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Construction of model Hamiltonians for the transition-metal impurities via the QSGW method

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Abstract

We show a method to construct model Hamiltonians for describing multiplet excitations of transition-metal impurities. Here we treat systems of a transition metal substituting Al in $\alpha$-Al$_2$O$_3$. Based on the results of quasiparticle self-consistent $GW$ (QSGW) calculations for the systems, we construct the model Hamiltonian of 3$d$ orbitals. We determine not only the crystal field parameters but also the parameters of effective interactions based on the theoretical correspondence between QSGW calculations and the model Hamiltonian, and investigate systematic change of these parameters. Finally, we discuss the structures of multiplet excitations calculated from these parameters.

Keywords: first-principles calculations, QSGW method, multiplet excitations, transition metals
1 INTRODUCTION

Light emission from luminescent centers of transition metals (TMs) is one of the most important physical phenomena for white LED applications [1–6] as well as the tunable laser applications [7]. Ruby, Cr\(^{3+}\)-doped \(\alpha\)-\(\text{Al}_2\text{O}_3\) (\(\alpha\)-\(\text{Al}_2\text{O}_3\);\(\text{Cr}^{3+}\)), was utilized for the first solid-state laser developed by Maiman [8]. \(\alpha\)-\(\text{Al}_2\text{O}_3\);\(\text{Ti}^{3+}\) is widely used these days, while other TM elements in \(\alpha\)-\(\text{Al}_2\text{O}_3\) are also potentially applicable to the solid-state lasers [9–12]. Possible combinations of TMs with host materials are extensively examined [7]. To assist such examination by the computational material design (CMD), we have to figure out a reliable method to compute properties that control the light emission. Such a method should be applicable to any systems on the same footing without choosing computational settings by hand.

The luminescent centers are described well as the multiplets of 3\(d\) electrons. Excitations among these multiplets cause light emission. The spectrum of ruby is analyzed by the multiplet excitations [13, 14]. If we assume the 3\(d\) electrons of the luminescent center are well isolated from the other electrons, we can regard the system as TM 3\(d\) electrons embedded in the crystal field (CF) with effective interactions between the electrons.

In order to treat the multiplets, we have to use a method to go beyond the mean-field theories which describe electronic structure by the single Slater determinant. A possible method is based on the idea of the configuration-interaction (CI) [15]. For instance, Cr\(^{3+}\) or V\(^{3+}\) in \(\alpha\)-\(\text{Al}_2\text{O}_3\) were examined by the single-electron cluster calculation [16, 17], where only a few positions of bands or lines of the spectrum were obtained from analytic relation between the molecular-orbital energies and the multiplet energies. Duan et al. calculated the whole multiplet structure of ruby while their method could not be applicable to the calculation of the emission spectra [18]. Ogasawara et al. developed a hybrid method combining density functional theory (DFT) and the CI to obtain multiplet structures [19–21]. However, such methods based on CI have some problems to treat TM in solids. At first, we have to choose the size of clusters including TM at the center; such a choice is not easy technically, therefore unsuitable for CMD. In addition, if the size of the cluster is not large enough, we may not reproduce properties of hosts such as band gaps. This can cause a problem because we should describe the levels of 3\(d\) electrons relative to the band structure of host materials so as to describe the localization of the 3\(d\) electrons. In fact, we saw a large reduction of the spin-orbit coupling because of the delocalization of 4\(f\) eigenfunction when Eu is doped into GaN [22].

On the other hand, we may describe the electronic structure of the ground state even in a mean-field theory by a Slater determinant; in the case of atom, we expect that \(L_z\) and \(S_z\) of the Slater determinant should be consistent with the Hund rule. Kitaoka et al. performed the constraint DFT in LSDA+\(U\) resulting \(\sim 1.0\text{eV}\) for transition energy from \(4\text{A}_{2g}\) to \(2\text{E}_g\) states of \(\alpha\)-\(\text{Al}_2\text{O}_3\);\(\text{Cr}^{3+}\) while experimental value is around 1.8\text{eV} [23]. Na-Phattalung et al. obtained the transition energies 2.12 \text{eV} between the state \(2\text{E}_g\) and
the \( ^4 \text{A}_{2g} \) ground state in the hybrid functional \([24]\). However, both LSDA+\( U \) and the hybrid functional are somehow ambiguous to describe their correct ground states. In addition, results can be changed so much depending on the semi-empirical parameters included in the theories.

We have another first-principles approaches to determine only the parameters of CF. Haverkort et al. demonstrated ab initio cluster calculations including the full Coulomb interactions using the localized Wannier orbitals based on non-magnetic GGA electronic structure \([25]\). Kuzian et al. performed calculations on local magnetic centers with open 3\( d \) and 5\( f \) shells using similar Wannier orbital method \([26]\). Though their approaches gave good agreement with the experimental CF parameters, their methods are not satisfactory from the view of CMD because the adopted Coulomb parameters are those of free ion or experimental analysis.

In this paper, we present a method to determine the model Hamiltonian of 3\( d \) electrons of the luminescent centers based on the quasiparticle self-consistent \( GW \) (QSGW) calculations \([27–30]\). This method, originally developed by Suzuki et al. \([22]\) for 4\( f \) multiplets, virtually overcomes problems in previous works mentioned above. The model Hamiltonian was made from the terms of the CF and the screened Coulomb interactions.

To determine the model Hamiltonian (in other words, to determine parameters in the Hamiltonian), we start from our core idea. The core idea is in the requirement that “QSGW applied to the model Hamiltonian” should reproduce the one-body Hamiltonian of QSGW. This is possible because the idea of QSGW is applicable not only to the first-principles calculations but also to the model Hamiltonians. This core idea satisfies a renormalization principle that the model Hamiltonian should be closer to the original Hamiltonian when we utilize larger model space, e.g., including electrons of ligands. Roughly speaking, QSGW is a screened Hartree-Fock method where the size of screening is self-consistently determined without parameters by hand. Not only the screened Coulomb interaction within atoms corresponding to \( U \) of LSDA+\( U \) but also that between different atoms (often referred to as \( V \)) are automatically included. Thus, QSGW is advantageous rather than the hybrid functionals where we use a kind of Fock term with a fixed size of screening.

In practice, we use QSGW80 instead of QSGW. QSGW80 means that we use 80 \% QSGW + 20 \% LSDA for exchange-correlation terms. This is to avoid the overestimation of exchange effects due to the underestimation of screening effects for the interaction between electrons. A justification of QSGW80 is given in Ref. \([31]\), where we show that the vertex correction adding to the random phase approximation (RPA) used in QSGW enhances the screening effects by \( \sim 20 \% \). QSGW80 is a quick remedy including the vertex correction. We had observed that QSGW80 works well for a wide range of materials.\([30]\) Applying QSGW80 to TM-doped Al\(_2\)O\(_3\) is justified by the fact that QSGW80 describes not only \( sp \)-block semiconductors/insulators but also TM oxides very well. For instance, the spin waves are well reproduced for TM and TM oxides
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[32, 33]. We will show our results for TM-doped $\alpha$-Al$_2$O$_3$ systematically in order to confirm the performance of our method.

2 RESULTS AND DISCUSSION

In Sec. 2.1, we will explain our model Hamiltonian $\mathcal{H}$ specified by six parameters. In Sec. 2.2, we will show our main results of the six parameters calculated by the method which is introduced at the end of Sec. 1. The details of the method will be described in Sec. 3. To have a better understanding of the results, we will show the calculated parameters of free ions in Sec. 2.3.

2.1 Model Hamiltonian

In the similar manner with Ref. [22], we assume our model Hamiltonian $H$ specified by six parameters as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{C}},$$

where we have $\mathcal{H}_0$ for the spherical mean-field term, $\mathcal{H}_{\text{CF}}$ for CF, $\mathcal{H}_{\text{C}}$ for the effective Coulomb interaction. The dimension of $\mathcal{H}$ is $10C_N$, where $N$ is the number of 3d electrons. Since we do not take into account hybridization with the other electrons, we put 3d electrons at the zero level, that is, we set $\mathcal{H}_0 = 0$. The spin-orbit coupling is neglected because it affects little in the 3d orbitals system.

$\mathcal{H}_{\text{CF}}$ and $\mathcal{H}_{\text{C}}$ are given as

$$\mathcal{H}_{\text{CF}} = \sum_{mm'} \sum_{\sigma\sigma'} (h^{C_3v}_{\text{CF}})^{mm'}_{mm'} \hat{c}^\dagger_{m\sigma} \hat{c}^\dagger_{m'\sigma'},$$

$$h^{C_3v}_{\text{CF}} = -7D_{\sigma}O_2^0 - (14Dq + 21D\tau) O_4^0 + 2\sqrt{70}Dq (O_4^3 - O_4^{-3}),$$

$$\mathcal{H}_{\text{C}} = \frac{1}{2} \sum_{m_1m_3m_2m_4} \sum_{\sigma\sigma'} g_{m_1m_2m_3m_4} \hat{c}^\dagger_{m_1\sigma} \hat{c}^\dagger_{m_2\sigma'} \hat{c}_{m_4\sigma'} \hat{c}_{m_3\sigma}. $$

Here $m$ and $\sigma$ are for the magnetic quantum number and spin. $\hat{c}_{m\sigma}$ is the electron-annihilation operator. We represent $\mathcal{H}_{\text{CF}}$ with the Stevens’ operator $O_i^0$ [34], where we have the octahedral CF parameter $Dq$, the trigonal CF parameters $D_{\sigma}$ and $D_{\tau}$ [35] in addition because a TM ion replacing Al$^{3+}$ in $\alpha$-Al$_2$O$_3$ has $C_{3v}$ symmetry.

$\mathcal{H}_{\text{C}}$ in Eq. (4) is given with

$$g_{m_1m_2m_3m_4} = (-1)^{m_1-m_3} \delta_{m_1+m_2,m_3+m_4} \sum_{p=0}^l F^{2p} c^{2p}(m_1,m_3)c^{2p}(m_2,m_4),$$

where we have the Gaunt coefficients $c^{2p}(m, m')$ and the Slater-Condon parameters $F^{2p}$ [36]. $F^{2p}$ are given by the modified Slater-Condon parameters $F_0$, ...
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\[ F_2, \text{ and } F_4 \] as

\[
\begin{align*}
F^0 &= F_0, \\
F^2 &= 49F_2, \\
F^4 &= 441F_4.
\end{align*}
\]  

(6)

Note that \( U \) and \( J \) in [38] are related as \( U = F_0 \) and \( J = (7/2)F_2 + (63/2)F_4 \).

As a summary, \( \mathcal{H} \) is determined by the six parameters, \( F_0, F_2, F_4, Dq, D\sigma, \) and \( D\tau \) via \( \mathcal{H}_C \) and \( \mathcal{H}_{CF} \). As shown in Sec.3, we can determine the six parameters by our matching method after we perform QSGW80 calculations for \( \alpha-Al_2O_3:TM \).

2.2 Calculated parameters in the model Hamiltonian

In Table 1, we show calculated six parameters in \( \mathcal{H} \) for TM\(^{2+}\), TM\(^{3+}\), or TM\(^{4+}\) in \( \alpha-Al_2O_3 \), together with the experimental ones derived from optical measurements. In cases as Fe\(^{3+}\), we have two results corresponding to two converged results of QSGW, the high spin (HS) and the low spin (LS) states. In cases shown in square brackets such as [Fe\(^{3+}\)(d\(^5\))...], we found that 3d occupied states are strongly hybridized with the oxygen 2\( p \) orbitals. Our current model including only 3d orbitals may not be suitable enough for such cases. Thus, data lines with square brackets should be taken as less reliable cases. The calculated DOS in supplementary information shows the size of hybridization (Figs. S2-S8).

For Cr\(^{3+}\), \( F_0 = 4.98 \) eV in QSGW80 is very different from 0.80 eV in LSDA. This is because LSDA does not include onsite non-locality of one-body potential which is usually described by \( U \) of LSDA+U. This causes the difference of positions of 3d bands (see Figs. 3 in Sec.3). On the other hand, we see just \(~10\%\) differences as for \( F_2, F_4 \) and 10\( Dq \) between QSGW80 and LSDA. This means that difference in the screening effects given in QSGW80 and in LSDA does not affect to the anisotropic part of interactions so much. \( F_2 = 0.108 \) eV in QSGW80 gave a little better agreement with experimental values 0.136, or 0.133 eV than \( F_2 = 0.092 \) eV in LSDA. Since we usually expect that varieties of experimental values fall between QSGW80 and LSDA, we feel still remaining difference of 0.136-0.108=0.028 eV sounds a little too large while we have no definite idea to identify the main cause of the difference. A cluster theory \([21]\) shows better agreement with experiments, however, it is not simple enough as a method for CMD. Note that we cannot determine \( F_2 \) and \( F_4 \) for the case where all of the majority spin states are filled completely (HS with d\(^5\)) because degeneracy of 3d bands in QSGW80 gives insufficient pieces of information for determining all the six parameters. We have room to improve this point by adding bias fields in QSGW80 to have enough pieces of information.

Let us compare our results of QSGW80 with experimental analysis. In the case of V\(^{3+}\) as well as Cr\(^{4+}\), we see good agreement as in Cr\(^{3+}\). To make an overall comparison, we plot the data in Table 1 (only lines without square
Table 1 Calculated six parameters of TM ions in $\alpha$-Al$_2$O$_3$. The number of 3$d$ occupancy is shown as $d^m$ ($m = 1, \ldots, 9$). $N^\uparrow - N^\downarrow$ mean the spin moment in $\mu_B$. HS is for high spin, LS for low spin. Some of ‘—’ for $d^5$ means no data in our current treatment. The systems with bracket means strong hybridization with 2$p$ orbitals (see text).

<table>
<thead>
<tr>
<th>TM ion</th>
<th>$N^\uparrow - N^\downarrow$</th>
<th>method</th>
<th>$F_0$ (eV)</th>
<th>$F_2$ (eV)</th>
<th>$F_4$ (eV)</th>
<th>$10Dq$ (eV)</th>
<th>$D\sigma$ (eV)</th>
<th>$D\tau$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{2+}$ ($d^2$)</td>
<td>2</td>
<td>QSGW80</td>
<td>4.46</td>
<td>0.093</td>
<td>0.0070</td>
<td>2.68</td>
<td>-0.005</td>
<td>0.000</td>
</tr>
<tr>
<td>V$^{2+}$ ($d^3$)</td>
<td>3</td>
<td>QSGW80</td>
<td>4.92</td>
<td>0.087</td>
<td>0.0104</td>
<td>2.64</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Cr$^{2+}$ ($d^4$) HS</td>
<td>4</td>
<td>QSGW80</td>
<td>5.50</td>
<td>0.166</td>
<td>0.0081</td>
<td>2.10</td>
<td>0.281</td>
<td>-0.023</td>
</tr>
<tr>
<td>Cr$^{2+}$ ($d^4$) LS</td>
<td>0</td>
<td>QSGW80</td>
<td>4.44</td>
<td>0.250</td>
<td>0.0135</td>
<td>2.35</td>
<td>0.029</td>
<td>0.009</td>
</tr>
<tr>
<td>Mn$^{2+}$ ($d^5$) HS</td>
<td>5</td>
<td>QSGW80</td>
<td>9.55</td>
<td>—</td>
<td>—</td>
<td>1.82</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Fe$^{2+}$ ($d^5$) HS</td>
<td>4</td>
<td>QSGW80</td>
<td>5.78</td>
<td>0.151</td>
<td>0.0148</td>
<td>1.97</td>
<td>0.144</td>
<td>-0.030</td>
</tr>
<tr>
<td>[Co$^{2+}$ ($d^7$) HS</td>
<td>3</td>
<td>QSGW80</td>
<td>6.00</td>
<td>0.195</td>
<td>0.0119</td>
<td>2.11</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>[Ni$^{2+}$ ($d^8$) HS</td>
<td>2</td>
<td>QSGW80</td>
<td>5.49</td>
<td>0.142</td>
<td>0.0130</td>
<td>2.44</td>
<td>0.004</td>
<td>0.007</td>
</tr>
<tr>
<td>[Cu$^{2+}$ ($d^9$) HS</td>
<td>1</td>
<td>QSGW80</td>
<td>5.54</td>
<td>0.220</td>
<td>0.0112</td>
<td>2.13</td>
<td>-0.115</td>
<td>-0.008</td>
</tr>
<tr>
<td>Ti$^{3+}$ ($d^1$)</td>
<td>1</td>
<td>QSGW80</td>
<td>4.59</td>
<td>0.095</td>
<td>0.0124</td>
<td>2.73</td>
<td>0.004</td>
<td>-0.001</td>
</tr>
<tr>
<td>V$^{3+}$ ($d^2$)</td>
<td>2</td>
<td>QSGW80</td>
<td>4.77</td>
<td>0.117</td>
<td>0.0099</td>
<td>2.40</td>
<td>-0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Cr$^{3+}$ ($d^3$)</td>
<td>3</td>
<td>QSGW80</td>
<td>4.98</td>
<td>0.108</td>
<td>0.0113</td>
<td>2.17</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn$^{3+}$ ($d^4$) LS</td>
<td>0</td>
<td>QSGW80</td>
<td>4.15</td>
<td>0.256</td>
<td>0.0112</td>
<td>2.04</td>
<td>-0.021</td>
<td>0.005</td>
</tr>
<tr>
<td>Fe$^{3+}$ ($d^5$) LS</td>
<td>1</td>
<td>QSGW80</td>
<td>4.00</td>
<td>0.141</td>
<td>0.0054</td>
<td>1.25</td>
<td>-0.199</td>
<td>0.013</td>
</tr>
<tr>
<td>Ni$^{3+}$ ($d^6$) HS</td>
<td>5</td>
<td>QSGW80</td>
<td>10.6</td>
<td>—</td>
<td>—</td>
<td>1.19</td>
<td>—</td>
<td>—</td>
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<tr>
<td>[Co$^{3+}$ ($d^7$) HS</td>
<td>4</td>
<td>QSGW80</td>
<td>5.06</td>
<td>0.170</td>
<td>0.0150</td>
<td>1.19</td>
<td>-0.133</td>
<td>0.021</td>
</tr>
<tr>
<td>Ni$^{3+}$ ($d^7$) LS</td>
<td>3</td>
<td>QSGW80</td>
<td>5.72</td>
<td>0.129</td>
<td>0.0107</td>
<td>1.21</td>
<td>-0.152</td>
<td>0.027</td>
</tr>
<tr>
<td>V$^{4+}$ ($d^1$)</td>
<td>1</td>
<td>QSGW80</td>
<td>3.85</td>
<td>0.116</td>
<td>0.0132</td>
<td>2.68</td>
<td>0.021</td>
<td>-0.002</td>
</tr>
<tr>
<td>Cr$^{4+}$ ($d^2$)</td>
<td>2</td>
<td>QSGW80</td>
<td>3.61</td>
<td>0.119</td>
<td>0.0116</td>
<td>2.52</td>
<td>0.010</td>
<td>0.000</td>
</tr>
<tr>
<td>Mn$^{4+}$ ($d^3$)</td>
<td>3</td>
<td>QSGW80</td>
<td>5.56</td>
<td>0.103</td>
<td>0.0124</td>
<td>2.23</td>
<td>0.006</td>
<td>-0.001</td>
</tr>
<tr>
<td>Fe$^{4+}$ ($d^4$) LS</td>
<td>2</td>
<td>QSGW80</td>
<td>3.60</td>
<td>0.141</td>
<td>0.0100</td>
<td>2.12</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Co$^{4+}$ ($d^5$) HS</td>
<td>5</td>
<td>QSGW80</td>
<td>6.87</td>
<td>—</td>
<td>—</td>
<td>1.33</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Co$^{4+}$ ($d^5$) LS</td>
<td>1</td>
<td>QSGW80</td>
<td>3.34</td>
<td>0.226</td>
<td>0.0124</td>
<td>2.57</td>
<td>-0.503</td>
<td>0.051</td>
</tr>
</tbody>
</table>
Fig. 1 The parameters of effective Coulomb interactions and cubic CF interaction as a function of 3d electron number in \( \alpha\text{-Al}_2\text{O}_3 \) compared with those in free ions. The trends of four parameters are shown in these figures: a and e: The modified Slater-Condon parameter \( F_0 \); b and f: \( F_2 \); c and g: \( F_4 \); and g: cubic CF parameter 10Dq. Left figures show results of TM ions in \( \alpha\text{-Al}_2\text{O}_3 \), and right ones of free TM ions. In the all figures, following symbols are employed: red circles denote the QSGW80 of TM\( ^{2+} \), blue triangles the QSGW80 of TM\( ^{3+} \), and open symbols experimental analysis. Circles express TM\( ^{2+} \), and triangle TM\( ^{3+} \).
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brackets) in Figs. 1a, b, c, and d. \( F_0 \) shows monotonic behavior except \( d^5 \) where we have fewer screening effects due to the missing of spin-preserving transitions among 3d electrons. For \( F_2 \) in cases without square brackets, we have agreements within \( \sim 20\% \). For example, \( V^{2+} \) for \( F_2 \) has agreement with the difference only 0.112eV(Expt.)/0.087eV(QSGW80). We see similar agreements for \( F_4 \). On the other hand, the experimental 10\( D_q \) for TM\(^{2+} \) show too much difference; experimental value is only \( \sim 70\% \) of QSGW values; 1.69eV/2.64eV for \( V^{2+} \) and 1.25eV/1.82 eV for Mn\(^{2+} \). A reason might be in the background charge used for our supercell (see Sec.3) to keep the given valency. In fact, we may expect TM\(^{2+} \) replacing Al\(^{3+} \) should introduce one half of oxygen vacancy near TM\(^{2+} \). This may reduce the octahedral symmetry, resulting in smaller \( e_g-t_{2g} \) splitting effectively.

We calculated the multiplet excitation energies by the exact diagonalization of \( \mathcal{H} \) with the parameters in Table 1. Fig. 2 is the Tanabe-Sugano diagram of \( \alpha\text{-Al}_2\text{O}_3:Cr^{3+} \), showing multiplet energies relative to the ground state \( 4A_{2g} \) as a function of 10\( D_q \). We show a label of multiplet for each branch. Fig. 2a is for the set of parameters of the QSGW80, Fig. 2b for the set of the experimental analysis \([46]\) as well. We see how the difference of the sets results in the difference of the multiplet excitations. Because of the non-negligible size of \( D\sigma = -0.057 \) eV, Fig. 2b shows minor splittings of branches as well as kinky behaviors of branches near 10\( D_q=0 \) whereas Fig. 2a do not show them.

Considering the fact that 10\( D_q \) are similar in Fig. 2a and Fig. 2b, differences of excitation energies should be mainly from \( F_2 \) and \( F_4 \). In fact, the difference of excitation energies (\( \sim 20\% \)) is almost corresponding to the error ratio of \( F_2 \) between experimental analysis and QSGW80, (0.136 – 0.108)/0.136 \( \sim \) 0.21, and that of \( F_4 \), (0.131 – 0.113)/0.113 \( \sim \) 0.15. In contrast, we see quartets \( 4T_{2g} \) and \( 4T_{1g} \) shown by green are less affected by the ratio. Only multiplets starting from \( 2G \) show strong non-linear behaviors as a function of 10\( D_q \). This results in a little larger difference of \( 2T_{2g} \). We have to pay attention to this type of error enhancement mechanism, that is, small differences in parameters can cause large errors. We show the Tanabe-Sugano diagrams for other TM ions in the supplementary information (Figs. S11-S16).

2.3 Calculated parameter of free ions

To have a better understanding of Table 1, we have applied our method to free TM ions. See computational settings in Sec.3. Since we have no CF, we set \( D_q = D\sigma = D\tau = 0 \).

Figs. 1e, f, and g show \( F_0, F_2, \) and \( F_4 \) for TM\(^{2+} \) and TM\(^{3+} \), together with experimental values \([37]\). Our results follow the Hund rule. \( F_0 \) shows a monotonic increase along the atomic number for the former half up to \( d^4 \) as Fig. 1a. This monotonic behavior is due to two contributions, the orbital shrinkage and the screening effect in the RPA. The size of \( F_0 \) is completely different from the case of \( \alpha\text{-Al}_2\text{O}_3:TM \) due to the screening effect.

Our calculation for \( F_2 \) based on QSGW80 reproduced the experimental values very well, especially from \( d^3 \) to \( d^7 \). This will support the reliability of
Fig. 2 Tanabe-Sugano diagram of Cr$^{3+}$ in α-Al$_2$O$_3$ ($d^3$). a: Calculation results by using the parameters given by the QSGW80. The axis $10D_q=0$ roughly corresponds the energy splitting of free ion states, namely multiplet structure without CF parameters. Multiplet symbols are assigned to each state and these are distinguished by spin multiplicity of doublet (red) and quartet (green). The symbols of irreducible representation of $O_h$ symmetry are shown in the QSGW80 multiplet structure. The red broken line means $10D_q$ value of the QSGW80. The intersection points of this red broken line and black curves give multiplet states. b: Result of experimental analysis. The horizontal axis in b is opposite to that in a. Corresponding multiplet states between a and b are connected by dotted lines.

Our method. On the other hand, we have some systematic disagreements for $F_2$: we see a jump between the former half and the latter half. We have no definite idea to explain the disagreements. $F_2$ in α-Al$_2$O$_3$ are a little lower than free ions because of anisotropic screening effects.

2.4 Summary

We have developed a new method to determine parameters in the effective Hamiltonian of 3$d$ electrons for the α-Al$_2$O$_3$:TMs based on the results of QSGW80. Determined parameters are consistent with experimental results. Moreover, our method was able to predict some reasonable systematic trends of effective interactions in α-Al$_2$O$_3$ as well as in TM free ion states, and reduction of effective Coulomb parameters in α-Al$_2$O$_3$ compared to those of free ion.

However, we have faced some problems of hybridization of TM 3$d$ orbitals with 2$p$ orbitals of surrounded oxygen atoms, insufficient information to determine parameters, and shifts of $10D_q$ due to background charge. For constructing a more precise model, the effect of 2$p$ orbitals of oxygen atoms around TM ions should be included in the future. Consideration of delocalization effects may improve especially the estimation of CF parameters.
We evaluated the mechanism of numerical errors as shown in Fig. 2. A little numerical difference in the parameters can change the energy ordering of multiplets. This may indicate that our method should be combined with some data assimilation techniques for obtaining reliable results for CMD.

3 METHOD

After showing computational setting of our first-principles calculations in Sec. 3.1, we illustrate the determination of parameters in model Hamiltonian of 3d orbitals in TMs in Sec. 3.2.

3.1 First-principle calculations

$\alpha$-$\text{Al}_2\text{O}_3$ has a corundum structure: oxygen atoms around aluminum ion are located at the vertices of a distorted octahedron. When an aluminum ion is substituted by a TM ion, its structure should be relaxed to become a more stable one. For structure optimization, we prepared a $2 \times 2 \times 2$ rhombohedral supercell of $\alpha$-$\text{Al}_2\text{O}_3$ substituted one aluminum ion with a TM ion for structure relaxation. Both the lattice volume and atomic positions were optimized using the projected augmented wave method with revised Perdew-Burke-Ernzerhof functional for solids implemented in the QUANTUM ESPRESSO package [49, 50]. The cut-off energy is 60Ry, and $k$-mesh is $6 \times 6 \times 6$. Since the optimized structure differs from the original one mainly around TM ions, we extract the local $1 \times 1 \times 1$ structure around TM ion from the supercell and assume $C_{3v}$ symmetry around the TM ion. The charge neutrality is conserved by imposing background charges to the cell: Positive (Negative) charge $+e$ ($-e$) was added in the case of TM$^{4+}$ (TM$^{2+}$). This optimized crystal structure was employed for the QSGW80 calculation (see results in Table S1).

The first-principles QSGW calculations, as well as the LDA calculations for comparison, were performed with the ecalj package at http://github.com/tkotani/ecalj. We used $k$-point mesh $8 \times 8 \times 8$ for the band structure part while $4 \times 4 \times 4$ for the self-energy part. We used $10 \times 10 \times 10$ for producing MLWFs of 3d orbitals.

3.2 Determination of parameters in model Hamiltonian

Based on the core idea given in the introduction, we have to determine the six parameters so that the one-body Hamiltonian of QSGW for 3d electrons $H_{3d}^{QSGW}$ is reproduced when we apply QSGW to $H$. Note that we can apply QSGW even to the model Hamiltonian.

Here we make a further approximation for simplicity. We first apply the first-principles method, QSGW80 to the systems where we substitute one of Al sites in the host material $\alpha$-$\text{Al}_2\text{O}_3$ with one TM ion. From this result of QSGW80, we obtain $H_{3d}^{QSGW}$ in the procedure of the maximally localized Wannier functions (MLWFs) [51]. We expect QSGW80 gives a good description of the screening effect [31]. Then we determine the six parameters so that $H_{3d}^{QSGW}$
is in agreement with the result calculated by the Hartree-Fock approximation (HFA) applied to $\mathcal{H}$. This is under our assumption that applying HFA to $\mathcal{H}$ gives virtually the same results as applying QSGW to $\mathcal{H}$. We think this assumption is reasonable since we expect $\mathcal{H}$ show a small screening effect in the RPA.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{The electronic structure and parameter determination of $\alpha$-Al$_2$O$_3$:Cr$^{3+}$. a and d: The band structure of majority and minority spins together with DOS calculated in LSDA. Red lines are for the MLWFs of Cr 3d orbitals. Red filled region is for the partial DOS of Cr 3d; b and e: in QSGW80; c and f: Red lines in the left panel of c, f (MLWF panel) show the eigenvalues of $\mathcal{H}_{\text{QSGW}}$ (see text). In the right panel (HFMH panel), the contributions of six parameters are resolved (see text). Inset illustrates $D_\sigma$ and $D_\tau$ split $t_{2g}$ into $e_g$ and $a_{1g}$.}
\end{figure}

Let us illustrate the case of Al$_2$O$_3$:Cr$^{3+}$. In Figs. 3 b (majority spin) and e (minority spin), we show the band structure of $\alpha$-Al$_2$O$_3$:Cr$^{3+}$ in QSGW80, together with that in LSDA as references (a and d). We use a supercell of $\alpha$-Al$_2$O$_3$ with one Cr substituting Al (see Fig. S1). QSGW80 gives the band gap of 9.2eV for Al$_2$O$_3$, in good agreement with experimental value (8.7eV [52]), while LSDA gives too small value 6.5eV. Impurity levels of 3d orbitals relative
to the host bands can affect the localization of the 3d orbitals and hybridization with host electrons. To our knowledge, QSGW80 is the best available choice to obtain band gaps as well as the impurity levels correctly without adjustable parameters. To avoid uncontrollable ambiguities, we use QSGW80 which describes both transition metal compounds and semiconductors/insulators on the same footing. This is the advantage of QSGW80 over LSDA+$U$ and hybrid functionals.

In the left panels of Figs. 3 c and f (the MLWF panels), we show ten eigenvalues (five for each spin) of $H_{QSGW}^{3d}$, which is calculated in the manner of MLWFs for the results of QSGW80. We see $t_{2g}$ states are almost degenerated, $e_g$ states as well. This means that octahedral symmetry is almost preserved. $H_{QSGW}^{3d}$ is thus specified essentially by three levels relative to the occupied $t_{2g}$ states of majority spin.

The HFA to $H$ gives the one-body Hamiltonian $H_{HF}$ as

$$
H_{HF} = H_{CF} + H_{C}^{HF},
$$

$$
H_{C}^{HF} = \sum_{m_1m_3} \sum_{\sigma} \left[ \sum_{m_2m_4} \left( g^{\sigma\sigma}_{m_1m_2m_3m_4} - g^{\sigma\sigma}_{m_1m_2m_4m_3} \right) \langle c^\dagger_{m_2\sigma} c_{m_4\sigma} \rangle + g^{\sigma\sigma}_{m_1m_2m_3m_4} \langle c^\dagger_{m_2\sigma} c_{m_4\sigma} \rangle \right] \hat{c}^\dagger_{m_1\sigma} \hat{c}_{m_3\sigma}.
$$

(7)

Here $\bar{\sigma}$ is opposite spin to $\sigma$. $\langle \cdots \rangle$ is the expectation value for the ground state. We name $H_{HF}$ the Hartree-Fock model Hamiltonian (HFMH). We determine the six parameters so that $H_{HF}$ is in agreement with $H_{QSGW}^{3d}$ as good as possible, without paying attention to the matrix elements. Since $H_{QSGW}^{3d}$ has the freedom of a five-dimensional Hermitian matrix for each spin, we cannot expect perfect agreement.

We have to determine the six parameters so as to minimize the difference between $H_{HF}$ and $H_{QSGW}^{3d}$. Here we only require that $H_{HF}$ should reproduce these ten eigenvalues of $H_{QSGW}^{3d}$ as good as possible. This is because the matching of eigenvalues is the main part of the minimization; we guess that it is not meaningful to consider the matching of matrix elements within our current model of 3d only. Our minimization virtually gives $D\sigma = D\tau = 0$ for $\text{Al}_2\text{O}_3 : \text{Cr}^{3+}$ because of the almost-preserved octahedral symmetry. Two degrees of freedom due to $10Dq$ and $F_0$, are not enough to reproduce the three levels. Thus, we need these two contributions due to $F_2$ and $F_4$. In Figs. 3 c and f (the MFMH panels), we resolve contributions from $F_0, F_2, F_4$ and $10Dq$. We see that the degeneracy of octahedral symmetry is preserved well. In Figs. 3 c, We see that the degeneracy of occupied states of majority spin is recovered by adding the contribution from $F_4$, although the degeneracies of other states are not completely recovered because of our limited degree of freedom. As we showed in Table 1, $D\sigma$ and $D\tau$ are essentially needed in cases, especially for the case of Fe, Ni, and Cu.
DATA AVAILABILITY
The authors declare that the code supporting this is available on Github under the link https://github.com/ktszk/eigloc.

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Construction of model Hamiltonians via the QSGW method


Construction of model Hamiltonians via the QSGW method


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**ADDITIONAL INFORMATION.**

Supplementary information.

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