Excitonic Wave Function Reconstruction from Near-Field Spectra Using Machine Learning Techniques

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All the information about a quantum system is contained in eigenstate wave functions. A general problem in quantum mechanics is the reconstruction of eigenstate wave functions from measured data. In the case of molecular aggregates, information about excitonic eigenstates is vitally important to understand their optical and transport properties. Recently, it was suggested to use the near-field of a metallic tip to obtain spatially resolved spectra by scanning the tip along the aggregates. One open question is if these spectra can be used to reconstruct the excitonic wave functions belonging to the different eigenstates. In the present work we show that this is indeed possible using a convolutional neural network. The performance of the trained architecture is robust to various types of disorder.

INTRODUCTION

Self-assembled molecular aggregates on dielectric surfaces have attracted increasing attention and are promising candidates for optoelectronic devices.¹⁻⁵ One appealing feature of dielectric surfaces is that they do not strongly quench molecular fluorescence,¹⁻⁶,⁷ in contrast to metallic surfaces. On dielectric surfaces, aggregate properties are dominated by intermolecular coupling instead of relatively weak molecule-surface interactions.¹ As a result of the strong intermolecular electronic coupling these aggregates exhibit coherently delocalized excitonic eigenstates where the excitation is shared by many molecules.⁸⁻¹¹ Knowledge of these excitonic eigenstates is crucial for understanding the optical and transfer properties of aggregates. Optical spectroscopy is a typical tool to characterize the excitonic structure of molecular aggregates. However, conventional optical far-field spectroscopy cannot provide the full spectrum of these states as most of excitonic eigenstates are optically dark due to selection rules.

One possibility to tackle this problem is to apply an electromagnetic field that is spatially inhomogeneous on the nanometer scale.¹² This can be achieved by the near-field of a nearby excitation source. Near-field light-matter interaction can provide not only extremely high resolution microscopy of the samples circumventing the diffraction limit,¹³⁻²², but also reveal optical transitions beyond selection rules as has been discussed for several systems.²²⁻²⁶ Recent experiments have realized localized fields focusing on the sub-10 nm regime.¹³⁻¹⁶,¹⁷,²⁷⁻³⁰

In our previous study,¹² we considered the setup described in the upper panel of Fig. 1. Near-field absorption spectra are measured for a one-dimensional (1D) 3,4,9,10-perylenetetracarboxylic acid dianhydride (PTCDA) chain aggregated on the KCl surface. The localized field is generated by applying an electric field to a metallic tip. We found that most excitonic eigen-
calculated from the eigenstate coefficients via a nonlinear equation [see Eq. (3)], an analytical mapping from the spectra to the eigenstate coefficients has not been found to the best of our knowledge. A feasible way to perform this nonlinear inversion task is to apply machine learning techniques. Machine learning has gained widespread popularity since the AlphaGo beat the top Go players [31]. Beyond image recognition, machine learning techniques have penetrated many fields, such as material science, chemistry, and physics. Thanks to its excellent performance and great adaptability, machine learning has attracted increasing attention recently from physicists and has been applied to solve some physical problems which are difficult for pure numerical approaches, such as discovering phase transitions of various systems [32], and estimating quantum states [33–35]. Considering the capability of these machine learning techniques, we train a convolutional neural network (CNN) in the current work to reconstruct the eigenstate wave functions from the near-field absorption spectra. Here we show that it is possible to construct the complete excitonic wave functions from the spatially resolved near-field absorption spectra.

THE AGGREGATE

Basic Hamiltonian of the aggregate In our theoretical modeling we use a widely adopted description of the aggregate [12,36]. For each monomer in the aggregate we take two electronic states into account: the ground state \(|g)n\rangle\) and the first excited state \(|e)n\rangle\), where the index \(n\) labels the monomers. The transition dipole between these two states is denoted by \(\vec{\mu}_n\). Initially the aggregate, which consists of \(N\) molecules (monomers), is in the global ground state \(|g)_{agg}\rangle\) = \(|g)_1\cdots|g)_N\rangle\) in which all monomers are in their ground state. For linear absorption we are interested in states with one excitation. Using a basis state \(|m\rangle\) = \(|e)m\prod_{n\neq m}|g)n\rangle\) the excited state Hamiltonian for the system is written as

\[
H_{ex} = \sum_m \varepsilon_m |m\rangle\langle m| + \sum_{m\neq n} V_{mn} |m\rangle\langle n|.
\]

Here \(\varepsilon_m\) is excitation energy for the monomer \(m\) and \(V_{mn}\) is the transition dipole-dipole interaction, which for our calculations we take as \(V_{mn} = \frac{1}{R_{mn}}(\vec{\mu}_m \cdot \vec{\mu}_n - 3(\vec{\mu}_m \cdot \vec{R}_{mn})(\vec{\mu}_n \cdot \vec{R}_{mn}))\) with \(\vec{R}_{mn}\) the distance vector from monomer \(m\) to \(n\) and \(R_{mn} = |\vec{R}_{mn}|\). From solving the time-independent Schrödinger equation \(H_{ex}|\phi_\ell\rangle\) = \(E_\ell|\phi_\ell\rangle\) one obtains the \(N\) eigenenergies \(E_\ell\) with corresponding eigenstates

\[
|\phi_\ell\rangle = \sum_{m=1}^N c_{m\ell}|m\rangle.
\]

The coefficients \(c_{m\ell}\) depend on the arrangement of the molecules in the aggregate.

The Specific arrangement used in the present work We consider a 1D linear chain consisting of \(N = 20\) molecules as shown in the upper panel of Fig. 1. All the monomers are aligned parallel (\(\mu_n = \mu\), for all \(n\)). The center-center distance between neighboring molecules is fixed to \(a\). The center of molecule \(m\) is \(\vec{R}_m = (x_m, 0, 0)\) with \(x_m = (m - \frac{N-1}{2})a\). Note that the middle of the aggregate is located at \(x = 0\).

ABSORPTION FOR A SPATIALLY VARYING ELECTROMAGNETIC FIELD

![FIG. 2. Eigenstate wave functions (left column) and spectra \(A(x_{\text{tip}})\) (right column).](image)

Absorption for a spatially varying electromagnetic field. An electromagnetic field with strong variation on the scale of a few molecules is created by a Hertzian dipole with dipole moment \(\vec{d}\) perpendicular to the surface. This field even changes sign along the \(x\)-direction (where the aggregate is aligned). The absorption strength from the ground state to the eigenstate \(\phi_\ell\) for fields that vary over the extent of the aggregate (but have only a small variation over the extent of a single molecule) can be written as [12]

\[
A_\ell(\vec{R}_{\text{dip}}) = \left|\sum_{m=1}^N c_{m\ell} \vec{\mu}_m \cdot \vec{E}(\vec{R}_m; \vec{R}_{\text{dip}})\right|^2.
\]

Note that \(A_\ell\) has an explicit dependence on the position of the dipole \(\vec{R}_{\text{dip}}\). Here, as in Eq. (S2) of the Supplemental Material [37], \(\vec{E}(\vec{R}_m; \vec{R}_{\text{dip}})\) denotes the electric field.
component at the position of monomer $m$, when the excitation dipole is placed at position $\vec{R}_{\text{dip}}$. Since we scan the tip along the $x$ axis, $\mathcal{A}(\vec{R}_{\text{dip}})$ is simply denoted as $\mathcal{A}(x_{\text{dip}})$. In the following we will for brevity drop the eigenstate-index $\ell$ and write $c_m$ for the wave-function coefficients and $\mathcal{A}(x_{\text{dip}})$ for the corresponding absorption strength at position $x_{\text{dip}}$. We focus on an ideal scenario where the tip only creates an spatially inhomogeneous field and therefore ignore any interaction between the molecular dipoles and the tip. To obtain a feeling about the relationship between eigenstate coefficients $c_m$ and corresponding spectra, in Fig. 2 we show three examples. All spectra are normalized to unit area.

**RECONSTRUCTION OF THE WAVE FUNCTIONS**

We now investigate the possibility to obtain the eigenstate coefficients $c_m$ from the spatially resolved near-field absorption spectra $\mathcal{A}(x_{\text{dip}})$. Since $c_m$ are mapped to $\mathcal{A}(x_{\text{dip}})$ via the nonlinear equation Eq. (3), an analytical method for the inversion has not been established as far as we know. To this end we use machine learning techniques and train a CNN to realize the eigenstate reconstruction. Since we only intend to show the feasibility of such an inversion, we do not focus on the architecture optimization of the artificial neural network.

**Procedure.** We use a CNN to reconstruct the eigenstate wave functions from the near-field absorption spectra. The chosen network architecture is shown in Fig. S1 (a) in the Supplemental Material [37]. The network contains nine convolutional layers and has in total 417364 trainable parameters. The input data are spatially discretized near-field spectra $\mathcal{A}(x_{\text{dip}})$, where $\mathcal{A}$ is evaluated at equally spaced points. The metallic tip generating the localized field scans along the molecular chain with $\vec{R}_{\text{dip}} = (x_{\text{dip}}, 0, 2a)$. The scan interval is chosen as $x_{\text{dip}} \in [-20a, 20a]$, where $a$ is the distance between neighboring molecules in the aggregate (note that we consider an aggregate of length $N = 20$ which is symmetrically placed around $x = 0$.) The input for the CNN is therefore a real-valued array with $N_{\text{tip}} = 512$ elements, where $N_{\text{tip}}$ denotes the number of positions at which $\mathcal{A}$ is evaluated. The outputs are the corresponding predicted coefficients $c_m^{\text{pre}}$ of the wave function. The dimension of the output is equal to the number of molecules $N = 20$.

In order to train and validate the neural network, we prepare a huge number of spectra stemming from a broad range of wave-function coefficients. Since these wave functions are related to the 1D molecular aggregate considered in this work, the following procedure is adopted to generate enough data which also allows to treat other relevant situations besides the perfect chain discussed so far. In the Hamiltonian Eq. (1) we add disorder $\delta \varepsilon_m \sim \mathcal{N}(0, \sigma_d)$ to the molecular site energy $\varepsilon_m$. Various disorder strengths ($\sigma_d \in (0.02, 0.04, 0.06, 0.08, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, \ldots, 5.0)$) are used to capture a wide range of situations. The examples shown in Fig. 2 actually are particular realizations of the $10^{\text{th}}$ eigenstate (sorted according to increasing energy) for the case without disorder (panel a), $\sigma_d = 0.3$ (panel b) and $\sigma_d = 3$ (panel c). In addition, we also generate some data by adding disorder to the transition dipole-dipole interaction, by using $\tilde{V}_{mn} = \frac{1}{R_{mn}^3} (\vec{m}_m \cdot \vec{m}_n - 3(\vec{m}_m) \cdot (\vec{m}_n \cdot \frac{\vec{R}_{mn}}{R_{mn}}))$ for the wave-function coefficients $\vec{m}_m$ and $\vec{m}_n$. Various disorder strengths ($\sigma_{\text{od}} \in [0.1, 0.2, 0.3, 0.4, 0.5]$) and $\sigma_{\text{od}} \in [0.1, 0.2, 0.3, 0.4, 0.5]$.

For each disorder strength, $10000$ realizations are calculated, producing $4.6$ million data samples in total. $80\%$ of these data are used for training and the rest for validation.

The “loss function”

$$\text{Loss} = \frac{\sum_{m=1}^{N} (c_m - c_m^{\text{pre}})^2}{N} \cdot \frac{N}{4},$$

is adopted to evaluate the quality of the prediction. $c_m^{\text{pre}}$ are the predicted coefficients and the factor $N/4$ is introduced so that the maximum value of the loss function is one. The loss function is minimized to optimize the parameters inside the CNN during the training with the details presented in the Supplemental Material [37].

![Fig. 3](image-url)  

**FIG. 3.** Left column: comparison of the eigenstate wave functions and predictions from the trained CNN. Right column: near-field absorption spectra calculated from the wave functions shown on the left.

**Wave function reconstruction.** All the training and validation data have been used in training the architecture. Additional new data are prepared and supplied to the trained CNN for performance test. These new near-
field absorption spectra are fed to the network, which predicts corresponding wave-function coefficients.

Shown in the left column of Fig. 3 are the results for three excited states without any disorder. The results for all eigenstates of a disorder-free chain are given in Fig. S2 in the Supplemental Material [37]. The coefficients obtained by diagonalizing the Hamiltonian Eq. (1) and those reconstructed by the trained CNN show excellent agreement even for the highest excitonic state. The values of loss for most of the states are in the order of $10^{-4}$. This means that our trained CNN can successfully reconstruct the eigenstate wave functions from the near-field absorption spectra. Predicted wave functions are then used to calculate the corresponding near-field absorption spectra with representative results shown in the right column of Fig. 3. As expected, the spectra from the predicted wave functions agree well with those obtained from the eigenstates.

![Graph showing averaged loss over 100 realizations](image)

**FIG. 4.** (a) Averaged loss over 100 realizations of the test data for each state with different disorders. Lower panels: distribution of the loss for all the states with $\sigma_d = 2.75$ (b), 0.25 (c), and 0.05 (d).

In addition to the case without disorder, we use data obtained with different kinds of disorders to further check the validity of the trained CNN. For the disorder added to the site energies, we consider $\sigma_d = 2.75$, 0.25, and 0.05. For the disorder added to the inter-molecular coupling, we use $\sigma_{od} = 0.25$ to generate new data. We calculate 100 realizations for each disorder strength and analyze the averaged loss for individual states with the results shown in Fig. 4 (a). For each state the averaged loss is less than 0.05 for all the disorder strengths considered here. We also show the distribution of the loss for each disorder strength in the lower panels of Fig. 4. Most of the values of the loss are very small ($< 0.05$) for all the cases. In order to intuitively illustrate the performance of the trained CNN for the situations with disorder, we pick the results of a single realization for each disorder strength, and plot the comparisons between the exact coefficients and the predicted values in Figs. S3-S6, respectively. As can be seen from the figures, the trained CNN successfully predicts the wave-function coefficients for all the states and the performance is robust to various spectra. All these results strongly support the validity of the CNN trained in current work to reconstruct the eigenstate wave functions from the near-field absorption spectra of a 1D molecular aggregate.

**CONCLUSIONS**

Knowledge of excitonic eigenstates in molecular aggregates is crucially important to the understanding of the optical and transfer properties of the systems. The present study paves the way to construct the eigenstate wave functions from spatially resolved near-field absorption spectra which could be measured experimentally. To the best of our knowledge, an analytic inversion of the nonlinear equation (3) has not been developed and possibly is infeasible, we take advantages of the machine learning techniques and train a convolutional neural network to tackle the task. For the example of a linear chain consisting of 20 molecules, we can precisely reconstruct the wave-function coefficients not only for an ideal situation, but also for cases with various types of disorder.

In the presented examples we use spectra with a quite high spatial resolution (which is in the order of 1 Å for a typical distance $a \approx 1$ nm as $x_{dip} \in [-20a, 20a]$ and $N_{tip} = 512$). In Figs. S7 and S8 of the Supplemental Material we show that also for lower resolutions (around 2 Å and 4 Å) a trained CNN is able to reconstruct the wave-function coefficients [37].

Our main goal is to demonstrate the possibility of the inversion from the near-field spectra to the eigenstate wave functions. Therefore, we do not focus on the optimization of the network architecture and the training data. For the relatively small aggregate that we have considered we could easily diagonalize millions of Hamiltonians. For larger two-dimensional aggregates (number of molecules $N > 100$) one would want to diagonalize many fewer Hamiltonians. One way of generating enough training data is to perform diagonalizations only for the Hamiltonian without noise, and then simply add noise to the so obtained wave-function coefficients. Since for large aggregates the input and output of the CNN have larger sizes one probably also has to use a slightly more optimized architecture than the one we have used in the present work. We also tried to obtain the wave-function coefficients by using various optimizers, including Gaussian process regression. These methods only worked for quite small aggregates (linear chain with $N \lesssim 10$) and for wave functions with a small number of nodes, cementing...
the need for sophisticated machine learning techniques such as we have used. Further details can be found in the Supplemental Material [27].

Considering the objective stated above, we consider an ideal situation (no coupling to environments, no interactions between the molecular dipoles and the tip, etc.) in the current work. In next step we plan to investigate the feasibility of the inversion if these effects are taken into account.

In addition to the application to near-field spectra of molecular aggregates, the methodology adopted in present work can be applied to other optical spectra of various systems, such as the electron energy-loss spectroscopy of silver nanowires [38]. All of these varied applications require a similar inversion as for Eq. (3), and hence the implementation of machine learning as we have proven here can open up huge possibilities to extract key insight from experimental data.

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[37] See Supplemental Material at [URL will be inserted by publisher] for the details of the spatially varying light field applied in current study, the architecture and training procedures of the CNN, eigenstate wave function reconstruction with Gaussian Process Regression, the performance of the trained CNN and the performance of the CNN trained with lower resolution spectra. The Supplemental Material includes Refs. [1–4].
Excitonic Wave Function Reconstruction from Near-Field Spectra Using Machine Learning Techniques

In this Supplemental Material we provide additional details on the following items:

I. Descriptions of the spatially varying light field applied in current study to calculate the near-field spectra.

II. Architecture and training procedures of the convolutional neural network (CNN).

III. Eigenstate wave function reconstruction with the trained CNN.

IV. Eigenstate wave function reconstruction using the CNN trained with lower resolution spectra.

V. Eigenstate wave function reconstruction from the near-field spectra with Gaussian Process Regression.

I. SPATIALLY VARYING LIGHT FIELD

We consider electromagnetic radiation of frequency $\omega$ with an electric field component that at time $t$ and position $\vec{r}$ given by

$$\vec{E}(\vec{r},t) = \text{Re}\{\vec{E}(\vec{r})e^{i\omega t}\}.$$  \hspace{1cm} (S1)

Note the explicit dependence of the electric field on the position $\vec{r}$.

Here a Hertzian dipole with dipole moment $\vec{d}$, located at $\vec{R}_{\text{dip}}$ creates an electromagnetic field. In the near field zone this field can be written as

$$\vec{E}(\vec{R}_m; \vec{R}_{\text{dip}}) = \frac{3(\vec{R}_m - \vec{R}_{\text{dip}})[(\vec{R}_m - \vec{R}_{\text{dip}}) \cdot \vec{d}]}{|\vec{R}_m - \vec{R}_{\text{dip}}|^5} - \frac{\vec{d}}{|\vec{R}_m - \vec{R}_{\text{dip}}|^3}. \hspace{1cm} (S2)$$

Here $\vec{R}_m$ denotes the position of molecule $m$.

II. ARCHITECTURE OF THE CONVOLUTIONAL NEURAL NETWORK

The one-dimensional (1D) CNN applied in present study is constructed and trained using Keras. The architecture of the CNN is illustrated in Fig. S1 (a) with the output shape of each layer shown in brackets. Input data for the network are spatially resolved near-field absorption spectra for a certain eigenstate and are 1D arrays containing 512 entries. The outputs of the CNN are predicted wave-function coefficients which are arrays consisting of $N = 20$ elements (for the considered case of an aggregate with 20 molecules). There are 417364 trainable parameters in the architecture.

The neural network is trained with the optimizer $Adam$ \cite{S1}. Among the 4.6 million data samples, randomly selected 80% are used to train the CNN and the rest for validation. The model is trained for 500 epochs with a batch size of 512. As shown in Fig. S1 (b), both the training loss and validation loss saturate to a small value around 0.012 indicating that the network has been well trained.

III. WAVE FUNCTIONS RECONSTRUCTED WITH THE TRAINED CNN

In order to test the performance of the trained network, we feed some new data samples to it and compare the predicted eigenstate coefficients with the exact ones. The “loss function” defined in the main text is used to quantify the deviations between the exact eigenstate coefficients and the predicted ones.

For the case without disorder added to the Hamiltonian, three examples are shown in the left column of Fig. 3 in the main text. Results for all the 20 eigenstate are displayed in Fig. S2. Predictions perfectly agree with exact coefficients for all states. The values of loss are in the order of $10^{-4}$ for most of the states (the maximum value of the loss is normalized to unity).
FIG. S1. (a) Architecture of the neural network with the output shape of each layer shown in brackets. There are 417364 trainable parameters in the neural network. (b) Training loss and validation loss during training.

FIG. S2. Comparison of the exact and predicted eigenstate coefficients for the Hamiltonian without disorder.

To further check the validity of the trained network, we also use some new data obtained from disordered Hamiltonian to test the network. We adopt $\sigma_d = 2.75, 0.25, \text{ and } 0.05$ for the disorder added to the site energies, and $\sigma_{od} = 0.25$ for the disorder added to the inter-molecular coupling. For each disorder strength, 100 realizations are launched and the averaged loss for individual state is presented in Fig. 4 (a) in the main text. We select the results from one single realization for each disorder strength and plot the comparisons between the exact coefficients and the predicted ones in Figs. S3-S6. It can be seen that the trained network can reconstruct the eigenstate coefficients for all the cases, highlighting the robustness of the trained neural network to various spectra.
FIG. S3. Comparison of the exact and predicted eigenstate coefficients for a realization with large diagonal disorder $\sigma_d = 2.75$.

FIG. S4. Comparison of the exact and predicted eigenstate coefficients for a realization with intermediate diagonal disorder $\sigma_d = 0.25$. 
FIG. S5. Comparison of the exact and predicted eigenstate coefficients for a realization with small diagonal disorder $\sigma_d = 0.05$.

FIG. S6. Comparison of the exact and predicted eigenstate coefficients for a realization with off-diagonal disorder $\sigma_{od} = 0.25$. 
IV. WAVE FUNCTION RECONSTRUCTION USING THE CNN TRAINED WITH LOWER RESOLUTION SPECTRA

As mentioned above, the spectra used to train the CNN are arrays with 512 elements, indicating that the spectra are evaluated at a spatial resolution with around 10 data points for the center to center distance of the molecules. To explore the validity of the architecture to the spatial resolution of the spectra, we also train the CNN using the spectra with reduced resolutions. Shown in Fig. S7 are the comparisons between the exact eigenstate coefficients for the disorder-free Hamiltonian and the predict values from the CNN trained with the spectra containing 256 (128) elements, with an averaged loss of 0.00037 (0.00070). For both cases, the trained CNN can perfectly reconstruct all the eigenstate coefficients, indicating that the wave function reconstruction from near-field spectra is also feasible by using the CNN trained with low resolution spectra.

FIG. S7. Comparison of the exact and predicted eigenstate coefficients for the disorder-free Hamiltonian. The CNN is trained using the spectra containing 256 elements.

V. GAUSSIAN PROCESS REGRESSION

In addition to the neural network we have also tried to use Gaussian process regression [S2] to reconstruct the eigenstate coefficients from near-field spectra. As in our previous work [S3] we used the optimization package MLOOP [S4]. Firstly, we obtain the eigenstate coefficients by diagonalizing the Hamiltonian and calculate the near-field spectra in turn. We set the maximum and minimum boundaries for the predicted coefficients to 1 and \(-1\), respectively. The predicted coefficients are normalized before they are used to calculate the near-field spectra. Then the optimization proceeds by minimizing the cost function, which is defined as the mean-squared-error between the near-field spectra calculated from the exact coefficients (\(A\)) and that obtained from the predicted coefficients (\(A^{\text{pre}}\)), and is written as

\[
\text{Cost} = \frac{\sum_{i=1}^{N_{\text{tip}}} \left( A(x_i) - A^{\text{pre}}(x_i) \right)^2}{N_{\text{tip}}}, \tag{S3}
\]

with \(N_{\text{tip}} = 400\) referring to the number of positions at which the spectra is evaluated. We tried several optimization methods, including the Gaussian process method, the Nelder-Mead method, and the differential evolution method.
FIG. S8. Comparison of the exact and predicted eigenstate coefficients for the disorder-free Hamiltonian. The CNN is trained using the spectra containing 128 elements.

which are all implemented in the MLOOP package. We set the maximum iteration number to 1000 and the target cost to $10^{-10}$. Finally the optimization will be terminated either the maximum iteration number is reached or the target cost is achieved. For a small system, e.g., $N=5$, all the wave-function coefficients can be effectively predicted from the corresponding spectra. However, for a little larger system with $N=8$ molecules, wave functions of high energy eigenstates cannot be reproduced by any optimization approaches mentioned above.

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