Effective Coulomb interaction in multiorbital system

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Abstract. Transition metal atom generally takes various valences, and sometimes there are some ‘missing valences’, for example Fe usually takes 2+,3+ and 5+, but does not take other valences so often. We have calculated the atomic multiplet energies for the high-spin and low-spin configurations within the ligand-field theory and the Hartree-Fock approximation, and found that the Coulomb interaction energy \( U_{\text{eff}} \) becomes small when the valence is ‘missing’. In case \( U_{\text{eff}} < 0 \), this valence is not stable and segregates to other valences, and if the system is metallic, this cation site behaves as an attractive center between two conduction electrons. This result might explain one of the mystery of the iron-pnictide superconductor, e.g. the LDA+U approach can reproduce the experimental magnetic moment \( \sim 0.3\mu_B/\text{Fe} \) only when \( U < 0 \) is adopted. We have also investigated the effect of the distortion with symmetry lower than the regular octahedron. We have found that the value of \( U_{\text{eff}} \) increased in most cases, but in some special cases \( U_{\text{eff}} \) decreases and falls below the value \( U - 3J \), which is the least value of the undistorted system.

1. Introduction
Every atom in an ionic compound takes a valence, for example, Fe in FeO takes 2+ valence. Generally speaking, transition metal atom takes many valences, for example, Fe takes +2,+3,+5 valences. However, Fe scarcely takes +4 valence. In fact, SrFeO\(_3\) takes Fe\(^{4+}\) valence, but isovalent CaFeO\(_3\) and Sr\(_3\)FeO\(_7\) takes mixed valence\([1, 2, 3]\), i.e. Fe\(^{3+}\):Fe\(^{5+}\) = 1:1. This clearly shows that Fe\(^{4+}\) valence is not stable for some reason. This kind of ‘missing valence’ is also found in IIIB- or VB-group elements. For example, Bi in BaBiO\(_3\) does not takes Bi\(^{4+}\) but segregates into Bi\(^{3+}\) and Bi\(^{5+}\) valences. In this Bi site the electrons are ‘attractive’, because when the outermost valence (6s) electron is singly occupied (Bi\(^{4+}\)) it is unstable, and favors the (6s)\(^0\) (i.e. Bi\(^{3+}\)) and (6s)\(^2\) (i.e. Bi\(^{5+}\)) configurations. This attractive potential can induce the high-\( T_c \) superconductivity in (Ba,K)BiO\(_3\)\([4, 5, 6]\). However, why the missing valence takes place in the d-electron system is still not clear, because the Coulomb repulsion between the d-electrons is usually very large.

In this paper we consider a transition metal ion M surrounded by the \( A_6 \) octahedron, where A denotes an anion. We investigate that how the effective Coulomb interaction changes with varying \( n \), which is the number of d-electrons on the M site. This paper is organized as follows: In section 2, we calculate the atomic multiplet energies and the effective Coulomb interaction energies \( U_{\text{eff}} \) for the high-spin and low-spin configurations for the \( MA_6 \) octahedron using the Hartree-Fock approximation. General trend of \( U_{\text{eff}} \) for the number of d-electrons is discussed. In section 3, we take the distortion of the \( MA_6 \) octahedron into account and show that in some special cases, \( U_{\text{eff}} \) decreases and falls below the value \( U - 3J \), which is the least value of the undistorted system. Summary is given in section 4.
2. Octahedral case

Our treatment is based on the ligand-field theory. Since we are interested in the on-site effective Coulomb interaction of a MA₆ octahedron, we consider the following MA₆ cluster multiorbital d-p Hamiltonian:

\begin{align}
H &= H_t + H_U, \\
H_t &= \sum_{ij} \epsilon_{d} d_{i\sigma}^\dagger d_{j\sigma} + \sum_{j\sigma} \epsilon_{p} p_{j\sigma}^\dagger p_{j\sigma} + \sum_{ij\sigma} t_{ij} (d_{i\sigma}^\dagger p_{j\sigma} + h.c.) \\
H_U &= U \sum_i n_{i\uparrow} n_{i\downarrow} + U' \sum_{i\neq j} n_{i\uparrow} n_{j\downarrow} + J \sum_{ij} (d_{i\uparrow}^\dagger d_{j\uparrow} d_{j\downarrow}^\dagger d_{i\downarrow} + h.c.)
\end{align}

Here, \( \epsilon_d \) (\( \epsilon_p \)) denotes the one-electron energy of d- (p-) orbitals on the cation (anion). \( t_{ij} \) denotes the transfer energy between the \( i \)th d-orbital of cation and the \( j \)th p-orbital of anion. The suffix \( j \) also denotes the six anion sites. \( \sigma \) is the spin index. For simplicity, we use the Kanamori parameter \( U \), \( U' \) and \( J \) for the Coulomb and exchange interaction terms [7]. \( U \) and \( U' \) are the intra-orbital and inter-orbital Coulomb interaction energy. \( J \) is the exchange integral which leads to the Hund’s coupling. These parameters have a relation \( U' = U - 2J \).

First we consider the one-electron term \( H_t \). If the cation M is surrounded by A₆ octahedron, the degeneracy of the 5-fold d-orbitals is partially lifted by the hybridization with anion p-orbitals. The one-electron energies of the d-orbitals are

\begin{align}
\epsilon(d\gamma) &= \frac{1}{2} \{ \epsilon_d + \epsilon_p \} + \sqrt{ (\epsilon_d - \epsilon_p)^2 + 8(pd\sigma)^2 }, \\
\epsilon(d\epsilon) &= \frac{1}{2} \{ \epsilon_d + \epsilon_p \} + \sqrt{ (\epsilon_d - \epsilon_p)^2 + 8(pd\pi)^2 }
\end{align}

Here \( (pd\sigma) \) and \( (pd\pi) \) are the standard matrix elements between the neighboring d- and p-orbitals. Since \( (pd\sigma) > (pd\pi) \), \( \epsilon(d\gamma) > \epsilon(d\epsilon) \) if \( \epsilon_d > \epsilon_p \). This splitting \( \Delta_c \equiv \epsilon(d\gamma) - \epsilon(d\epsilon) \) leads to the octahedral crystal field 10\( D_q \) in the crystal field theory.

Next we consider the Coulomb interaction term \( H_U \). We adopt the Hartree-Fock approximation and the atomic energy for every \( d^{n+m} \) electron configuration \( (t_{2g})^{n_1}(t_{2g})^{m_1}(e_g)^{n_2}(e_g)^{m_2} \) can be obtained. The result is

\begin{align}
E((t_{2g})^{n_1}(t_{2g})^{m_1}(e_g)^{n_2}(e_g)^{m_2}) &= U \ast (\# \text{ of pairs which occupy a single orbital}) \\
&+ U' \ast (\# \text{ of pairs other than } U\text{-pairs}) \\
&- J \ast (\# \text{ of pairs which have the same spins})
\end{align}

We can calculate the Hartree-Fock energy for each spin configuration in this way. For a given \( n \) (number of d electrons), many spin and orbital configurations are possible, but as is well known, if the crystal field is octahedral, then the spin configuration of the ground state is either the high-spin (HS) state or the low-spin (LS) state. Which spin state is most stable depends on the magnitude of \( \Delta_c \). Table 1 shows the ground state energy for each \( d^n \) configuration. Here we set the origin of energy is at \( \epsilon(d\epsilon) \), and added the crystal-field splitting \( \Delta_c \) to the energy of \( \epsilon_d \) orbital. We also included the effect of the distortion of the octahedron, as described in section 3. For undistorted case, \( \Delta_c = \Delta_s = 0 \). In this case, the HS state becomes the ground state if \( \Delta_c < 5J \) for \( n=4,5 \) and \( \Delta_c < 4J \) for \( n=6,7 \), respectively. Therefore, if \( \Delta_c < 4J \) then the ground state is always the HS state, and if \( \Delta_c > 5J \) then the ground state is always the LS state.
Table 1. The ground state energy for each $d^n$ configuration. The intermediate spin configuration is $(t_{2g})^4(e_g)^1$ and $(t_{2g})^4(e_g)^2$ for $n=5$ and 6, respectively.

| $n$ | High spin | Low spin | Intermediate spin |
|-----|-----------|----------|-------------------|
| 1   | $-\Delta'_t$ | $U - 3J - \Delta'_t$ | $6U - 18J + \Delta_c - \Delta_t$ |
| 2   | $U - 3J - \Delta'_t$ | $10U - 20J - \Delta'_t$ | $10U - 24J + \Delta_c - \Delta_t - \Delta'_t$ |
| 3   | $3U - 9J$ | $10U - 20J - \Delta'_t$ | $15U - 30J$ |
| 4   | $6U - 18J + \Delta_c - \Delta_t$ | $15U - 30J$ | $15U - 33J + \Delta_c - \Delta_t - \Delta'_t$ |
| 5   | $10U - 30J + 2\Delta_c$ | $21U - 45J + \Delta_c - \Delta_t$ | $28U - 63J + 2\Delta_c$ |
| 6   | $15U - 38J + 2\Delta_c - \Delta'_t$ | $21U - 45J + \Delta_c - \Delta_t$ | $36U - 80J + 3\Delta_c - \Delta_t$ |

The effective Coulomb interaction $U_{\text{eff}}$ is written by

$$U_{\text{eff}}(n) = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n) \quad (9)$$

where $E(d^n)$ denotes the ground state energy within the $d^n$ configurations, given in Table 1.

Figure 1 shows the curves that effective Coulomb interaction $U_{\text{eff}}(n)=0$. Therefore, if $U/J$ is below these lines then $U_{\text{eff}}(n) < 0$, namely, this valence is unstable. In other words, this site behaves as an attractive potential for electron pairs. The region $U_{\text{eff}}(n) < 0$ is the shadow area in Fig.1. The upper panel is for the LS state. For the LS state, this $U_{\text{eff}}(n) < 0$ area is wide when $n=1, 2, 4, 5, 7, 9$. Or we can say that if $n=3, 6, 8$ then the valence is more stable. This is natural because in this case $t_{2g}$ and $e_g$ orbitals are ‘closed’. The lower panel is for the HS state. Similarly, the stable states are $n=3, 5, 8$, in which the $t_{2g}$ and $e_g$ orbital are ‘closed’. If we set $\Delta_c=0$, $U_{\text{eff}}(n) = 0$ curve has a large dip at $n=5$. In this case the 5-fold degeneracy of the d electrons are not lifted, and the only stable state is $n=5$. These results agree with the previous report[8] for the HS case.

Here we comment for the tetrahedral field. The crystal field induced by the tetrahedral configuration of anions has a duality with the octahedral one, i.e. 5-fold d-orbitals split into two-fold $e_g$ and three-fold $t_{2g}$ orbitals, and the energy of $e_g$ orbital is lower than that of $t_{2g}$. Therefore, we can use electron-hole symmetry for the tetrahedral field. For example, the Fe atom in LaOFeAs is surrounded by four As atoms, forming FeAs$_4$ tetrahedron. Its valence state is Fe$^{2+}$, i.e. the $d^6$ configuration. Using the electron-hole symmetry, it corresponds to the $d^4$ configuration in the octahedral ligand field. This $d^4$ configuration is the missing valence, as seen in CaFeO$_3$ and Sr$_3$Fe$_2$O$_7$[1, 2, 3]. Katayama-Yoshida et al. also claims that the $d^4$ state can be superconducting[6]. This concept of ‘missing valence’ can explain one of the mystery of iron-pnictide superconductor, which is that the LDA+U approach can reproduce the experimental magnetic moment $\sim 0.3\mu_B$/Fe only when $U < 0$ is adopted[9].

3. Distorted case

Next we consider a small D$_{4h}$ distortion of the MA$_6$ octahedron. In the crystal field theory, due to the anisotropic crystal field, the degeneracy of the $t_{2g}$ and $e_g$ orbitals are lifted. In view of the ligand-field theory, this energy splitting is ascribed as the anisotropic transfer matrix $(pd\sigma)$ and $(pd\pi)$ in eqn.(4) and (5). If the MA$_6$ octahedron is elongated along z-direction, then $(pd\sigma)$ and $(pd\pi)$ along z-direction decreases, the energy of the $d_{z^2}, d_{z^2}$ and $d_{yz}$ orbitals decreases, while
Figure 1. A phase diagram for $U$ vs $n$. Shaded region means $U_{\text{eff}}(n) < 0$, for $\Delta_c = 5J$ (HS) and $\Delta_c = 4J$ (LS). Only $U > 0$ has physical meaning.

$d_{x^2-y^2}$ and $d_{xy}$ do not change the energy. Anyway, we write this energy splitting as $\Delta_t$ for $e_g$ orbitals, and $\tilde{\Delta}_t'$ for $t_{2g}$ orbitals, respectively. If we fix the volume of the MA$_6$ octahedron, the center of gravity of the orbital energy is unchanged. And if the $t_{2g}$ and $e_g$ orbitals are partially occupied, then the system can gain energy by the distortion. As for the $e^1$ and $e^3$ configurations, the energy gain is $\Delta_t = \Delta_t/2$. As for the $t_{2}^1$ and $t_{3}^2$ ($t_{2}^1$ and $t_{3}^2$) configurations, the collapse (elongation) of the MA$_6$ octahedron lowers the electronic energy, and the energy gain is $\Delta_t' = \frac{5}{3}\Delta_t$. This is the Jahn-Teller effect[10]. We included this energy for $E(d^n)$, and the result is shown in Table 1. In case of $\Delta_t \neq 0$ and $\Delta_t' \neq 0$, the intermediate spin (IS) state can become the ground state for $n=5,6$. The energy $E(d^n)$ of IS states are also shown in Table 1.

Next we calculate $U_{\text{eff}}(n)$. In case of the undistorted octahedron, the least value of $U_{\text{eff}}(n)$ is $U - 3J$. However, in case of the distorted octahedron, $U_{\text{eff}}(n)$ can become further smaller. We consider the case that the ground states of $d^4$ and $d^6$ are the HS state, and the ground state of $d^8$ is the LS state. From $E(d^n)$ given in Table 1, these conditions are described as follows:

$$\Delta_t + \Delta_t' < 6J - \Delta_c \hspace{1cm} (10)$$
$$\Delta_t' < 10J - 2\Delta_c \hspace{1cm} (11)$$
$$-\Delta_t + \Delta_t' < 5J - \Delta_c \hspace{1cm} (12)$$
$$\Delta_t' < -8J + 2\Delta_c \hspace{1cm} (13)$$
$$\Delta_t + \Delta_t' < -3J + \Delta_c \hspace{1cm} (14)$$

If we put a value on $\Delta_c$, these inequalities give a region in the $(\Delta_t, \Delta_t')$ plane. In this case $U_{\text{eff}}(5) = U + 12J - 3\Delta_c - \Delta_t$, and if $f = 3\Delta_c + \Delta_t - 15J > 0$, $U_{\text{eff}}(5)$ becomes lower than $U - 3J$. Figure 2 shows this region for $\Delta_c = 4.9J$. In this case we obtain $f = 0.8J$ at $(\Delta_t, \Delta_t') = (1.1J,0)$.

Figure 2. The region which satisfies eqn.(10-14) in the $(\Delta_t, \Delta_t')$ plane. For example, (13) shows the line which satisfies eqn.(13). In the shaded area $f = 3\Delta_c + \Delta_t - 15J$ is positive, and $U_{\text{eff}}(5)$ is lower than $U - 3J$. In this figure we set $\Delta_c = 4.9J$. 

\begin{align*}
\Delta_t + \Delta_t' &< 6J - \Delta_c \\
\Delta_t' &< 10J - 2\Delta_c \\
-\Delta_t + \Delta_t' &< 5J - \Delta_c \\
\Delta_t' &< -8J + 2\Delta_c \\
\Delta_t + \Delta_t' &< -3J + \Delta_c 
\end{align*}
However, since $\Delta_t$ and $\Delta'_t$ both come from the same distortion of the octahedron, $\Delta_t$ and $\Delta'_t$ are not independent each other. The relation between $\Delta_t$ and $\Delta'_t$ changes when we change $\epsilon_d$, $\epsilon_p$, and the wave functions of anions. Thus we cannot determine the minimum value of $U_{\text{eff}}(5)$, but it can still be smaller than $U - 3J$, which is the least value of any $U_{\text{eff}}(n)$ in the undistorted case.

Similarly, in the case that the ground states of $d^5$ is the HS state, and the ground state of $d^6$ and $d^7$ are the LS state, $U_{\text{eff}}(6)$ becomes below $U - 3J$ in some region in the $(\Delta_t, \Delta'_t)$ plane. Interestingly, if we set $\Delta_c = 4.1J$, this region becomes identical with the region of Fig.2. More generally speaking, the $(\Delta_t, \Delta'_t)$ region which makes $U_{\text{eff}}(6) < U - 3J$ corresponds to the region which makes $U_{\text{eff}}(5) < U - 3J$, if we perform the transformation $\Delta_c \rightarrow 9J - \Delta_c$.

4. Summary

Using the Hartree-Fock approach, we have calculated the effective Coulomb interaction energy $U_{\text{eff}}(n)$ in the octahedral and distorted-octahedral ligand field. In the octahedral ligand field, the ground state is the either high-spin state or the low-spin state, depending on the strength of the octahedral crystal field. In the distorted-octahedral ligand field, intermediate spin can also become the ground state. Moreover, as for the $d^5$ and $d^6$ case, $U_{\text{eff}}(n)$ can become lower than $U - 3J$, which is the least value of $U_{\text{eff}}(n)$ for the octahedral ligand field.

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