SHAP Interpretable Machine learning and 3D Graph Neural Networks based XANES analysis

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Abstract

X-ray absorption spectroscopy (XAS) is an indispensable tool to characterize the atomic-scale three-dimensional local structure of the system, in which XANES is the most important energy region to reflect the three-dimensional structure. However, quantitative analysis of three-dimensional structure from XANES requires users to have a deep understanding and accurate judgment of structural information and summarize several structural parameters, which is often difficult to achieve. In this work, we construct a graph neural network model for calculating XANES from the input three-dimensional structure; we improve the efficiency of the model based on the physical meaning of XAS; then we combine the model and optimization algorithm to fit the three-dimensional structure of the given system. This method does not require users to summarize the structural parameters, has wide application range. It can be applied to the three-dimensional structure analysis of solid materials and has positive significance for the study of structure-function relationship in the fields of energy and catalysis. In addition, this method is expected to be developed into an online three-dimensional structure analysis method for XAS related beamlines.

Keywords: X-ray Absorption Spectroscopy, XANES, Machine Learning, Graph neural network, Optimization Algorithm

1 Introduction

X-ray absorption spectroscopy (XAS) is one of the most powerful tools to detect the local three-dimensional structure. X-ray absorption near edge structure (XANES) is the important region containing the three-dimensional structure of the given system. XAS three-dimensional structure analysis focuses on the XANES region. The detection of three-dimensional structure plays an important role in revealing the microscopic mechanism of material strain, chemical reaction mechanism and in-depth study of the relationship between structure and function of the system. EXAFS fitting accounts for the vast majority of XAS quantitative
analysis work, and quantitative analysis of XANES three-dimensional structure is relatively few. XAS analysis methods based on machine learning are divided into two categories: "spectrum to parameter" and "parameter to spectrum". The "spectrum to parameter" model is the method predicting structural parameters results from the input XAS. The "spectrum to parameter" model related method has not yet been used to predict the three-dimensional coordinates of the system directly from the XAS. There is another class of methods called XANES fit. In XANES fit, the module for calculating the spectrum, which we call the "core" for short and the fitting of the structural parameters is usually controlled by optimization algorithms. The "core" module used to calculate the spectrum can be either multiple scattering calculation[1] or machine learning model calculation. XANES fitting work is mostly applied in the complex and metalloprotein system. There is still room for development of three-dimensional structure analysis method of XANES.

The XANES fit softwares combining multiple scattering calculation and optimization algorithm includes MXAN software[2] developed by Benfatto research group combined with MINUIT optimization algorithm package, XANES fitting method developed by Rehr research group combined with Bayesian optimization algorithm[3], XANES fitting method combined with deterministic global optimization algorithm[4], etc. The XANES fit softwares adopting "parameter to spectrum" machine learning method includes Pyfitit[5] based on random forest algorithm and Fitit[6] based on interpolation method. Based on the above methods, researchers have carried out the analysis of the three-dimensional structure of various systems. Shanghai Institute of Hematology used MXAN software to analyze the three-dimensional local structural changes around the metal ions before and after the binding of PML protein to As. The changes in the local spatial structure led to the function loss of it[7]. Veen et al. applied the Bayesian XANES fitting method to study the excited-state structural changes of the Pt complex PtPOP[8]. Xiong Yujie’s research group used the deterministic global optimization XANES fitting method to study the time-resolved XAS of the photocatalytic CO2 reduction system of Ni complexes, and analyzed the three-dimensional structure changes of the reaction intermediates[9]. Smolentsev et al. used FITIT software to study the system of CoII(aPPy) catalytic decomposition of water to produce hydrogen, and analyzed the four-nitrogen atom coordination intermediate [10]. Most of the above works are complex and metalloprotein systems.

Based on the "spectrum-to-parameter" machine learning method, researchers have developed machine learning models that predicting various parameters. In 2017, Timoshenko et al. first introduced machine learning into XAS analysis[11], and successively applied fully connected networks to analyze the coordination number, radial distribution function[12] and coordination bond length[13] of metal clusters. Frenkel et al. Applied two fully connected networks to analyze the coordination number of bimetallic sites in nanocluster systems[14]. Zheng et al. applied the random forest model to analyze the coordination mode identifier of the system[15]. To our best knowledge, there is no relevant research on the "spectrum-to-parameter" model which takes the three-dimensional structure of
the system as the direct output.

In this work, first we construct a graph neural network (GNN) model for calculating XANES from the input three-dimensional structure. We study the importance of different geometric quantities and coordination atom types to the GNN model. Then we combine the model and optimization algorithm to fit the three-dimensional structure of given system. This method does not require users to summarize the structural parameters, has wide application range. It can be applied to the three-dimensional structure analysis of solid materials and has positive significance for the study of structure-function relationship in the fields of energy and catalysis. In addition, this method is expected to be developed into an online three-dimensional structure analysis method for XAS related beamlines.

2 Method

There are two possible methods for the XANES 3D structure analysis of the system. One method is implemented via "spectrum-to-parameter" machine learning model, that is, to design a 3D structure output coding mode. At present, the output parameters are constantly enriched, from the initial coordination number and bond length to the radial function and coordination motif, while to our best knowledge there is no model output that can be directly converted into the three-dimensional coordinates of the system. Another method is the XANES fit mentioned above. At present, there are two types of methods for spectrum calculation in XANES fitting, full multiple scattering algorithm and "parameter to spectrum" machine learning model. Research works using XANES fit is mostly seen in complex, protein systems, which can fix ligands, peptides and other rigid bodies, and in which 3D structure fitting can be converted into a small amount of rigid body motion fitting to reduce the required fitting parameters, that is, the fundamental purpose is to reduce the degree of freedom of fitting. Specific to the two types of XANES fit methods, the purpose of reducing the degree of freedom is different. Although the XANES fitting software based on full multiple scattering to calculate spectrum has the function of rigid body grouping to reduce the degree of freedom, in principle, a single atom can be regarded as a rigid body, that is, the three dimensional degrees of freedom of all atoms can be considered. The purpose of reducing the degrees of freedom in this method is mainly to reduce the total fitting time. The high degree of freedom brings more optimization steps, and the total time consumption is long regarding the time-consuming of full multiple scattering calculation of each step. Taking the Mn doped $Co_3O_4$ system as an example, when the multiple scattering calculation used cluster with radius of 5 Å, the FDMNES software[16] under 8-core parallel took about 4 minutes. In this case, FDMNES used the "Green" mode, the finite difference method is turned off. When the unit cell contains 28 atoms, the total 84 internal coordinates required for fitting. Suppose 5000 steps need to be fitted, the total time consuming is about 13.9 days, which is unacceptable. In addition, the theoretical spectrum calculated in this method is difficult to be
effectively reused. XANES fit based on "parameter to spectrum", using trained model to approximate full multiple scattering calculation results. The model is trained on the theoretical spectral data set. The XANES calculation based on the machine learning model greatly reduces the time consumption, which is enough to deal with the high degree of freedom system, while model needs to be carefully designed. In the Mn doped Co$_3$O$_4$ system, different machine learning models were trained with the 84 internal coordinates as the input and XANES as the output. The performance of the model on the 10% validation set is shown in the Fig.1 and Tab.1 in which the solid line is the multiple scattering calculation spectrum and the dashed line is the machine learning model calculation spectrum. It can be seen that the use of machine learning models such as support vector machines, multi-layer perceptrons, random forests, extreme random trees and so on can not achieve a good agreement with the results of multiple scattering calculations. One possible reason is that the use of user defined structural parameters rather than direct 3D coordinates as input reduces the pressure of machine learning models. It is a feasible technical route to improve the ability of machine learning model to deal with the 3D coordinates input and to improve the consistency between the model predicted spectrum and the multiple scattering calculated spectrum. Here Three-dimensional graph neural network is a good basic model.

We chose the 3D graph neural network as the basis model. 3D graph neural network\[17\] is a kind of graph neural network specially designed to deal with 3D coordinates input of the system, with atoms as nodes and atom pairs as edges. The 3D graph is defined as $G(V,A,P)$. The dimension of atom feature (node feature) matrix $V = [v_1;v_2;...;v_n]$ is $N_{atom} \times N_v$ where $v_i,i=1...N_{atom}$ is feature vector of given atom, $N_v$ is dimension of the feature vector which is hyperparameters. The dimension of the adjacency matrix $A$ is $N_{atom} \times N_{atom}$ which is a sparse matrix of dimension $2 \times N_{edge}$ in the program. There is an edge $e_{ij}$ in graph $G$ when $A[i][j] = 1$, $e_{ij}$ is the pair of atoms included in the model. The position matrix $P$ consisting of the three-dimensional coordinates of the atoms. The three-dimensional graph neural network takes the interaction layer as the basic unit, as shown in the Fig.2. The main part of the model is usually composed of several interaction layers, and the number of interaction layers is a hyperparameter. In Fig.2 the interaction layer calculates the distance $r$, angle $\theta$, dihedral angle $\phi$ and other geometric features corresponding to the atom pairs (e.g. edges in graph) through the input atom coordinates, next calculates the feature function values based on the geometric features, then updates the feature vector of the atom via graph convolution, XANES is the output after pooling of the graph. The main differences between different 3D GNN models such as SchNet\[17\], SphereNet\[18\],DimeNet++\[19\] lie in the completeness of the definition of geometric features, the computational efficiency of geometric features and the definition of characteristic functions. In this work, a 3D GNN model is constructed, it takes 3D coordinates as input and XANES spectrum as output. In the definition of geometric features, we choose the most efficient definition at present\[20\]. It can be seen from the discussion part that the importance of twist angle $\tau$ in XANES prediction is low, and we select $F(r, \theta, \phi)$
Figure 1: Multiple scattering calculated XANES(solid lines) and machine learning model predicted XANES(dashed lines) on validation set.

Table 1: XANES prediction performance of machine learning models.

| Machine learning model   | MAE   | R factor |
|--------------------------|-------|----------|
| Multiple perceptron      | 0.0565| 0.00733  |
| Support Vector Machine   | 0.0478| 0.00560  |
| Random Forest            | 0.0449| 0.00558  |
| Extra Trees              | 0.0454| 0.00570  |

as the feature function to improve the training efficiency of the model. This model is abbreviated as XAS3D for short. We replace the multiple scattering calculation with the constructed XAS3D GNN model, and the flow chart of the XANES fitting is shown in the Fig. 3. When the system is a complex system, the three-dimensional Cartesian coordinates are directly input of XAS3D. When the system is a solid material, the lattice parameters and internal coordinates are first converted into Cartesian coordinates of a cluster centered on the absorbing atoms, which are then used as the input of XAS3D.

3 Application and results

We applied our method to a Mn doped $Co_2O_4$ system, where Mn atom is located in the octahedral coordination environments, as shown in the Fig. 4. The system contains 28 atoms in crystal cell, total 84 internal coordinates to be fitted. The data set was calculated using full multiple scattering algorithm adopting FDMNES software. Cartesian coordinates variation ranges is [−0.3Å, 0.3Å], Latin hypercube sampling[21] was adopted, and the data set size was 3000, 90% as the training set and 10% as the validation set. Graph neural networks are im-
Figure 2: The flowchart of XAS3D GNN model.

Figure 3: The flowchart of XANES fit combined GNN model and optimization algorithm.
implemented based on Pytorch\textsuperscript{22} and PyTorch Geometric\textsuperscript{23} framework. We tested the importance of different geometric features to the model. The training history of models including different geometric features $r, \theta, \phi, r$, is shown in the Fig.\textsuperscript{5}. It can be seen that $r$ is the most important geometric features among them, mae of model using $r$ as geometric feature is the lowest. Meanwhile angle $\theta$ is more important than dihedral angle and torsion angle. Dihedral angle and torsion angle are of low importance. One possible reason is that this data set is built for a single system and does not involve the problem of torsion angle to be considered, such as isomer judgment \textsuperscript{20}. So, the feature function $F(r, \theta, \phi)$ regardless of torsion angle is selected here based on the test results. In addition to geometric features and feature functions, we also test graph definition influence. In the graph definition, the general scheme is to select the atom $j$ around atom $i$ as its neighbor atom within a uniform distance cutoff. Here, we extract the absorber atom and its neighbors to form a graph, and as a contrast we remove the atomic pairs (e.g. edges in graph) associated with absorber atom to form another graph. We plotted the training history of models on the two graphs. In Fig.\textsuperscript{6} it can be seen that the local structure around absorber is more important than that all other atoms. This is consistent with the physical meaning of X-ray absorption spectrum, which can detect the local structure around absorber atoms. The test results show that the cutoff in the definition of the model graph needs to be divided into two hyperparameters for consideration. The cutoff of absorbing atoms are set large enough to fully consider the local structure around absorber, and the cutoff of other atoms can be appropriately
reduced its value to reduce the amount of computation and avoid redundant information. The performance of XAS3D model on the system validation set is shown in the Fig. It can be seen that even the 10 spectra with the worst prediction performance can be reconstructed by the XAS3D model. After confirming the model performance, we performed XANES fitting based on XAS3D model. In inner fit, energy shift fitting range is [-10eV,10eV], and the normalization factor fitting range is [0.7,1.3]. Nelder-Mead optimization algorithm was used for the outer layer fitting. The fitting range of atomic cartesian coordinates was [-0.3Å,0.3Å]. The fitting went through 5621 steps. The fitting results showed that the average axial bond length of Mn was 2.36Å and the average plane bond length was 1.94 Å, indicating that the local environment of doped Mn site had a J-T effect, which was in line with the expectation. The fitting spectrum is shown in the Fig. It can be seen that all features of the experimental spectrum are reconstructed by fitting, including the shoulder peak at 6573eV and the scattering peak at 6616eV. Furthermore, the multiple scattering theoretical spectra was calculated based on the fitted 3D structure, and the features of theoretical spectra was consistent with that of model predicted spectra. Compared with the experimental spectra, the fitting intensity of the pre-edge peak was enhanced, maybe because there was no restriction on coordinates of each atom in the fitting, and the symmetry of fitted structure was broken. Subsequently, we consider adding geometric and energy stability constraints to the fitting process in order to improve this. In conclusion, the method proposed is applied in the Mn-doped Co3O4 system. Verifying the practicality of this method in actual solid material systems. It is of positive significance for expanding the application of XANES fitting in high degrees of freedom systems such as solid materials.
Figure 6: The validation loss function MAE versus the training epoch of GNN models with different graph definition.

Figure 7: Multiple scattering calculated XANES(solid lines) and GNN model predicted XANES(dashed lines) on validation set.
4 Conclusion and Outlook

In this work, we construct a graph neural network model for calculating XANES from the input three-dimensional structure; we improve the efficiency of the model based on the physical meaning of XAS and then we combine the model and optimization algorithm to fit the three-dimensional structure of given system. This method does not require users to summarize the structural parameters, has wide application range. It can be applied to the three-dimensional structure analysis of solid materials and has positive significance for the study of structure-function relationship in the fields of energy and catalysis. In addition, this method is expected to be developed into an online three-dimensional structure analysis method for XAS related beamlines.

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