Optimization of first-principles calculation conditions for multiplet energies of Fe$^{3+}$ and Co$^{3+}$ in α-Al$_2$O$_3$

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Abstract. Corundum can contain various transition metals as impurities, for example, ruby. Ruby is used as solid state laser. The prediction of the electronic state of these transition metals is very important for the development of novel optical materials. The CI calculation used finite Slater determinants, the calculated multiplet energies is overestimated generally. In this study, we optimized the calculation multiplet energy of transition metals in α-Al$_2$O$_3$ by considering some corrections.

1. Introduction
The prediction of multiplet energies of d$^n$ ions such as transition metal ions in crystals is important for the development of novel optical materials. Although the multiplet energies calculated by Configuration-Interaction (CI) calculations are generally overestimated, the overestimation can be corrected by considering the Configuration-Dependent Correction (CDC) and the Correlation Correction (CC). However, for d$^5$ and d$^6$ ions in Al$_2$O$_3$, the conditions of CDC-CC such as the considered transition processes have not been established. In this study, in order to optimize the conditions of CDC-CC, we performed first-principles calculations of the multiplet energies of Fe$^{3+}$ and Co$^{3+}$ in α-Al$_2$O$_3$ considering CDC-CC based on various transition processes.

2. Methods
2.1 DV-Xα and DVME
We used Discrete Variational Xα method (DV-Xα) [1] and Discrete Variational Multi-Electron (DVME) method [2] in this study. These methods are way to perform First-Principles Calculation. The wave function of the molecular orbit and the orbital energies are acquired by DV-Xα method. The multiplet energies are acquired by DVME method. The number of sampling points for numerical integration was 100000 for central transition metal ion, 10000 for the first proximity oxygen ions, and 1000 for others

2.2 Corrections
In DVME method, the obtained multiplet energies are generally overestimated because of considering the finite Slater determinants. Therefore, we performed some corrections to calculate the multiplet energies more precisely.

First, we performed Configuration Dependent Correction (CDC) [2], CDC is a method to correct the center of gravity of each electronic configuration by using the orbital energies obtained by DV-Xα method.
Second, we performed Correlation Correction (CC) [2]. CC is a method to consider the underestimated electron correlation effect by spin-flip energies obtained by spin-unrestricted DV-Xα method.

Finally, we performed lattice relaxation [3][4]. Lattice relaxation is a method to consider the change of bond distance between the ligand and the central atom in replacing the central atom.

\[ d_{relax} = d_0 \times \frac{r(M^{3+}) + r(O^{2-})}{r(Al^{3+}) + r(O^{2-})} \]  

We can take account for many spin inversion transitions in CC, so we considered various spin inversion transition in CC and investigated optimal correction in the calculation of multiplet energy of Fe$^{3+}$ and Co$^{3+}$.

3.3 Crystal constructure and model cluster

Figure 1. The crystal constructure of α-Al$_2$O$_3$ (a), The 7-atom cluster of α-Al$_2$O$_3$ (b) and 63-atom cluster of α-Al$_2$O$_3$ (c)

We showed the crystal constructure of α-Al$_2$O$_3$ [5]. We made 7-atom cluster and 63-atom cluster which have Al$^{3+}$ ion in center and O$^{2-}$ ion as ligands. We replaced Al$^{3+}$ with Fe$^{3+}$ or Co$^{3+}$ in calculation.

3. Results

We performed both calculation with lattice relaxation and calculation without lattice relaxation. We considered various spin inversion energies in CC respectively.

Figure 2. The best result about multiplet energy of Fe$^{3+}$ in the 7-atom cluster and the transition considered in CC

in CC without lattice relaxation. We also considered CDC and spin inversion transition energies of $t_2g_{up} \rightarrow t_2g_{down}$ in high spin, $e_g_{up} \rightarrow e_g_{down}$ in high spin, $e_g_{up} \rightarrow t_2g_{down}$ in high spin and $t_2g_{up} \rightarrow e_g_{down}$ in low spin in CC with lattice relaxation. Finally, we also performed calculation
without CC and CDC. As a result, the calculation considered CDC and spin inversion energy of $e_{g,up} \rightarrow t_{2g,down}$ in high spin in CC without lattice relaxation is the best result. The mean square error of the best result is minimum in all calculation. In the case of multiplet energy of Fe$^{3+}$ in the 7-atom cluster, the calculated multiplet energies decreased by considering the transition showed at Figure 2 in CC.

In the calculation of 63-atom cluster for Fe$^{3+}$, we considered CDC and spin inversion transition energies of $t_{2g,up} \rightarrow t_{2g,down}$ in high spin, $e_{g,up} \rightarrow e_{g,down}$ in high spin, $t_{2g,up} \rightarrow e_{g,down}$ in high spin and $e_{g,up} \rightarrow t_{2g,down}$ in low spin in CC without lattice relaxation. We also considered CDC and spin inversion transition energies of $t_{2g,up} \rightarrow t_{2g,down}$ in high spin, $e_{g,up} \rightarrow e_{g,down}$ in high spin, $t_{2g,up} \rightarrow e_{g,down}$ in high spin and $t_{2g,up} \rightarrow e_{g,down}$ in low spin in CC with lattice relaxation. Finally, we also performed calculation without CC and CDC. As a result, the calculation considered only lattice relaxation is the best result. The mean square error of the best result is minimum in all calculation. In the case of multiplet energy of Fe$^{3+}$ in the 63-atom cluster, the calculated multiplet splitting decreased by considering only lattice relaxation.

![Figure 3. The best result about multiplet energy of Fe$^{3+}$ in the 63-atom cluster](image1)

In the calculation of 7-atom cluster for Co$^{3+}$, we considered CDC and spin inversion transition energies of $t_{2g,up} \rightarrow t_{2g,down}$ in high spin, $e_{g,up} \rightarrow e_{g,down}$ in high spin, $t_{2g,up} \rightarrow e_{g,down}$ in high spin and $e_{g,up} \rightarrow t_{2g,down}$ in high spin in CC without lattice relaxation. We also considered CDC and spin inversion transition energies of $t_{2g,up} \rightarrow t_{2g,down}$ in high spin, $e_{g,up} \rightarrow e_{g,down}$ in high spin and $e_{g,up} \rightarrow t_{2g,down}$ in high spin in CC with lattice relaxation. Finally, we also performed calculation without CC and CDC. As a result, the calculation considered CDC and spin inversion energy of $t_{2g,up} \rightarrow e_{g,down}$ in high spin in CC with lattice relaxation is the best result. The mean square error of
the best result is minimum in all calculation. In the case of multiplet energy of Co\textsuperscript{3+} in the 7-atom cluster, the calculated multiplet splitting decreased by considering lattice relaxation and the transition showed at Figure 4 in CC.

Finally, in the calculation of 63-atom cluster for Co\textsuperscript{3+}, we considered CDC and spin inversion transition energies of $t_{2g}^{\uparrow}\rightarrow t_{2g}^{\downarrow}$ in high spin, $e_{g}^{\uparrow}\rightarrow e_{g}^{\downarrow}$ in high spin, $t_{2g}^{\uparrow}\rightarrow e_{g}^{\downarrow}$ in high spin and $e_{g}^{\uparrow}\rightarrow t_{2g}^{\downarrow}$ in high spin in CC without lattice relaxation. We also considered CDC and spin inversion transition energies of $t_{2g}^{\uparrow}\rightarrow t_{2g}^{\downarrow}$ in high spin, $e_{g}^{\uparrow}\rightarrow e_{g}^{\downarrow}$ in high spin and $e_{g}^{\uparrow}\rightarrow t_{2g}^{\downarrow}$ in high spin in CC with lattice relaxation. Finally, we also performed calculation without CC and CDC. As a result, the calculation considered CDC and spin inversion energy of $t_{2g}^{\uparrow}\rightarrow e_{g}^{\downarrow}$ in high spin in CC with lattice relaxation is the best result. The mean square error of the best result is minimum in all calculation. In the case of multiplet energy of Co\textsuperscript{3+} in the 63-atom cluster, the calculated multiplet splitting decreased by considering lattice relaxation and the transition showed at Figure 5 in CC.

4. Conclusion
We could optimize the conditions of CC and CDC for Fe\textsuperscript{3+} and Co\textsuperscript{3+} in $\alpha$-Al\textsubscript{2}O\textsubscript{3}, and successfully reproduced the experimental multiplet energies. By consideration of CC and CDC, the repulsion between electrons was suppressed and the overestimation of the multiplet splittings was reduced.

References
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