Spectroscopic signatures of molecular orbitals on a honeycomb lattice.

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A tendency to form benzene-like molecular orbitals has been recently shown to be a common feature of the 4d and 5d transition metal oxides with a honeycomb lattice. This tendency competes with other interactions such as the spin-orbit coupling and Hubbard correlations, and can be partially or completely suppressed. In the calculations, SrRu2O6 presents the cleanest, so far, case of well-formed molecular orbitals, however, direct experimental evidence for or against this proposition has been missing. In this paper, we show that combined photoemission and optical studies can be used to identify molecular orbitals in SrRu2O6. Symmetry-driven election selection rules suppress optical transitions between certain molecular orbitals, while photoemission and inverse photoemission measurements are insensitive to them. Comparing the photoemission and optical conductivity spectra one should be able to observe clear signatures of molecular orbitals.

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Introduction. Low dimensional ruthenates with a honeycomb lattice have been attracting a lot of attention in recent years. α–RuCl3, which has one hole in the t2g manifold, shows hallmarks of Kitaev physics.1,2, Li2RuO3 with two t2g holes dimerizes in the low-temperature phase3,4 and exhibits a valence bond liquid behavior at high temperatures3,5,6, while SrRu2O6 with a half-filled t2g band shows rather unusual magnetic properties7. It has been argued8 that the physics of these compounds is underscored by competition between the spin-orbit coupling and Hubbard correlations, on one side, direct Ru-Ru one-electron hopping, on the other side, and O-assisted indirect hopping that leads to formation of molecular orbitals (MO), on the third side9. Ab initio calculations show that MOs appear to dominate in the last compound8. In the first two they are mostly suppressed, but at least in α–RuCl3 (and in a similar compound, Na2IrO3) they manifest themselves via an anomalously large third-neighbor coupling10.

MOs inevitably occur if transition metals with active t2g orbitals form a honeycomb lattice and t2g electrons can only hop via oxygen p orbitals11. In this case, the electronic structure problem maps onto that of the benzene molecule, essentially, a 6-member ring with nearest and next-nearest neighbor hoppings only (t1 and t2, respectively). The electronic structure then consist of four levels, A1g, E1u, E2g, B1u (E1u and E2g are doubly degenerate), formed by six molecular orbitals. Their energies are: E_{A1g} = 2(t_1' + t_2'), E_{E1u} = (t_1' - t_2'), E_{E2g} = -(t_1' + t_2'), and E_{B1u} = -2(t_1' - t_2')12. In this approximation, an electron occupying one of the MOs remains fully localized within one of the Ru hexagons, in spite of the fact that the lattice itself is uniform without any dimerization or clusterization13.

In real materials t_1'/3 - t_2' > 0 and the two highest MO levels, A1g and E1u, turn out to be nearly degenerate8,13. This is conducive for the spin-orbit coupling (SOC) and is the reason why the SOC is so efficient in the case of one t2g hole as in α–RuCl3 or in Na2IrO3. Moreover, for the whole range between the weak and the strong SOC limit the highest energy state (j_{eff} = 1/2 or 1) is half-filled and therefore Hubbard correlations are important.

Increasing number of holes, i.e. going from Ru3+ to Ru4+ makes E1u band half-filled. One may lift the degeneracy and gain some energy not due to the SOC or formation of molecular orbitals on hexagons, but dimerizing lattice (if the elastic energy penalty would not be too large). In this case the system gains considerable covalent energy due to direct d–d hopping (which may be large in the common edge geometry) and forms singlet dimers. This scenario is realized in Li3RuO28,9.

In the case of three t2g holes, Ru5+, we arrive at the situation, when A1g and E1u states are completely empty and the MOs with their large gap between the E1u and E2g states are energetically favorable. In the ionic approximation the energy gain is of the order of E_{E1u} - E_{E2g} \sim 2t'_1. Interestingly, the long range Neel antiferromagnetic (AFM) order does not destroy MOs, but even increases this energy gain8. These are the reasons why the MOs are so clearly seen in the band structure calculations in SrRu2O68.

While MO scenario has been very successful in explaining the physical properties of SrRu2O68, no direct observation of MOs has been effected so far, and other, albeit, in our opinion, less convincing, scenarios have been proposed14. In this paper we suggest that a combination of the spectroscopic techniques sensitive and insensitive to the dipole selection rules may provide direct evidence of the formation of MOs in SrRu2O6. These can be,
Figure 1: The nonmagnetic GGA band structure (upper panel) and total DOS obtained by GGA calculation for the Neel antiferromagnetic structure (lower panel). The contributions from different molecular orbitals are labeled according to Refs. [8, 12].

e.g., optical absorption and photoemission measurements (the latter are mostly determined by the electronic density of states, DOS), properly corrected for corresponding cross sections. We will show both analytically and numerically that the optical conductivity in the MO picture is dramatically different from the joint DOS, because of unusually restrictive optical selection rules.

Optical properties of molecular orbitals. The dipole selection rules prohibit optical transitions between states of the same parity. In the MO picture, this leaves four transitions: $B_{1u} \rightarrow E_{2g}$ (at $h\omega = t_1' - 3t_2'$), $E_{2g} \rightarrow E_{1u}$ (at $2t_1'$), $E_{1u} \rightarrow A_{1g}$ (at $t_1' + 3t_2'$), and $B_{1u} \rightarrow A_{1g}$ (at $4t_1'$). For the half filling, representative of SrRu$_2$O$_6$, that would generate two absorption peaks, corresponding to the $E_{2g} \rightarrow E_{1u}$ and $B_{1u} \rightarrow A_{1g}$ transitions, the latter at a twice larger energy than the former. However, there is an additional symmetry in the problem that forbids some of these transitions. Indeed, to assure a nonzero optical matrix element, the direct product of the representations of the initial and final states must contain a representation of the corresponding component of the dipole operator $p^\alpha$ (see, e.g., Ref. [15]). In the case of an ideal hexagon with the point group symmetry $D_{6h}$, the $p^x$ and $p^y$ components are transformed according to the $E_{1u}$ representation [16]. Since

\begin{align*}
B_{1u} \times A_{1g} &= B_{1u} \\
B_{1u} \times E_{2g} &= E_{1u} \\
E_{2g} \times E_{1u} &= B_{1u} + B_{2u} + E_{1u} \\
E_{1u} \times A_{1g} &= E_{1u}
\end{align*}

the point symmetry will suppress $B_{1u} \rightarrow A_{1g}$, but not $B_{1u} \rightarrow E_{2g}$, $E_{2g} \rightarrow E_{1u}$, and $E_{1u} \rightarrow A_{1g}$ transitions. In SrRu$_2$O$_6$ only $E_{2g} \rightarrow E_{1u}$ transitions are allowed, but in other hexagonal systems with different number of d electrons one may also expect $B_{1u} \rightarrow E_{2g}$ and $E_{1u} \rightarrow A_{1g}$ transitions. In the Appendix we show explicitly the matrix elements of $p^\alpha$ in the nearest- and next-nearest-neighbor tight binding approximation. The out-of plane matrix element is zero and corresponding optical transitions are absent in the MO approximation.

Together with the selection rules forbidding transitions between states with the same parity this additional selectivity offers a direct test of the MO scenario. It suggests that despite the double-hump structure of the DOS (Fig. 1), and, correspondingly, joint DOS, the optical absorption $\sigma(\omega)$ will have a one peak structure. Importantly, this is a qualitative, not quantitative test. While the exact positions and relative intensities of different peaks in DOS and $\sigma(\omega)$ may differ from the density function theory predictions (due to many-body effects), the general structure described above should qualitatively hold. This way one can directly verify by spectroscopic means (comparing optical, photoemission and inverse photoemission spectra) the concept of molecular orbitals.

DFT calculations of $\sigma(\omega)$ in SrRu$_2$O$_6$. We used the full-potential linearized augmented plane-wave (LAPW) method as implemented in the WIEN2k code [17] to calculate optical properties of SrRu$_2$O$_6$. We used the exchange-correlation potential of Ref. [18]. Integration was performed using the tetrahedron method on a mesh consisting of 4096 k-points in the Brillouin zone (BZ). The radii of atomic spheres were chosen to be 2.36, 1.93 and 1.72 a.u. for Sr, Ru, and O, respectively. The parameter of the plane wave expansion was set to 1.72 and 1.57 a.u. for Sr, Ru, and O, respectively. The number of $k$-points in the Brillouin zone (BZ) was 1000, 2000, and 1500 for Sr, Ru, and O, respectively. The parameter of the plane wave expansion was set to 2.36, 1.93 and 1.72 a.u. for Sr, Ru, and O, respectively.

\begin{align*}
\text{Im} \varepsilon_{\alpha\beta}(\omega) &= \frac{e^2}{\pi m^2 \omega^2} \sum_{c,v} \int \langle c, k|p^\alpha|v, k\rangle \langle v, k|p^\beta|c, k\rangle \\
&\times \delta(\epsilon_c(k) - \epsilon_v(k) - \hbar \omega) dk.
\end{align*}

where $m$ is the electron mass, $\{\alpha, \beta\} = \{x, y, z\}$, summation runs over all pairs of conduction (c) and valence (v) bands, and $\epsilon(k)$ gives the energy of corresponding band, while $\langle c, k|p^\alpha|v, k\rangle$ is the momentum operator's matrix
The peak also becomes sharper, reflecting the fact that, while suppressed in \( \text{Im} \) transitions, while the second peak of what more of the energy part of the corresponding manyfold has some-
tensor, are only two independent components in the dielectric
material, \( \epsilon_{\alpha\beta} \) (blue dotted line) and \( \epsilon_{\alpha\beta} \) (green dotted line). The imaginary part of the frequency-
dependent dielectric functions, \( \epsilon_{xx} \) (c) and \( \epsilon_{zz} \) (d) are shown by solid blue and green lines, correspondingly.

\[
J(\omega) = \sum_{c,v} \int \delta(\epsilon_c(k) - \epsilon_v(k) - \hbar\omega)dk,
\]

and the effects of the matrix elements. The \( J(\omega) \) obtained within the AFM GGA calculations is shown in Fig. 2(a). One observes a broad maximum in the joint DOS at 1.1–1.4 eV, due to the transitions between the \( E_{2g} \) and the \( E_{1u} + A_{1g} \) manifolds, and another maximum at 1.6–1.8 eV, due to the \( B_{1g} \to E_{1u} + A_{1g} \) transitions.

Since SrRu\(_2\)O\(_4\) has a trigonal crystal structure there are only two independent components in the dielectric tensor, \( \epsilon_{xx} \) and \( \epsilon_{zz} \). Fig. 2(c), (d) shows the calculated imaginary part of dielectric tensor components for SrRu\(_2\)O\(_4\). The amplitude of the \( \epsilon_{xx} \) component is about 8 times larger than the one of \( \epsilon_{zz} \), reflecting the fact that it only appears through deviations from the MO model. More interestingly, we observe that \( \text{Im} \epsilon_{xx}(\omega) \) has one strong peak “A”at \( \sim 1 \) eV, corresponding to \( E_{2g} \to E_{1u} \) transitions, while the second peak of \( J(\omega) \) is completely suppressed in \( \text{Im} \epsilon_{xx}(\omega) \) (Fig. 2(c)). Moreover, the first peak also becomes sharper, reflecting the fact that, while the \( E_{1u} \) and \( A_{1g} \) orbitals are strongly mixed, the higher energy part of the corresponding manyfold has somewhat more of the \( A_{1g} \) character, leaving less room for the \( E_{2g} \to E_{1u} \) transitions (remember that the \( E_{2g} \to A_{1g} \) transitions are forbidden by parity). This is exactly the qualitative effect we were looking for.

Note that if the matrix elements in Eq. 5 are set to a constant, \( \langle c | p | v, k \rangle = \text{const} \), then \( \omega \sigma(\omega) = \text{const} \cdot J(\omega) \), and, indeed often in computational papers joint DOS is compared to \( \omega \sigma(\omega) \). However, in real materials, \( |\langle c | p | v, k \rangle|^2/m \) usually grows with energy, roughly as \( (E_c - E_v) \) \( \delta \), so one can elucidate the suppression of particular transitions by comparing \( J(\omega) \) (Fig. 2(a)) with \( \sigma(\omega) \) (Fig. 2(b)).

It is worth noting that the structure of \( \text{Im} \epsilon_{xx}(\omega) \), which cannot be derived from the MO model, is nonetheless quite interesting. Indeed, the \( p^2 \) matrix element appears to be strongly enhanced in the very low frequency region, from the absorption edge to about 0.7 eV (the feature denoted “C” in Fig. 2(d)). The matrix elements for next feature, “D”, are suppressed by a factor of \( \approx 1.5 \) \( [2.2-2.3 \text{ in } \text{ Im} \epsilon_{xx}(\omega)/J(\omega)] \), and the high-energy region corresponding to the \( B_{1g} \to E_{1u} + A_{1g} \) transitions by an additional factor of \( \approx 1.8 \) (feature “E”).

Compared to iridates Na\(_2\)IrO\(_3\) and Li\(_2\)IrO\(_3\), often quoted in the context of MOs, SrRu\(_2\)O\(_4\) has a clear advantage in the sense that in iridates the MO picture is contaminated by a strong spin-orbit interaction that makes selection rules not well expressed. Indeed, while DFT calculations for iridates \( \delta \) agree well with experimental data, they cannot be interpreted in such a simple way as ours presented above, and cannot provide such a qualitative assessment of the MO picture.

**Conclusions.** We presented first principle calculations of the optical properties of the putative molecular orbital solid SrRu\(_2\)O\(_4\), as well as an analytical analysis of the optical absorption in the molecular orbitals model. We have identified a qualitative signature of molecular orbitals in optical properties. There are only four possible transitions allowed by the parity of the wave functions, but one of these parity-respecting optical transitions is suppressed by the point group symmetry, an unusual effect directly related to molecular orbitals. Different distortions of the crystal lattice, spin-orbit coupling, correlation effects etc. may completely suppress formation of molecular orbitals or strongly modify their structure. Our results show that one may use optical spectroscopy as a probe to study molecular orbital physics in transition metals oxides consisting of honeycomb layers.

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**Appendix: tight-binding treatment of optical properties in an ideal MO system.** While there are three \( t_{2g} \) orbitals...
on each Ru site, so that formally the tight-binding (TB) Hamiltonian is $18 \times 18$, only one $t_{2g}$ orbital per site contributes to any given MO \cite{23}, so the problem is reduced to $6 \times 6$. This allows us to map the full $t_{2g}$ problem onto a simple tight-binding model on an ideal hexagon with one s-orbital per site:

$$
H = \begin{pmatrix}
0 & t_1' & 0 & t_2' & t_1' \\
t_1' & 0 & t_1' & 0 & t_2' \\
0 & t_2' & 0 & t_1' & 0 \\
t_1' & 0 & t_1' & 0 & t_2' \\
0 & t_2' & 0 & t_1' & 0
\end{pmatrix},
$$

(6)

where $t_1'$ and $t_2'$ are the nearest and next-nearest neighbor hoppings via oxygen. Diagonalization of this Hamiltonian gives the spectrum described in the introduction.

The dielectric function $\Im \varepsilon_{\alpha\beta}(\omega)$ in Eq. (5) is determined by matrix elements of momentum operator $\langle \mathbf{c}, \mathbf{k} | p^\alpha | \mathbf{v}, \mathbf{k} \rangle$, which can be easily calculated using the matrix elements of the momentum operator in the initial TB basis of $s$–orbitals, defined as \cite{22}

$$
p_{ij} = \frac{iq}{\hbar} H_{ij} (\mathbf{R}_i - \mathbf{R}_j),
$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ are corresponding sites in the hexagon.

The optical transitions can be characterized by their oscillator strengths

$$
f_{cv} = \frac{2}{m} \frac{|\langle \mathbf{c}, \mathbf{k} | p^\alpha | \mathbf{v}, \mathbf{k} \rangle|^2}{E_v - E_v},
$$

which can be calculated in the basis of the MOs using eigenvectors of Eq. \ref{MOs} as a transformation matrix. In our model there are only three nonzero momentum operator matrix elements for arbitrary filling of the $d$ shell

$$
\begin{align*}
    f_{B_{1u}, E_{2g}} &= \frac{ma^2}{2\hbar^2} (t_1' - 3t_2'), \\
f_{E_{2g}, E_{1u}} &= \frac{ma^2}{\hbar^2} t_1', \\
f_{E_{1u}, A_{1g}} &= \frac{ma^2}{2\hbar^2} (t_1' + 3t_2'),
\end{align*}
$$

(7, 8, 9)

where $a$ is the distance between the nearest neighbors (3.0053 Å in SrRu$_2$O$_6$). This is in agreement with symmetry consideration presented above and results to a single optical $E_{2g} \rightarrow E_{1u}$ transition in SrRu$_2$O$_6$.

For other fillings, e.g., four or two electrons per transition metal site, one may expect two other transitions, which can be, however, suppressed not due to the symmetry or parity reasons, but because of a particular ratio between hopping parameters. E.g., in both RuCl$_3$ and SrRu$_2$O$_6$, as well as in Na$_2$IrO$_3$, the hopping $t_2'$ was found to be of order of $-t_1'/3$ \cite{11, 23}, which will result in a strong suppression of the $E_{1u} \rightarrow A_{1g}$ transition. If one chose $t_1' = 0.3$ eV and $t_2' = -0.1$ eV as it was estimated for SrRu$_2$O$_6$ by Wang et al. \cite{23}, then indeed $f_{E_{1u}, A_{1g}} \sim 0$, while $f_{E_{1u}, E_{2g}} = f_{E_{2g}, E_{1u}} = 0.356$.

This provides us with an interesting quantitative check of the validity of the MO model as regards to the full all-electron DFT calculations. A major integral characteristic of the optical absorption is given by the optical sum rule, conveniently written in terms of the effective number of electrons:

$$$
\int_{0}^{\infty} \omega \Im \varepsilon_{\alpha\alpha}(\omega) d\omega = \frac{2\pi^2 e^2}{m\Omega} N_{\text{eff}}(\omega),
$$

(10)

where $\Omega$ is the unit cell volume.

The $N_{\text{eff}}$ obtained within \textit{ab initio} calculation from $xx$ component of the dielectric function for SrRu$_2$O$_6$ is shown in Fig. 3 A plateau in $N_{\text{eff}}(\omega)$ curve clearly points to a presence of a single transition in agreement with model and symmetry considerations. For the energy of 2 eV $N_{\text{eff}}^{xx} = 1.44$ \cite{24}. In the MO model there is one allowed transition, $E_{2g} \rightarrow E_{1u}$, $f = 0.356$ (using the parameters presented above), and, accounting for symmetry and spin degeneracies, $N_{\text{eff}}^{\text{model}} = 4f = 1.424$, in excellent agreement with the DFT calculations.

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