Applicability of approximated effective Hamiltonian method to first-principle study on magnetic clusters

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Abstract. In the first-principle study on the magnetic interactions in transition metal dimer complexes, we have shown that the effective Hamiltonian method can be effectively utilized (J. Phys.: Condens. Matter 23 375502). To extend our method to clusters with higher nuclearity, some approximations are needed since the number of the parameters of the effective Hamiltonian is too large. In the present paper, how to decrease the number of parameters of our effective Hamiltonian and how to determine the parameters from the calculations based on the density functional theory are shown. Then, approximated Hamiltonians are examined for its applicability in the first-principle study on the magnetic interactions in transition metal clusters. From the calculations of the Ti$_2$Cl$_6^-$ cluster whose parameters of the effective Hamiltonian are already determined, it is found that small differences caused by the symmetry of the each orbital can be neglected and not only kinetic exchange but also potential exchange terms are needed for quantitative calculation of the magnetic susceptibility. The appropriately approximated Hamiltonian reproduces the global structure of the lower energies so as to realize the nature of the magnetic interaction.

1. Introduction
First-principal studies on the magnetic interactions of transition metal complexes have been attracted much interest for long years. In the case of orbitally non-degenerate metal ions, the density functional theory (DFT) is often used to calculate the coupling constant of the isotropic Heisenberg model Hamiltonian. For example, the broken symmetry approach [1–7] and the DFT-based ligand field model method [8–11] are known as methods to obtain the coupling constant. Conversely, for orbitally degenerate metal systems, quantitative study of the magnetic properties becomes complicated because the Hamiltonian of the system must be written by not only spin operators but also operators acting within the orbital spaces.

Recently, we have investigated the magnetic interactions in the orbitally degenerate transition metal dimer complexes [12,13]. In our calculations, an effective Hamiltonian method is effectively utilized. Note that the term “effective Hamiltonian” in the present paper is used in the extensive interpretation as have been mentioned in ref. [12, 13] (In the field of the molecular magnetism, the effective Hamiltonian often means the expression of the Hamiltonian by irreducible tensor operators and spin operators, which has been applied to a kinetic exchange interaction for a pair of orbitally degenerate metal ions [14–20]). By using a set of one-electron localized orbitals as basis of the effective Hamiltonian, we can analyze the magnetic interactions on the basis of the Anderson theory [21]. In the straightforward extension of our methodology to more than...
trimer complexes, the number of the parameters of the effective Hamiltonian matrix will increase drastically and it becomes laborious to evaluate all parameters by DFT calculations, so that it is needed to approximate the parameters.

In the present paper, we consider how to decrease the number of parameters of the effective Hamiltonian and show how to determine the parameters using DFT calculations. Then we discuss the applicability of approximated Hamiltonians to the investigations of the magnetic interactions between transition metal complexes. For this purpose, we consider the Ti$_2$Cl$_9$ - cluster [12, 22, 23] whose parameters of the effective Hamiltonian are already determined in ref. [12]. Then, another simple example that orbitally non-degenerate trimer complex is also presented.

2. Effective Hamiltonian

To investigate the magnetic interactions using the effective Hamiltonian, we need to generate a set \( L \) of the local orbitals by the DFT calculations. However, the DFT calculations are carried out using the delocalized molecular orbitals, and it is hard to directly provide the local orbitals. Therefore, the local orbitals are defined by the linear combinations of molecular orbitals.

Here, for example, we consider the M$_2$X$_3$ type cluster which contains two octahedra sharing a face so that it has \( D_{3h} \) cluster symmetry [12]. The molecular orbitals are generated in the average-of-configuration (AOC) calculation [10,11], where the AOC is the spin-restricted system in which all molecular orbitals are equally occupied. Then we obtain six molecular orbitals \( \alpha'_1 \) and \( \alpha'_2 \) which belong to the \( A'_1 \) and \( A'_2 \) terms under \( D_{3h} \) cluster symmetry, respectively, and the doubly degenerate molecular orbitals \( (\xi, \eta) \) and \( (\epsilon, \zeta) \) which belong to the \( E'' \) and \( E' \) terms, respectively. The set \( L \) of the local orbitals is composed of the following orbital functions:

\[
\begin{align*}
  a_1 &= \frac{1}{\sqrt{2}} (\alpha'_1 + \alpha'_2), \quad x_1 = \frac{1}{\sqrt{2}} (\xi + \epsilon), \quad y_1 = \frac{1}{\sqrt{2}} (\eta - \zeta), \\
  a_2 &= \frac{1}{\sqrt{2}} (\alpha'_1 - \alpha'_2), \quad x_2 = \frac{1}{\sqrt{2}} (-\xi + \epsilon), \quad y_2 = \frac{1}{\sqrt{2}} (-\eta - \zeta),
\end{align*}
\]

where the orbital \( a_{1,2} \) belongs to the \( A_1 \) term and doubly degenerate orbitals \( x_{1,2} \) and \( y_{1,2} \) belong to the \( E \) term under the \( C_{3v} \) site symmetry of the cluster. Generally in the cases of the complexes with other symmetries, it is possible to represent the local orbitals by linear combinations of molecular orbitals which is generated by the AOC calculations.

It is assumed that a d-electrons in the transition metal clusters occupies one of the local orbitals \( i \in L \). Then, the effective Hamiltonian can be represented by the following form:

\[
H_{\text{eff}} = \sum_{i,j \in L} \sum_{\sigma} f_{ij} c_{i,\sigma}^\dagger c_{j,\sigma} + \sum_{i,j,k,l \in L} \sum_{\sigma,\sigma'} g_{ijkl} c_{i,\sigma}^\dagger c_{j,\sigma'}^\dagger c_{k,\sigma'} c_{l,\sigma} = H_1 + H_2, \quad (2)
\]

where \( c_{i,\sigma} \) and \( c_{i,\sigma}^\dagger \) denote annihilation and creation operators of an electron on a local orbital \( i \ (\in L) \) with a spin \( \sigma \ (= \pm 1/2) \). The “effective” Hamiltonian means that the exchange and correlation effects on the electron interaction are renormalized in the elements \( f_{ij} \) and \( g_{ijkl} \) of the one-body operator \( H_1 \) and the two-body operator \( H_2 \), respectively. Note that the elements \( g_{ijkl} \) are not two-body integrals of \( 1/|r_1 - r_2| \) because the renormalized Coulomb interaction contains a screening effect.

The number of the parameters of the above Hamiltonians is too large to extend to the complexes of higher nuclearity. In the case of the Ti$_2$Cl$_9$ - cluster, the effective Hamiltonian has 30 independent parameters (table 1). The notations of the Coulomb and exchange integrals are summarized in table 2, where the intra-atomic and inter-atomic Coulomb integrals are given by \( j_{\phi \phi'} = \int dV_1 V_2 \phi_1 (r_1) \phi'_2 (r_2) H_2 \phi_1 (r_1) \phi'_2 (r_2) \) and \( J_{\phi \phi'} = \int dV_1 dV_2 \phi_1 (r_1) \phi'_2 (r_2) H_2 \phi_1 (r_1) \phi'_2 (r_2) \), respectively, and the intra-atomic and inter-atomic

\[
\begin{align*}
  a_1 &= \frac{1}{\sqrt{2}} (\alpha'_1 + \alpha'_2), \quad x_1 = \frac{1}{\sqrt{2}} (\xi + \epsilon), \quad y_1 = \frac{1}{\sqrt{2}} (\eta - \zeta), \\
  a_2 &= \frac{1}{\sqrt{2}} (\alpha'_1 - \alpha'_2), \quad x_2 = \frac{1}{\sqrt{2}} (-\xi + \epsilon), \quad y_2 = \frac{1}{\sqrt{2}} (-\eta - \zeta),
\end{align*}
\]
exchange integrals are given by \( K_{\phi\phi'} = \int dV \int dV' \phi_i(r_1)\phi_i'(r_2) \mathcal{H}_2 \phi_i(r_1)\phi_i(r_2) \) and \( K_{\phi\phi'} = \int dV \int dV' \phi_i(r_1)\phi_i'(r_2) \mathcal{H}_2 \phi_i(r_1)\phi_i(r_2) \), respectively.

To decrease the number of the parameters of the effective Hamiltonian, we approximate the parameters on the basis of our previous result [12] as follows: (i) The two-body effects in the transfer integrals are neglected, for example, the values of \( T_{aa} = t_{aa} + \int d\tau_1 \int d\tau_2 \phi_i(r_1)\phi_i'(r_2) \mathcal{H}_2 \phi_i(r_1)\phi_i(r_2) \) and \( T_{ae} = t_{ae} + \int d\tau_1 \int d\tau_2 \phi_i(r_1)\phi_i'(r_2) \mathcal{H}_2 \phi_i(r_1)\phi_i(r_2) \) are equal to \( t_a \). Note that \( t_a \) and \( t_e \) are discriminated from one-body transfer integrals \( t_{aa} \) and \( t_{ee} \), because the two-body effects will be renormalized in the evaluation procedure of the parameters. (ii) The intra-atomic integrals are reduced to three kinds of integrals, namely, intra-atomic Coulomb integral between identical orbitals \( (j_{aa} = j_{ee} = j) \) and deferent orbitals \( (j_{ae} = j_{ee} = j') \) and intra-atomic exchange integral \( (k_{ae} = k_{ee} = k) \). This approximation corresponds to the small distortion of the \( C_{3h} \) site symmetry from the \( O_h \) symmetry. (iii) All inter-atomic Coulomb integrals are equal \( (J_{aa} = J_{ae} = J_{ee} = J) \) and all inter-atomic exchange integrals are equal \( (K_{aa} = K_{ae} = K_{ee} = K) \). The distance between two metals is enough large to neglect small differences caused by the symmetry of the each orbital. (iv) All the other integrals which are related to two-electron hopping terms, for example, \( K_{111}^{22} = \int d\tau_1 \int d\tau_2 \phi_i(r_1)\phi_i'(r_2) \mathcal{H}_2 \phi_i(r_1)\phi_i(r_2) \) and \( Y_{111}^{22} = \int d\tau_1 \int d\tau_2 \phi_i(r_1)\phi_i'(r_2) \mathcal{H}_2 \phi_i(r_1)\phi_i(r_2) \) are set to zero. Thus the approximated effective Hamiltonian \( \mathcal{H}_{\text{eff,1}} \) is written in terms of the creation and annihilation operators as follows:

\[
\mathcal{H}_{\text{eff,1}} = \sum_{m=1,2} \sum_{\sigma = \pm 1/2} \left( \varepsilon_{a} c_{a\sigma}^\dagger c_{a\sigma} + \varepsilon_{e} \sum_{\gamma = x,y} c_{\gamma \sigma}^\dagger c_{\gamma \sigma} \right) + \sum_{\sigma = \pm 1/2} \left( t_{a} c_{a1\sigma}^\dagger c_{a2\sigma} + t_{e} \sum_{\gamma = x,y} c_{\gamma 1\sigma}^\dagger c_{\gamma 2\sigma} + \text{h.c.} \right) + \sum_{m=1,2} \left( (j - J) \sum_{\gamma = a,x,y} n_{\gamma m} n_{\gamma m} + (j' - J') \sum_{\gamma = a,x,y} n_{\gamma m} n_{\gamma m} \right) + k \sum_{m=1,2} \sum_{\gamma \neq \gamma'} \sum_{\gamma''} c_{\gamma \sigma}^\dagger c_{\gamma' \gamma'' \sigma} c_{\gamma'' \gamma'' \sigma} + K \sum_{\gamma,\gamma' = a,x,y} \left( c_{\gamma 1\sigma}^\dagger c_{\gamma 2\sigma}^\dagger c_{\gamma 1\sigma} c_{\gamma 2\sigma} + \text{h.c.} \right)
\]
Table 2. Coulomb and exchange integrals between the local orbitals $\phi_k$ and $\phi'_l$.

| $\phi_k$ | $\phi'_l$ |
|---------|-----------|
| $\psi_1$ | $j_{aa}^{\psi_1} j_{ae}^{\psi_1} j_{ae}^{\psi_1} j_{ae}^{\psi_1}$ |
| $\psi_2$ | $j_{aa}^{\psi_2} j_{ae}^{\psi_2} j_{ae}^{\psi_2} j_{ae}^{\psi_2}$ |

where $n_{\sigma \pi} = \sum_{\sigma=\pm 1/2} C_{\alpha \sigma}^l C_{\beta \sigma}^m$.

We also consider another approximated Hamiltonian $H_{\text{eff},2}$ which is the Hamiltonian eq.(3) with putting $K = 0$. The inter-atomic exchange integrals $K$ correspond to the potential exchange terms in the magnetic interaction, so that only the kinetic exchange term is contained in $H_{\text{eff},2}$.

To determine the matrix elements of the effective Hamiltonian, the DFT-based ligand field model is utilized. By using the energy expectation values $E_{\text{DFT}}(\Psi_i)$ in states $\Psi_i$ which is one of the Slater determinants (SD) of the molecular orbitals, the Coulomb and exchange integrals between two molecular orbitals are able to be determined as shown in ref. [12]. For the effective Hamiltonian without above approximation, $H_{\text{eff}}$, the all parameters are explicitly related to the Coulomb and exchange integrals between the molecular orbitals. Therefore, in ref. [12], at first we have determined the Coulomb and exchange integrals between the molecular orbitals by using the least square fitting, and then we have obtained the parameters of the effective Hamiltonian. Conversely in the cases of the approximated Hamiltonians $H_{\text{eff},1}$ and $H_{\text{eff},2}$, the relations between the parameters of the effective Hamiltonians and the integrals between molecular orbitals does not hold. Therefore, the parameters of $H_{\text{eff},1}$ and $H_{\text{eff},2}$ are needed to directly determine from the least square fitting of the energy expectation values $E_{\text{DFT}}(\Psi_i)$ as follows.

By a unitary transformation $U$, the basis of the effective Hamiltonian composed of the local orbitals can be transformed to that of molecular orbitals. The diagonal elements of the transformed matrix, $[U H_{\text{eff},1,2} U^{-1}]_{ii}$, correspond to the energy expectation values $E_{\text{DFT}}(\Psi_i)$. From the least square fitting, namely, minimizing the following value

$$\sum_i \left\{ \left[ U H_{\text{eff},1,2} U^{-1} \right]_{ii} - E_{\text{DFT}}(\Psi_i) \right\}^2,$$

the parameters are determined.

3. Numerical results

The following DFT calculations have been carried out with the ADF 2010.02 program package using a triple-$\zeta$ basis set with polarization function. We utilize the PBE0 functional which is hybrid 25% Hartree-Fock (HF) exchange form of PBE functional [24] proposed by Ernzerhof-Scuseria [25] and by Adamo-Barone [26].

By minimizing eq.(4), we obtain the parameters of $H_{\text{eff},1}$ and $H_{\text{eff},2}$ as shown in table 3. All values reasonably coincide with the values of the parameters of $H_{\text{eff}}$ obtained in ref. [12].

Figure 1 shows the energy expectation values of the single SD’s of molecular orbitals obtained from the effective Hamiltonians $H_{\text{eff}}$, $H_{\text{eff},1}$ and $H_{\text{eff},2}$ with parameters in table 3. All effective Hamiltonians can be reproduce the values of $E_{\text{DFT}}(\Psi_i)$, although small disagreements appear in the result of $H_{\text{eff},1}$ and $H_{\text{eff},2}$.

The energy eigenvalues obtained by numerically diagonalization of the effective Hamiltonians are shown in figure 2. First excitation energy of $H_{\text{eff},1}$ accurately coincide with the results...
Table 3. Numerical values of parameters in eV obtained from least square fit.

|                  | $e_e - e_a$ | $T_{aa}$ | $T_{ae}$ | $T'_{ae}$ | $T_{ee}$ | $T'_{ee}$ | $k_{ae}$ | $k_{ee}$ |
|------------------|-------------|----------|----------|-----------|----------|-----------|----------|----------|
| ref. [12]        | 0.0515      | -0.5083  | -0.4765  | 0.0222    | 0.0240   | 0.0502    | 0.3710   | 0.3717   |
| $\mathcal{H}_{\text{eff.1}}$ | 0.0578      | $t_a = -0.3932$ | $t_e = 0.0471$ | $k = 0.3872$ |
| $\mathcal{H}_{\text{eff.2}}$ | 0.0578      | $t_a = -0.3932$ | $t_e = 0.0471$ | $k = 0.4108$ |

|                  | $j_{aa} - j_{aa}$ | $j_{ee} - j_{ee}$ | $j_{ae} - j_{ae}$ | $j'_{ee} - j'_{ee}$ | $K_{aa}$ | $K_{ae}$ | $K_{ee}$ | $K'_{ee}$ |
|------------------|------------------|------------------|------------------|------------------|---------|---------|---------|---------|
| ref. [12]        | 3.4142           | 3.5530           | 2.5594           | 2.5645           | 0.0543  | 0.0104  | 0.0135  | 0.0317  |
| $\mathcal{H}_{\text{eff.1}}$ | $j - J = 3.7317$ | $j' - J' = 2.6412$ | $K = 0.0236$ | $K = 0$ |
| $\mathcal{H}_{\text{eff.2}}$ | $j - J = 3.7789$ | $j' - J' = 2.6884$ | $K = 0$ |

|                  | $F_{11}^{22}$ | $K_{11}^{21}$ | $K_{11}^{12}$ | $K_{11}^{21}(=K_{11}^{21})$ | $Y_{11}^{22}$ | $X_{11}^{12}$ | $X_{11}^{12}(=X_{11}^{21})$ |
|------------------|---------------|---------------|---------------|--------------------------|---------------|---------------|--------------------------|
| ref. [12]        | 0.0129        | -0.0157       | 0.0030        | 0.0015                   | 0.0042        | -0.0109       | 0.0013                   |
| $\mathcal{H}_{\text{eff.1,2}}$ | 0             | 0             | 0             | 0                        | 0             | 0             | 0                        |

Figure 1. Energy expectation values of the single SD's of molecular orbitals calculated by DFT, and that of the systems $\mathcal{H}_{\text{eff}}$, $\mathcal{H}_{\text{eff.1}}$ and $\mathcal{H}_{\text{eff.2}}$ with the parameters given in table 3.

Figure 2. Energy eigenvalues of the system described by the effective Hamiltonian $\mathcal{H}_{\text{eff}}$, $\mathcal{H}_{\text{eff.1}}$ and $\mathcal{H}_{\text{eff.2}}$.

of ref. [12]. As a result, the magnetic susceptibility (figure 3) is similar to that of $\mathcal{H}_{\text{eff}}$ and experimental result. At higher temperatures, both $\chi_\parallel(T)$ and $\chi_\perp(T)$ become larger than that of $\mathcal{H}_{\text{eff}}$ because the multiplet energy of the $^3\!A''_g$ term becomes lower compared with that of $\mathcal{H}_{\text{eff}}$. In the system $\mathcal{H}_{\text{eff.2}}$, the inter-atomic exchange integrals are neglected, namely, the ferromagnetic
potential exchange interaction is neglected. Therefore, the excitation energy from the singlet ground state to the triplet excitation state become larger, and thus the temperature dependences of the magnetic susceptibilities are flattened as shown in figure 3. The potential exchange term is not negligible to describe the magnetic interaction in the Ti$_2$Cl$_3$ cluster because this cluster is composed of face sharing octahedra.

Here, we present another example, trinuclear copper cluster called TrisOH [27–30]. This cluster contains three Cu$^{2+}$ ions bridged by OH$^-$ as shown in figure 4. The ligand field from surrounding ions are so strong that the orbital degeneracy of the d-electrons in Cu$^{2+}$ ions is resolved. The effective Hamiltonian contains too many parameters to determine its value by the least square fitting. Therefore, we consider the simplest model to describe the d-electrons in this cluster, the Hubbard model Hamiltonian:

$$ H = t \sum_{\langle i,j \rangle} c_i^\dagger c_j + U \sum_i n_{i\uparrow} n_{i\downarrow}. $$

Form the second order perturbation of the transfer integral $t$, the coupling constant of the spin Hamiltonian $J_s = \frac{8}{t^2} U$. Assuming the three copper ions form equilateral triangle, the local orbitals $a_i$ ($i = 1, 2, 3$) are represented by the following linear combinations of molecular orbitals $\psi_i$ ($i = 1, 2, 3$):

$$ a_1 = \frac{1}{\sqrt{3}} \psi_1 + \sqrt{\frac{2}{3}} \psi_2, \quad a_2 = \frac{1}{\sqrt{3}} \psi_1 - \frac{1}{\sqrt{6}} \psi_2 + \frac{1}{\sqrt{2}} \psi_3, \quad a_3 = \frac{1}{\sqrt{3}} \psi_1 - \frac{1}{\sqrt{6}} \psi_2 - \frac{1}{\sqrt{2}} \psi_3, \quad (5) $$

where $\psi_1$ and $\{\psi_2, \psi_3\}$ belong to $A_1$ term and $E$ term under $C_{3v}$ cluster symmetry, respectively.

By the least square fitting of the energy expectation values of the single SD’s of molecular orbitals $E_{\text{DFT}}(\Psi_i)$, we obtain the parameters of the Hubbard model Hamiltonian as $t = 0.0972$ eV and $U = 5.212$ eV. We obtain the calculated value of the coupling constant $J_s$ as 116 cm$^{-1}$ which is near the experimental value 104.7 cm$^{-1}$ [27–30]. The coupling constant is also calculated by the broken symmetry approach as $J_s = 111$ cm$^{-1}$ [28]. In contrast to the broken symmetry approach which can be evaluated only the coupling constant, important information of $t$ and $U$ for the electronic structure in the metal cluster can be obtained by using our effective Hamiltonian method. This simple Hubbard model for this system does not precisely reproduce each one of the calculated energies $E_{\text{DFT}}(\Psi_i)$, but the model reproduces the global structure of the lower energies so as to realize the nature of the magnetic interaction.
4. Summary
In the present paper, the applicability of our approximated effective Hamiltonian to the first-principle study of the magnetic interactions have been examined. From the calculation of the Ti$_2$Cl$_9$ cluster, it was found that small differences caused by the symmetry of the each orbital can be neglected and not only kinetic exchange but also potential exchange terms are needed for quantitative calculation of the magnetic susceptibility. The multiplet energy levels can be roughly estimated using approximated effective Hamiltonian. For the case of TrisOH, the Hubbard Hamiltonian is sufficient to obtain the coupling constant. Applications of our effective Hamiltonian method to clusters with higher nuclearity will be present in near future.

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