Orbital Phase Perspective of Goodenough-Kanamori-Anderson Rules (GKA Rules) in Superexchange Interaction

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ABSTRACT. Goodenough-Kanamori-Anderson rules (GKA rules) in superexchange interaction discriminate the magnetic properties of two magnetic metal ions bridged with an anion. We propose here that the GKA rules can be explained in terms of the orbital phase continuity-discontinuity property of cyclic orbital interaction including direct metal-metal orbital interaction.

1. Introduction
Goodenough-Kanamori-Anderson rules (GKA rules) in superexchange interaction discriminate the magnetic properties, ferro- or antiferromagnetic, of two magnetic metal ions bridged with an anion. Anderson introduced the use of orbital drawings to interpret this behavior. He considered Kramers’ final expression for superexchange interaction. Kramers showed that the superexchange matrix $H_{tt'}$ could be given as the third-order perturbation term of the interaction (eq. 1):

$$H_{tt'} = \sum_{u, u'} \frac{\langle t|H^{tr}|u\rangle\langle u|H^{ex}|u'\rangle\langle u'|H^{tr}|t'\rangle}{(E_u - E_t)(E_{u'} - E_t)}$$  \hspace{1cm} (1)

where $t$ and $t'$ refer to the various initially degenerate spin states of the ground state, while $u$ and $u'$ are various states of the excited state, and $E_u$, $E_{u'}$ and $E_t$ are the corresponding energy levels.

From this equation, the interactions among the electronic configurations were determined by the Hamiltonians, which correspond to the energy term. These considerations led to a quantitative treatment of superexchange interactions as Anderson demonstrated. Initially, it focused on the number of electrons of the two metal ions bridged with an anion to determine the magnetic properties. The geometry, i.e., linear or perpendicular, also affects the magnetic properties of the bridged metal ions. However, it is still difficult to understand why such a combination of metal ions and oxide ion is required.

On the other hand, Inagaki considered the interaction among three systems, including the interaction among three bonds, which interact with each other to establish ring closure. To achieve stabilization by electron delocalization among the electronic configurations, Inagaki considered the third-order perturbation term for this interaction (eq. 2):

$$H_{OO'}^{(3rd)} = \sum_{K, L \neq K} \frac{(H_{OK} - S_{OK}H_{OO})(H_{LO} - S_{LO}H_{OO})(H_{KL} - S_{KL}H_{OO})}{(H_{OO} - H_{KK})(H_{OO} - H_{LL})}$$  \hspace{1cm} (2)
where $O$ is the electronic state for the ground state and $O'$ is that with some perturbation from the ground state. The electronic states for $K$ and $L$ are those with delocalization. Electrons are delocalized among the electronic states of $O$, $K$ and $L$.

Both discussions begin with the third-order perturbation term of the Hamiltonian. Thus, we expected that the orbital phase requirements for cyclic orbital interaction could also be applied to the stability of the superexchange system.

Here we describe our investigation into whether the GKA rules can also be explained from an orbital phase perspective. The requirements for phase-continuity in cyclic orbital interaction can be applied to the GKA rules.

2. Theoretical background for the requirements of orbital phase continuity

Inagaki was focused on the orbital, the wave character of electrons. He was interested in the phase, which refers to the relationship of the signs of the orbital functions, starting from this energy term. He initially evaluated the interaction among three systems in which electrons are delocalized among the electronic structures. Electrons can delocalize among three electronic configurations. He concluded that, for this effective cyclic delocalization to produce stabilization, the product of the overlaps between the electronic configurations should be positive (eq. 3):

$$S_{OK}S_{OL}S_{KL} > 0 \quad (3)$$

The overlaps among the electronic configurations can be approximated by the overlaps $S$ among the interacting orbitals; one donating (occupied) orbital $a$ and two accepting (vacant) orbitals $b^*$ and $c^*$. Thus, this equation should be rewritten in the case of interaction among one donating orbital and two accepting orbitals, as in eq. 4,
\[ S_{OK}S_{OL}S_{KL} \cong S_{ab*}S_{ac*}S_{bc*} > 0 \quad (4) \]

and in the case of two donating orbitals and one accepting orbital, as in eq. 5:

\[ S_{OK}S_{OL}S_{KL} \cong -S_{ab*}S_{ac*}S_{bc*} > 0 \quad (5) \]

From these equations, the following requirements for orbital phase continuity can be deduced: (i) Donating orbitals are out-of-phase; (ii) Donating and accepting orbitals are in-phase; (iii) Accepting orbitals are in-phase (Figure 1).

(i) Donating orbitals are out-of-phase.

(ii) A donating orbital and an accepting orbital are in-phase.

(iii) Accepting orbitals are in-phase.

(iv) For interaction among more than three systems, the cyclic orbital interaction is monocyclic, i.e., the bonds interact with adjacent bonds but only little or negligibly with those in a remote position.

(v) The cyclic orbital interaction must be divided into only two parts, the donor \( D \) and acceptor \( A \) parts, and not into four, six, or so on.

**Figure 1.** The requirements of orbital phase continuity for cyclic orbital interaction
These requirements are initially deduced from a consideration of three systems. However, Inagaki extended this idea from interaction among three systems to interaction among more than three systems. The requirements of orbital phase continuity for cyclic orbital interaction are still applicable if (iv) the cyclic orbital interaction is monocyclic, i.e., the bonds interact only with adjacent bonds but not with those in a remote position; and (v) the cyclic orbital interaction must consist of only one donor and one acceptor.

3. Application of the requirements of orbital phase continuity to the GKA rules from the an orbital phase perspective

Now, let us consider electron delocalization among electronic structures. As a three-system model, we use magnetic metal ions M1 and M2 bridged with a lone pair of anion A (Figure 2). Anion A has an occupied orbital a, and the two magnetic metal ions M1 and M2 have singly-occupied orbitals m1 and m2, respectively. Initially, ignoring the spin exchange, we consider α- and β-spin electrons separately. Inagaki discussed the stability of diradicals of the singlet and triplet. He concluded that the triplet diradicals are stable when the cyclic orbital interaction is phase-continuous, while the singlet diradicals should be phase-discontinuous to avoid the electronic configuration of a closed shell by electron transfer. Here we applied Inagaki’s discussions to the magnetic metal ion complex system. It matters whether, in Kramers’ final expression, the ground states t and t’ correspond to the same electronic state, the ground configuration G, and the excited states u and u’ refer to the electron-transferred configuration T_A-M1 and T_A-M2.
Figure 2. Delocalization among the electronic configurations in a triplet model.

First, we consider the case of the triplet state in which each metal ion has one $\alpha$-spin electron. In this system, three $\alpha$-spin electrons do not delocalize since the orbitals are all filled. In contrast, the $\beta$-spin electron can delocalize among the electronic configurations $G$, $Ta-M1$ and $Ta-M2$. For effective delocalization among the electronic configurations, the product of the overlaps $S$ among the electronic configurations should be positive to produce stabilization (eq. 6):

$$S_{GT(A-M1)}S_{GT(A-M2)}S_{T(A-M1)T(A-M2)} > 0 \quad (6)$$

According to Inagaki’s discussion, this approximates the product of the overlaps $S$ among the orbitals of the lone pair on A and the orbitals on the magnetic metal ions $m1^*$ and $m2^*$. Assuming overlap between two magnetic metal ions, i.e., interaction between two magnetic metal ions as suggested by Kanamori\textsuperscript{12}, we can obtain the following equation by overlap among the lone pair and the orbitals on the metal ions (eq. 7):

$$S_{GT(A-M1)}S_{GT(A-M2)}S_{T(A-M1)T(A-M2)} \cong S_{nAm1^*}S_{nAm2^*}S_{m1^*m2^*} > 0 \quad (7)$$

This equation is the same as that Inagaki deduced regarding the requirements of orbital phase continuity in cyclic orbital interaction. Thus, after Inagaki’s discussion, the requirements for orbital phase continuity can also be applied to a system with two magnetic ions bridged with an anion.
Inagaki also discussed the orbital phase theory for singlet diradicals. He concluded that a stable singlet should not satisfy the requirements for orbital phase continuity in cyclic orbital interaction (Figure 3), since it contains the electronic configuration of the closed shell, and electron transfer results in a loss of the diradical property. Figure 3 shows the electron transfer of $\beta$-spin electrons among the electronic configurations, with $\alpha$-spin electrons fixed in the case of a bridged magnetic metal complex. The magnetic property of the complex should be greatly diminished due to the electron-transferred electronic configuration of the closed shell, such as $T_{\text{M1-M2}}$ in Figure 3. Thus, cyclic orbital interaction should be phase-discontinuous, with the electron localized to maintain the diradical singlet state.

**Figure 3.** Delocalization among the electronic configurations in a singlet model.

In the case where the electronic configurations $t$ and $t'$ are not the same for Kramers’ final expression for superexchange interaction, we should consider the interaction among the electronic structures of $G_1$, $G_2$, $T_{\text{AM1}}$ and $T_{\text{AM2}}$ (Figure 4). The electronic configurations of $G_1$ and $G_2$ are degenerate. Usually, the orbitals for the lone pairs are lower in energy than those of the singly-occupied orbitals on the magnetic metal ions, so that the degenerate ground states $G_1$ and $G_2$ correspond to the degenerate lone pairs $n_1$ and $n_2$ of the anion species $A$. Note that there are no interaction between $n_1$ and $n_2$ since they are orthogonal. To consider the cyclic orbital interaction, the orbitals $m_1$ and $m_2$ must not interact with each other for various reasons, e.g., (i) the orbitals $m_1$ and $m_2$ are orthogonal; (ii) they cannot interact with each other due to symmetry.
reasons; or (iii) they are located far from each other so that interaction between them should be negligible.

![Figure 4](image.png)

**Figure 4.** Ground configuration for the complex of two magnetic metal ions M1 and M2 bridged by two degenerate lone pairs on A.

Note that the overlap between two orbitals is always less than 1, i.e., $|S_{ij}| < 1$. Thus, fewer corresponding orbitals in the cyclic orbital interaction are often preferred. The magnetism property must be evaluated with the total of every cyclic orbital interaction.

4. **Examples of application of the orbital phase theory for the GKA rules**

4.1 **A linear M-O-M complex at the triplet state**

Here, we discuss the stability of a triplet linear M-O-M complex (Figure 5). Suppose that both electrons on the magnetic metal ions consist of d-orbitals and have an $\alpha$-spin, so that $\alpha$-spin electrons do not delocalize since all the orbitals are occupied. In contrast, the $\beta$-spin electron of the p-orbital on the oxide ion can delocalize among occupied $n$ and vacant $m_1^*$ and $m_2^*$ orbitals. The requirements of orbital phase continuity suggest that all the phase relationships between two of the corresponding orbitals should be in-phase. This satisfies the GKA rules, and is the same picture as when we only consider orbital symmetry.
Figure 5. Cyclic orbital interaction in the linear complex of two magnetic metal ions M1 and M2 bridged by a lone pair n on an anion A.

4.2 An L-shaped M-O-M complex at the singlet state

In previous reviews, an L-shaped M-O-M complex was introduced as a stable singlet that shows magnetism (Figure 6). The two orbitals for the lone pairs on oxygen are orthogonal, so that they cannot interact with each other. If we ignore the interaction between two singly-occupied orbitals m1 and m2 on the metal ions M1 and M2, they respectively interact with two lone pairs separately, and the authors concluded that the singlet state should be stable. However, the two orbitals for the lone pairs are degenerate. This can also be explained by a drawing of two orbitals for the lone pairs rotated by 45°. However, no explanation is available for this condition. Thus, this explanation is still plausible with some assumptions with a fixed-orbital.

Figure 6. The orbital interaction of two independent M-O interactions due to two orthogonal lone-pair orbitals.
From an orbital phase perspective, the cyclic orbital interactions among $n_s-m_1-n_a-m_2^*$ and $n_s-m_1^*-n_a-m_2$ are phase-discontinuous when there is no direct $M_1-M_2$ interaction (Figure 7). In addition, out-of-phase combinations of a donor-acceptor orbital interaction between $m_1-m_2^*$ and $m_1^*-m_2$ should greatly suppress the electron delocalization. This phenomenon results in avoiding the electronic configuration of the closed shell by electron transfer. Furthermore, when there is some direct $M_1-M_2$ interaction, the phase-continuous cyclic orbital interactions among $n_a-m_1-m_2^*$ with one lone pair are always accompanied by the inevitable phase-discontinuous cyclic orbital interaction among $n_s-m_1-m_2^*$, since the lone pairs $n_s$ and $n_a$ have different symmetries. Delocalizations between $m_1-m_2^*$ and, similarly, $m_1^*-m_2$ are also suppressed. Thus, we can predict that the singlet state should be stable due to the phase-discontinuous cyclic orbital interaction.
Figure 7. Orbital phase perspective of phase-discontinuous cyclic orbital interaction in the L-shaped M-O-M singlet complex.

5. Conclusion

We demonstrated that cyclic orbital interaction controls the magnetic property of magnetic metal ions bridged with an anion. Anderson evaluated the magnetic property with the third-order perturbation term of Kramers’ final expression. This is the same equation as that Inagaki deduced from the requirements for orbital phase continuity in cyclic orbital interaction. Thus, the same discussion should be applied to Kramers’ equations, and the requirements for orbital phase
continuity should also be applicable when there is direct interaction between two magnetic metal ions. We showed examples of the GKA rules, which can be explained in terms of an orbital phase perspective. Such an orbital phase perspective means that we can consider the complex of two magnetic metal ions bridged not only with lone pairs but also with a vacant orbital, such as M-Li-M and M-B-M. For example, the linear M1-Li-M2 complex in the triplet state, where \( \mathbf{m1} \) and \( \mathbf{m2} \) consist of p-orbitals, satisfies the requirements of orbital phase continuity for cyclic orbital interaction (Figure 9). Thus, the triplet state should be stabilized with superexchange interaction. The application of these results to the design of new materials with unique magnetic properties is under investigation.

\[
\begin{array}{c}
\text{in-phase in-phase} \\
\text{out-of-phase} \\
\text{M1 Li M2} \\
\text{in-phase in-phase} \\
\text{out-of-phase} \\
\mathbf{m1} \quad \mathbf{p^*} \quad \mathbf{m2}
\end{array}
\]

**Figure 9.** Phase-continuous cyclic orbital interaction in a linear M-Li-M complex as a model for two magnetic metal ions bridged with a vacant p*-orbital in the triplet state.

AUTHOR INFORMATION

**Author Contributions**

All authors have approved this version of the manuscript.

REFERENCES


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Delocalization is suppressed by phase-discontinuous cyclic orbital interactions