right) c_{\beta 1, \alpha} \right].$$

$$\Gamma_I = U \sum_{i} \sum_{\alpha, \beta} \left[ (S_{i, \alpha} S_{i, \beta} + \frac{1}{4} \delta_{\alpha, \beta} \delta_{\alpha, \beta}^\dagger) \langle c_{\beta i, \alpha} \epsilon_{\alpha i, \beta}^\dagger \epsilon_{\beta i, \alpha} \epsilon_{\alpha i, \beta} \epsilon_{\beta i, \alpha} \epsilon_{\alpha i, \beta} \epsilon_{\beta i, \alpha} \epsilon_{\alpha i, \beta} \rangle \right] - \sum_{\alpha, \beta} \epsilon_i c_{\alpha i, \beta}^\dagger c_{\beta i, \alpha}.$$
to the Hamiltonian eq. (1) and obtain χ_P = \(\frac{1}{N} \sum_k \chi_P(k) = \frac{1}{N} \sum_{k,a} \left( \frac{\partial \epsilon_a(k)}{\partial \mu} \right)^2 \left( -\frac{\partial f(\epsilon_a(k))}{\partial \mu} \right) \), and χVV = \(\frac{1}{N} \sum_k \chiVV(k) = -\frac{1}{N} \sum_{k,a} \left( \frac{\partial \epsilon_a(k)}{\partial \mu} \right) f(\epsilon_a(k) - \mu) \), with a Fermi distribution function, \(f(x) = \frac{1}{e^{x/T} + 1}\). We plot the temperature dependences of χ_P and χVV in Fig. 1 (a). χ_P shows a moderate increase with decreasing temperature, in contrast to χVV, which takes almost a constant value in a wide temperature range, 0 ≤ T ≤ 1.

Figures 1 (c) and 1 (d) show the momentum-resolved magnetic susceptibilities χ_P(k) and χVV(k) evaluated at \(T = 0.1\), respectively. The major contribution to χ_P comes from the vicinity of three Fermi surface sheets, while χVV comes from a wide area in a Brillouin zone (e.g., around \((\pi, 0)\) and \((0, \pi)\) ), where either the \(d_{yz}\) or \(d_{zx}\) orbital is occupied, and the other orbital is empty. We note that χVV is brought about by the hybridization of the \(d_{yz}\) and \(d_{zx}\) orbitals due to the magnetic field parallel to the \(z\)-axis. In particular, sharp peaks are located at \((p_x, p_y) \approx (±0.62\pi, ±0.62\pi)\), where these bands cross at the Fermi level.

Next, let us consider the effect of electron interaction. In Fig. 2, we show the χ_P and χVV divided by their non-interacting values \(\chi_P^{(0)}\) and \(\chiVV^{(0)}\). Here, we plot χ_P and χVV by varying \(U\), with \(U'/U\) and \(J/U\) fixed. Figures 2(a) and 2(d) show that both χ_P and χVV tend to increase with \(U\); however, their growth rates are quite different. Although χ_P is substantially enhanced by electron interaction, \(\chiVV/\chiVV^{(0)}\) remains \(\approx 1.1\), at most, in the interaction range considered here. Moreover, Figs. 2 clearly show that the inter-orbital repulsion \(U'\) and Hund coupling \(J\) affect χ_P and χVV, quite differently. Figures 2(a) and 2(b) show that χ_P monotonically increases with \(J\), while it is suppressed with increasing \(U'\). In contrast, Figs. 2(c) and 2(d) show that χVV decreases with \(J\), while it grows with increasing \(U'\). The contrastive behaviors of χ_P and χVV can be attributed to the difference in the way electron correlation affects spin and orbital fluctuations. In multi-orbital systems, a magnetic moment can be decomposed into the spin part and the orbital part, as \(M^2 = l^2 + 2s^2\). Without spin-orbit coupling, \(\chi_P (\chiVV)\) is equal to \(2s^2 (l^2)\) divided by the applied magnetic field. Accordingly, the magnitude of \(\chi_P (\chiVV)\) is affected by a spin (orbital) fluctuation.

Generally, the intra-orbital repulsion \(U\) and the Hund coupling \(J\) stabilize the high-spin states and enhance spin susceptibility. Accordingly, χ_P grows with increasing \(U\) or \(J\). On the other hand, the inter-orbital repulsion \(U'\) stabilizes the orbital moment by prohibiting two electrons occupying different orbitals at the same site. The Hund coupling \(J\) also destabilizes the orbital moment by facilitating the simultaneous occupancy of different orbitals. As a result, χVV grows with increasing \(U'\), while it decreases with increasing \(J\).

These contrastive correlation effects naturally lead to the different enhancement rates of χVV and χ_P noted above. Although χ_P is enhanced by a large intra-orbital repulsion \(U\), the increase in χVV is mainly brought about by a smaller inter-orbital repulsion \(U'\). Accordingly, \(\chiVV/\chiVV^{(0)}\) becomes relatively small compared with \(\chi_P/\chi_P^{(0)}\). We plot the ratio \(\chiVV/\chi_P\) in Fig. 2(e) for several values of \(U'/U\), under the relation \(U' = U - 2J\). Evidently, the correlation enhancement of χVV is smaller than that of χ_P for a wide parameter range.

Next, we will consider the correlation effects on χ_P and χVV under a finite spin-orbit coupling. In Fig. 3(a), we plot the \(\lambda\) dependence of χVV for several \(U's\), with \(U'/U = 0.4\) and \(J/U = 0.3\) fixed. With this choice of \(U'\) and \(J\), χVV is only slightly enhanced by inducing \(U\) for \(\lambda = 0\), consistent with Fig. 2. However, Fig. 3(a) clearly shows that χVV increases with \(U\) for moderate \(\lambda\). χVV/χ_P increases from 4.5 to 6.3 at \(\lambda = 1.2\) while sweeping \(U\) from 0.0 to 3.0.
To elucidate the origin of this marked enhancement, we introduce the spin fluctuation $\chi^S$ and orbital fluctuation $\chi^L$ as

\begin{align*}
\chi^S &= \frac{1}{N} \beta \int_0^\beta d\tau S^z(\tau)S^z \\
\chi^L &= \frac{1}{N} \beta \int_0^\beta d\tau (L^z(\tau)L^z),
\end{align*}

respectively, with $S^\alpha(L^\alpha) = \sum_i \langle \alpha | S^\alpha_i \rangle \langle \alpha | S^\alpha_i \rangle^\dagger$. In particular, $\chi^L$ corresponds to the fluctuation between $d_{xz}$ and $d_{x^2-y^2}$ orbitals, which is essential to $\chi_{VV}$ at $\lambda = 0$. We plot $\chi_{VV}$ together with $\chi^S$ and $\chi^L$ in Figs. 3(b)-(3)(d) with varying $J/U$. As Figs. 3(c) and(d) show, the correlation effects on spin and orbital fluctuations are not sensitive to $\lambda$. $\chi^S (\chi^L)$ monotonically increases (decreases) with $J$, consistent with the view that spin (orbital) fluctuation is enhanced (suppressed) by Hund coupling. In contrast, $\chi_{VV}$ shows a non-monotonic $\lambda$ dependence. For a small $\lambda$ ($\lambda \lesssim 0.2$), $\chi_{VV}$ decreases with $J/U$, consistent with the case of $\lambda = 0$, whereas, for an intermediate $\lambda$ ($\lambda \gtrsim 0.2$), $\chi_{VV}$ grows with $J/U$, as is clearly shown in Fig. 3(e).

This non-monotonic behavior of $\chi_{VV}$ can be assigned to the mixing of spin and orbital degrees of freedom due to spin-orbit coupling. Namely, the spin moment does not commute with the Hamiltonian for $\lambda \neq 0$; hence, the spin degree of freedom also contributes to $\chi_{VV}$. We define the spin- (orbital-) dominant region by the criterion $\chi_{VV}[J/U = 0.3] - \chi_{VV}[J/U = 0.0] > 0 (\leq 0)$, and show the two regions in Fig. 3(a). Figure 3(a) clearly shows that $\chi_{VV}$ is strongly enhanced in the spin-dominant region. Namely, in the orbital-dominant region, $\chi_{VV}$ is enhanced mainly by an inter-orbital electron interaction, whereas, in the spin-dominant region, a large intra-orbital electron interaction contributes to $\chi_{VV}$, and $\chi_{VV}$ becomes strongly enhanced. Our current analysis is based on the band structure of $\text{Sr}_2\text{RuO}_4$; however, we confirm that our results are generic in $t_{2g}$ systems by obtaining qualitatively the same behavior for other band structures. The details of our analysis will be reported elsewhere.

Here, let us discuss our results, in association with experiments. By adopting the band structure for $\text{Sr}_2\text{RuO}_4$, we revealed that $\chi_{VV}/\chi_P$ is $\sim 0.5$ in a non-interacting case. The electron interaction tends to make this ratio smaller for $\lambda \lesssim 0.2$. Actually, the spin-orbit coupling of $\text{Sr}_2\text{RuO}_4$ is rather weak. Therefore, it is reasonable to conclude that $\chi_P$ dominates $\chi_{VV}$ for $\text{Sr}_2\text{RuO}_4$, i.e., $\chi_P$ has a dominant contribution to the Knight-shift signal.

On the other hand, for most Ir compounds, spin-orbit coupling is estimated to be fairly large. In light of our analysis, $\chi_{VV}$ is highly enhanced by electron correlation, if the spin-orbit coupling is so large that the spin degree of freedom contributes to $\chi_{VV}$. This gives a possible clue to the anomalously large residual susceptibility of Ir compounds. We note that some of the Ir compounds are considered as Mott insulators, which are outside the scope of our current analysis based on a perturbative method. Nevertheless, we consider that our mechanism is also relevant to the large residual susceptibility of such compounds. It is an interesting future study to extend our analysis to the vicinity of metal-insulator transition.

In summary, we have studied the effects of electron correlation on the Pauli susceptibility $\chi_P$ and the Van Vleck susceptibility $\chi_{VV}$ on the basis of the multi-orbital Hubbard model. We adopt DMFT combined with IPT, and calculate $\chi_P$ and $\chi_{VV}$, following the definitions introduced by Kontani and Yamada. As a result, we found that the correlation enhancement of $\chi_{VV}$ is rather small for a small $\lambda$. Meanwhile, a substantial increase is found for an intermediate $\lambda$, where the spin degree of freedom contributes to $\chi_{VV}$.

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20) To avoid the unphysical deformation of the Fermi surface, we omit Fock terms by assuming that these terms are included in $H_0$ as a renormalization of hopping integrals.
21) We note that $\chi^0$ and $\chi^4$ show irregular $\lambda$ dependence for $\lambda \gtrsim 2.5$ (not shown), owing to the transition to a band insulator.