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Cite as: J. Chem. Phys. **153**, 074111 (2020); <https://doi.org/10.1063/5.0016009>

Submitted: 31 May 2020 . Accepted: 30 July 2020 . Published Online: 20 August 2020

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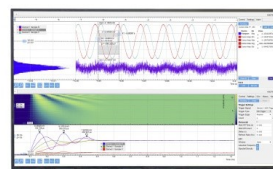
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Submitted: 31 May 2020 • Accepted: 30 July 2020 •

Published Online: 20 August 2020



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Note: This paper is part of the JCP Special Topic on Machine Learning Meets Chemical Physics.

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ABSTRACT

In this manuscript, we develop multiple machine learning (ML) models to accelerate a scheme for parameterizing site-based models of exciton dynamics from all-atom configurations of condensed phase sexithiophene systems. This scheme encodes the details of a system's specific molecular morphology in the correlated distributions of model parameters through the analysis of many single-molecule excited-state electronic-structure calculations. These calculations yield excitation energies for each molecule in the system and the network of pair-wise intermolecular electronic couplings. Here, we demonstrate that the excitation energies can be accurately predicted using a kernel ridge regression (KRR) model with Coulomb matrix featurization. We present two ML models for predicting intermolecular couplings. The first one utilizes a deep neural network and bi-molecular featurization to predict the coupling directly, which we find to perform poorly. The second one utilizes a KRR model to predict unimolecular transition densities, which can subsequently be analyzed to compute the coupling. We find that the latter approach performs excellently, indicating that an effective, generalizable strategy for predicting simple bimolecular properties is through the indirect application of ML to predict higher-order unimolecular properties. Such an approach necessitates a much smaller feature space and can incorporate the insight of well-established molecular physics.

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I. INTRODUCTION

The performance of organic-based semiconductors depends not only on their molecular composition but also on how molecules are arranged within the material. The inter- and intramolecular interactions that underlie this dependence are well understood, but predicting how many such interactions combine to produce macroscopic material properties remains a significant scientific problem. Because these materials are often amorphous, lacking in microscopic periodicity, this problem cannot generally be solved with analytical theory. Computational modeling has played and will continue to play a vital role in advancing our understanding of

these materials and guiding their development. Unfortunately, current methods for modeling materials with specific molecular structures include computational bottlenecks that limit their scope to system sizes that are too small to infer bulk properties. Here, we demonstrate that these bottlenecks can be effectively eliminated through the application of machine learning (ML), thereby enabling the existing frameworks for computational modeling to be extended to larger and more experimentally relevant system sizes.

Organic molecular semiconductors (OMs) provide an attractive alternative to the traditional inorganic semiconductors and have been increasingly utilized in the development of devices with

notable applications to lighting, solar energy conversion, and even nanoscale electronic circuitry.^{1–5} The performance of these materials is determined in large part by the properties of Coulombically bound excited electron–hole pairs, known as Frenkel excitons. When molecules within the material are weakly coupled, the static and dynamic properties of these excitons can be efficiently simulated with the Frenkel–Davydov model^{6,7} in which the molecular system is described in terms of a Hamiltonian for a coupled network of singly excitable chromophores. When appropriately parameterized, this efficient model has been shown to accurately reproduce experimental measurements^{8,9} and large scale electronic-structure calculations.^{9–12}

The Frenkel Hamiltonian can be parameterized directly from first-principles based on all-atom configurations of representative systems of many organic conjugated molecules.^{7,9,11,12} Unfortunately, the procedure for this parameterization requires performing, at a minimum, one excited-state electronic-structure (ES) calculation per fragment. This cost is further exacerbated if one incorporates time dependence into the parameters, for example, by analyzing a time-series of configurations generated from molecular dynamics (MD) simulation. Despite the computational cost, including explicitly derived time dependence in the Frenkel Hamiltonian provides several key advantages over static models or models with phenomenological time dependence. Most significantly, trajectory-based parameterizations allow one to systematically evaluate the consequences of molecular disorder and correlated environmental noise on exciton transport.^{9,13} However, even for a system containing ~ 10 chromophores (far below any reasonable approximation of the bulk), a 1 ns simulation can require $\sim 10^6$ ES calculations. Even with the least demanding ES methods,

this requirement represents an extremely large computationally expense.

Notably, however, many of the systems of interest, such as organic semiconductors,^{9,13–16} DNA nanowires,^{17,18} and biological light-harvesting complexes^{12,19–21} are composed of many *identical* chromophore units with very similar electronic-structure properties, e.g., differing in nuclear or environmental configuration. Here, we circumvent the costly model parameterization by developing a ML model to accelerate the computations associated with the ES calculations. This model utilizes the similarities across different configurations to rapidly predict molecular excitation energies and intermolecular electronic couplings. In this manuscript, we present this ML model and examine its application to two different OMSs morphologies made up of sexithiophene (T6) molecules.

The first system is a monolayer phase in which molecules are aligned longitudinally in a manner analogous to experimental structures obtained via vapor deposition.^{22–24} The second system is a completely amorphous bulk phase. We choose to study T6 because it has been widely characterized experimentally,^{22,24–35} and its optoelectronic properties can be generalized to polythiophenes (such as P3HT). Mechanistic insight into the interplay between spatial disorder and exciton transport in these systems and other OMSs is key to making them more efficient and tunable, and our ML approach is an important step for building computer models capable of giving such insight.

Our approach to building a ML model Frenkel Hamiltonian, as illustrated in Fig. 1, is to train separate models for the diagonal and off-diagonal elements, corresponding to the excitation energies, E_m , and intermolecular electronic couplings, V_{mn} ,

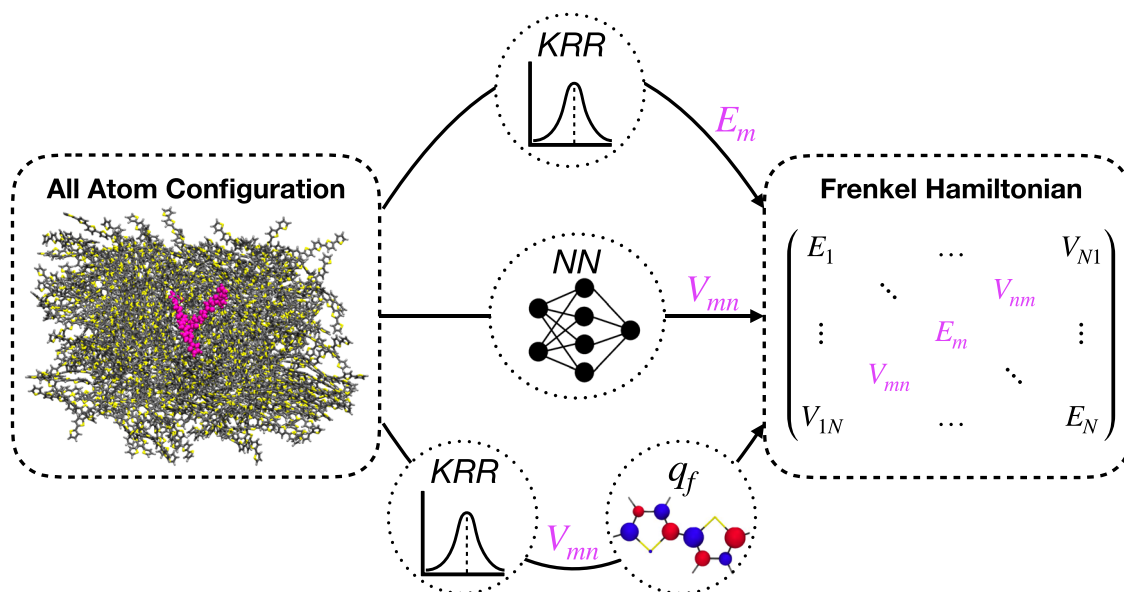


FIG. 1. Depiction of machine learning schemes described by this work. Three machine learning models are tested, one for the excitation energy and two for the excitonic couplings. The deep neural network (DNN) model for the direct prediction of couplings is shown to perform worse than the transition charge based kernel ridge regression (KRR) model.

using information only from the nuclear conformations of the constituent molecules. We consider two distinct approaches to building a ML model for V_{mn} . The first is to predict V_{mn} directly from bimolecular features. The second is to predict a set of atom-centered transition charges using unimolecular features from which the coupling may be obtained. We show that this transition charge approach is far superior to the direct approach, even when taking into account the additional error from the transition charge embedding.

In all cases, we evaluate the performance of our ML model through a set of four rigorous criteria. The first criterion is that the model applies to a broad range of ES methods, and therefore, we study its performance on both semi-empirical Pariser–Parr–Pople/Configurations Interaction Singles (PPP/CIS)³⁶ and time-dependent density functional theory (TDDFT) calculations. The second criterion is that the model requires no more than 10 000 ES calculations as training data to yield error levels below that of the intrinsic uncertainty in the ES method. Third, the model should produce significantly less error than the intrinsic fluctuations in E_m and V_{mn} , given by the interactions within the MD bath. The final criterion is that the model be *transferable*, meaning it should still perform well when encountering molecular conformations far outside what it was trained on. This criterion not only gives us added confidence in the performance of our model but also allows us to apply our model beyond the morphology it was originally trained on. We show that both our E_m ML model and our transition charge based V_{mn} ML model satisfy the aforementioned criteria.

The organization of this manuscript is as follows: We outline the derivation the Frenkel Hamiltonian and associated matrix elements from first-principles in Sec. II. We then give a description of methods used for data generation, organization, and machine learning in Sec. III. In Secs. IV–VI, we develop and evaluate the ML models for the excitation energies and intermolecular electronic couplings. Finally, in Sec. VII, we provide concluding remarks.

II. THE FRENKEL-DAVYDOV MODEL

The Frenkel–Davydov model supposes that the excited-state properties of an N molecule system may be expressed in terms of a reduced excitonic Hamiltonian

$$\hat{H}_F = \sum_m E_m |m\rangle \langle m| + \sum_{m \neq n} V_{mn} |n\rangle \langle m|, \quad (1)$$

where $|m\rangle$ represents the basis state where molecule m is in the excited state (all other molecules are assumed to be in the ground state), E_m is the excitation energy of molecule m , and V_{mn} is the coupling between excitations on molecules m and n . When using CIS or TDDFT with the Tamm–Dancoff approximation (TDDFT/TDA), the basis states in Eq. (1) may be expressed as

$$|m\rangle = \sum_{ia} D_{ia}^m \left| \psi_a^m \left(\prod_{j \neq i} \psi_j^m \right) \psi_1^m \psi_2^m \dots \psi_N^m \right|, \quad (2)$$

where ψ_i^m refers to the i th orbital of molecule m and D_{ia}^m is the CIS coefficient for an excitation from the occupied orbital i to virtual orbital a on molecule m . This basis can readily be expanded to the

full N molecule case by appending ground state MOs to the determinant. Assuming that the molecules interact weakly, we may optimize the CIS and MO coefficients for each fragment independently and derive the Frenkel Hamiltonian matrix elements by projecting the supersystem electronic Hamiltonian into this basis. The couplings (off-diagonal elements) that result from this procedure may be expressed as

$$V_{mn} = \sum_{iajb} D_{ia}^m D_{jb}^n [2(\psi_i^m \psi_a^m | \psi_j^n \psi_b^n) - (\psi_i^m \psi_j^n | \psi_a^m \psi_b^n)], \quad (3)$$

where $(ia|jb) = \int dr_1 dr_2 \psi_i(r_1) \psi_a^*(r_1) \frac{1}{r_{12}} \psi_j(r_2) \psi_b^*(r_2)$. It is common to make several additional approximations to make calculating this coupling more tractable. Many studies neglect the exchange terms in Eq. (3) under the assumption that the MOs on different molecules do not have a significant spatial overlap.^{7,37–42} We examined the contribution of exchange to the coupling in Sec. VI of this study; however, it is also worth noting that it is not clear if the Frenkel exciton model itself is appropriate in strong-coupling regimes where exchange is significant.

The Coulomb couplings in Eq. (3) may also be simplified in terms of an interaction between transition charge monopoles q_f on the atoms of each molecule,³⁷

$$V_{mn} \approx \sum_{f,g} \frac{q_f^m q_g^n}{|\mathbf{r}_f - \mathbf{r}_g|}, \quad (4)$$

where the summation is taken over pairs of atoms belonging to separate molecules, $\mathbf{r}_f$ is the position of atom f , and q_f^m is the charge of atom f of molecule m . The transition charges may be determined via a variety of methods. One popular approach is to use Mulliken population analysis on the transition density matrix,

$$q_f = \sum_{ia} \sum_{\mu} \sum_v N_{aof} D_{ia} C_{i\mu} C_{av} S_{\mu v}. \quad (5)$$

Here, the summation over μ and v is taken over the atomic orbitals. $C_{i\mu}$ are atomic orbital coefficients, and $S_{\mu v}$ is the overlap between orbitals μ and v . N_{aof} is the number of atomic orbitals on atom f . In PPP/CIS theory, Eq. (4) is essentially equivalent to the exact coupling integral due to the zero-differential overlap approximation and highly localized orbitals.⁹ However, for TDDFT and other *ab initio* methods, Eq. (4) is an approximation that should hold if the two molecules are sufficiently far apart. This approach has been adopted in several studies^{37,38,40,41,43} due to how it is significantly more computationally efficient than directly computing the two-electron integrals in Eq. (3). In Sec. VI A, we benchmark differences when calculating couplings using transition charges derived from Mulliken, Löwdin, and natural population analyses to the exact Coulomb coupling from TDDFT.

III. COMPUTATIONAL DETAILS

A. Data generation

We consider two materials, each with identical chemical composition, but differing molecular morphology. Specifically, we consider a monolayer morphology of 150 molecules, where molecules are in rough mutual alignment, as illustrated in Fig. 2(a), and an

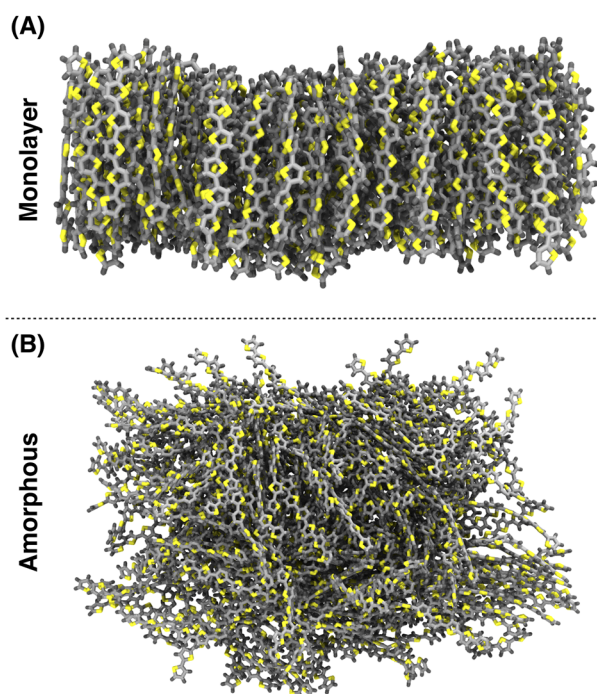


FIG. 2. Snapshots of different molecular morphologies used in this study. Panels (a) and (b) show the monolayer and amorphous morphologies, respectively.

amorphous bulk morphology of 343 molecules, as illustrated in Fig. 2(b). For each morphology, we generate a 10 ps trajectory of the nuclear dynamics using molecular dynamics (MD) simulations with the OPLS/2005 force field.^{44,45} Periodic boundary conditions were employed with the monolayer system periodically replicated in the plane parallel to the film, while the amorphous system was periodically replicated in three dimensions. All simulations were done in an NVT ensemble at 300 K with a Nosé–Hoover thermostat^{46,47} with a coupling constant of 2.0 ps after equilibration. Simulations were done with the DESMOND package⁴⁸.

We map the MD snapshots to the Frenkel Hamiltonians using a set of independent one-molecule excited-state electronic-structure (ES) calculations (see Sec. II). We use two different ES methods to calculate Frenkel Hamiltonians: PPP/CIS and TDDFT with the Tamm–Dancoff Approximation (TDDFT/TDA). For our TDDFT/TDA calculations, we employ the CAM-B3LYP functional,⁴⁹ along with 6-31 + G(d) basis set, due to the functional’s demonstrated performance at reproducing the coupled-cluster excitation energies of organic chromophores.^{50–52} Despite the functional’s incomplete use of long-range corrections, Lu *et al.* demonstrated that the accuracy of lowest singlet excitation energy increases with the size of the number of monomers in an oligothiophene.⁵⁰ TDDFT/TDA calculations were done with the PySCF package.⁵³

Using PPP/CIS, we mapped MD snapshots to Frenkel Hamiltonian calculations at 10 fs intervals, assuming that we may treat the Frenkel Hamiltonians to be roughly constant within 10 fs. Due to the significantly increased cost of TDDFT/TDA, a longer interval

of 100 fs was used when calculating Frenkel Hamiltonians. We note, however, that one of the advantages of our proposed ML model is that it may be used to calculate Frenkel Hamiltonians at intervals much smaller than even 10 fs with little added cost. Couplings for molecules at intermolecular separations greater than 20 Å are neglected due to the fact that they are extremely small (1 meV on average for the monolayer system). While the 20 Å cutoff has not been explicitly shown to have a negligible effect on exciton dynamics, we hope to use the efficiency of the ML model described herein to further elucidate the effects of coupling cutoffs in future studies.

B. Data preparation and machine learning

To train and evaluate our unimolecular ML models (for predicting E_m and transition charges using KRR), the data (features and associated values) were separated into training and testing sets. The term “features” refers to the inputs X of the regression algorithm: information about the molecular conformations. The term “values” refers to the quantities, $Y = f(X)$, we are trying to predict with the ML model. The training sets ranged in size from 100 to 10 000 datapoints, and the testing sets contained 5000 datapoints. We found that 5000 testing examples were sufficient to get an unbiased estimate of the error (Fig. S1 of the [supplementary material](#)). The training and testing data are always independent and randomly sampled, meaning that no two datapoints are shared between training and testing sets, and both are randomly chosen from the master dataset containing all of the available data.

To train and evaluate our deep neural network (DNN) for the direct prediction of V_{mn} , data were separated into independent randomly sampled training, validation, and testing sets. The training sets ranged in size 130 000–520 000 datapoints, the validation set contained 200 000 datapoints, and the testing set contained 3 000 000 datapoints. The validation set was used to pick the optimal number of epochs for early stopping during the training phase of the DNN. Only PPP/CIS data were used in the training of our direct V_{mn} model. In Sec. V, we report the sizes of the training sets in terms of the equivalent number of ES calculations needed to produce the couplings, as we believe the number of ES calculations to be a more informative measure when trying to ascertain the cost vs accuracy trade-off of the machine learning approach.

KRR models were trained using the scikit-learn Python package.⁵⁴ The KRR hyperparameters were selected via fivefold cross-validation. The DNN described in Sec. V was trained with Tensorflow 2.0.⁵⁵ The network consisted of three layers with 1200, 1000, and 800 neurons, respectively. The first and third layers used sigmoid activation functions, while the second layer used an exponential activation function to avoid the vanishing gradients’ problem. ADAM was used as the optimizer, and early stopping with the validation dataset was used to avoid overfitting.

IV. ML MODEL FOR EXCITATION ENERGIES

There are numerous ML models and featurizations that are very successful at predicting various molecular energies from unimolecular conformational data.^{56–65} Recently, Lu *et al.*⁵⁰ compared the performance of a series of molecular DNNs at predicting

excitation energies of high-temperature gas-phased T6 and showed a mean absolute error (MAE) of around 50 meV when compared to the actual TDDFT results. Here, we adopt a simpler approach using a kernel ridge regression (KRR) model with a Gaussian kernel. KRR offers several advantages to neural network models since it is generally much less expensive to train, has fewer hyperparameters, and is guaranteed to give the optimal solution (lowest training error) for a given set of training data and hyperparameters. Additionally, KRR is a well-understood, well-tested ML model that has already been shown to perform excellently as a way of accelerating non-adiabatic excited-state dynamics.^{65–68}

For features, we employ the Coulomb matrix (CM),⁵⁶

$$C_{ij} = \frac{Z_i Z_j}{r_{ij}}, \quad (6)$$

where Z_i are a set of atomic partial charges taken from semi-empirical model and r_{ij} is the distance between atoms i and j . While traditionally the diagonal elements of the CM are given by $0.5Z_i^{2.4}$, here, we neglect the diagonal elements since they give no additional information about the conformation of the molecule. We tested the performance of a series of four different charge models, as well as just using pairwise atomic distances without any charges, and found that

while performances were comparable, the Gasteiger charge model⁶⁹ gave the lowest error [Fig. 3(a)]. Thus, in subsequent analysis, the Gasteiger charge model was used whenever employing Coulomb matrix features.

We evaluate the performance of our ML model subject to the criteria outlined in the Introduction through a series of numerical experiments. We begin by evaluating the dependence of the testing set MAE on the size of the training set for both the monolayer and amorphous systems [Fig. 3(b)]. We see that, in both systems, the error converges well, with a difference of only 10 meV or less in the error between training with 5000 examples vs 10 000 examples. For both systems, the converged errors are significantly lower than the intrinsic uncertainty of a TDDFT calculation with CAM-B3LYP or similar range-separated hybrid functional, which based on previous studies we estimate to be around 200 meV.^{9,50} When training with 10 000 examples, the errors are only about 0.4% of the mean E_m in the monolayer system and 0.7% of the mean E_m in the amorphous system. However, comparing ML errors to the mean value of the excitation energy is not a very informative metric, as one can subtract any constant value out from the diagonal elements of the Frenkel Hamiltonian without changing the dynamics. It is more appropriate to compare the ML errors to the fluctuations (standard deviation) in E_m , as one would expect that ML errors that are of the

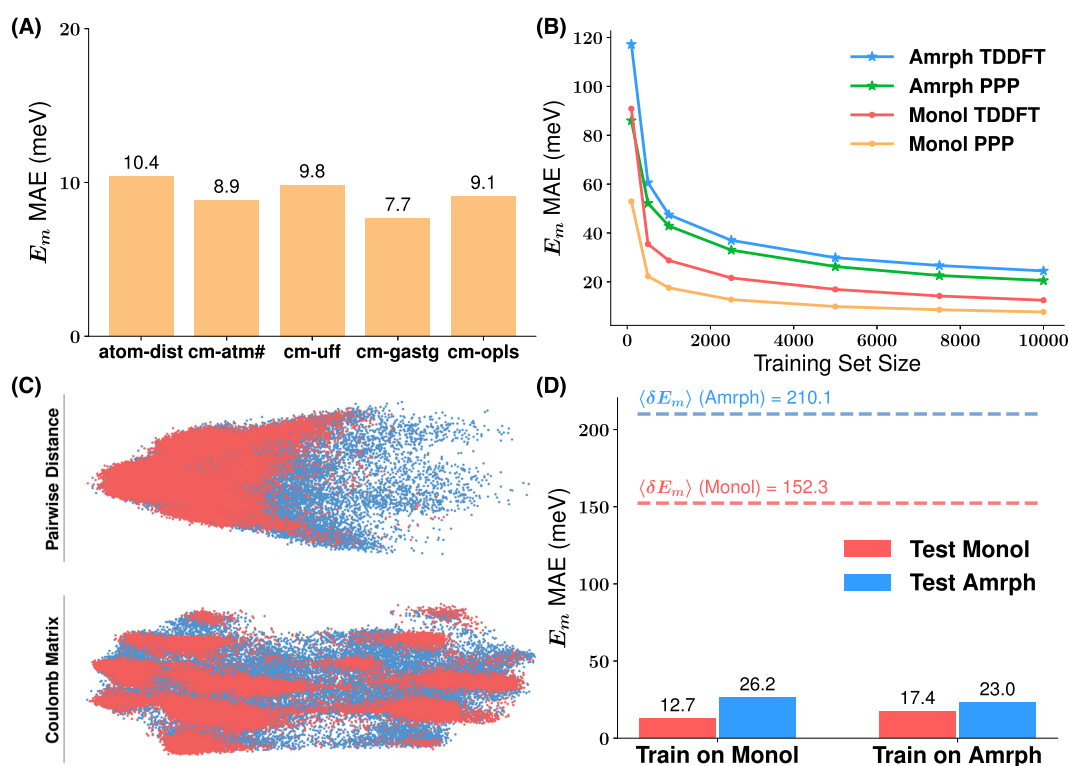


FIG. 3. (a) Differential performance of using several different charge models with the Coulomb matrix. Performances reported here are using the 10 000 example monolayer PPP/CIS training set. atom-dist = pairwise atomic distances (no charges), atm# = atomic numbers, uff = Universal Forcefield,⁷⁰ gastg = Gasteiger charges,⁶⁹ and opsls = OPLS/2005 Forcefield.⁴⁴ (b) Mean absolute error in E_m predictions vs training set size used. (c) 2D principal component analysis of pairwise atomic distances and Coulomb matrices taken from T6 conformations. (d) Cross-morphology error analysis on the predictions of E_m from TDDFT. Dashed lines indicate fluctuations (standard deviation) in E_m from the MD bath.

same order of magnitude or greater than the fluctuations would lead to significant errors in the exciton dynamics.¹³ The standard deviation in E_m from the MD bath is about 150 meV and 210 meV for the monolayer and amorphous systems, respectively, if calculated with TDDFT, and about 103 meV and 181 meV if calculated with PPP/CIS. These fluctuations are significantly higher than the MAE in Fig. 3(b) so long as 1000 or more training examples are used. Thus, our model satisfies our first three performance criteria. The strong performance of our model matches results from other studies using kernel based regression methods to predict unimolecular quantities.^{58,59,61,71}

Interestingly, the errors for the amorphous system tend to be higher than the MAE for the monolayer system. We attribute this increase to the greater range of intermolecular forces and larger conformational space sampled by the amorphous system. In Fig. 3(c), we demonstrate this larger sampling by performing principal component analysis (PCA) in two dimensions on the internal coordinates, showing that the area covered by the amorphous conformations is far larger than the area covered by the monolayer conformations. The wider range of intermolecular forces is also reflected in the larger standard deviation of E_m in the amorphous system.

Also of note is the fact that the error for the TDDFT data tends to be slightly higher than the error for the corresponding PPP/CIS data. The reduced performance on TDDFT data can be attributed to the increased complexity of the excited-state energy landscape from TDDFT as compared to PPP/CIS, which is a natural result of the more complex equations and much larger basis sets.

To evaluate the final performance criterion, transferability across morphologies, we take a model trained with 10 000 examples on a given morphology and test it against conformations from the other morphology. Despite the wider sampled space, the error of the model trained on monolayer conformations does not increase significantly when evaluated against conformations from the amorphous system [Fig. 3(d)]. Indeed, while the KRR model's predictive performance is best on the morphology it was trained on, the errors from the cross-morphology predictions are still small fractions of the fluctuations in E_m . We take this result to indicate that our model can generalize to morphologies of T6 beyond what it was originally trained (if at roughly the same temperature), satisfying our fourth performance criterion.

V. DIRECT ML MODEL FOR COUPLINGS

In principle, the increased scaling between the number of ES calculations and the number of coupling values merits using a different ML model than KRR. Each unique pair of molecules equates to a single coupling value, giving a total of $\frac{N(N-1)}{2}$ coupling datapoints per N molecules in a single time step. Roughly, this scaling equates to 10 000 ES calculations per 260 000 couplings in both the monolayer and amorphous systems. The $O(N^3)$ cost of inverting the kernel matrix makes KRR unsuitable for datasets much larger than 50 000 examples in size, but DNNs have been shown to be excellent at handling “big-data.” Thus, we chose to use a three-layer neural network model for the direct ML of the couplings. For features, we employ an intermolecular Coulomb matrix, with pairwise distances between atoms of separate molecules.

A very similar model for electron-transfer coupling using a much smaller dataset with KRR was recently reported by Wang *et al.*⁷² We decided to test this model only on the PPP/CIS data due to the poor convergence of the model and need for larger training sets.

The predictive performance of the direct V_{mn} model is significantly worse than the performance of the E_m ML model. Figure 4(a) demonstrates that the errors do not converge as quickly as they did in the E_m model. Although the errors here appear small, especially in comparison to the corresponding errors for E_m , one must keep in mind that the magnitude for V_{mn} is about two orders of magnitude smaller than the magnitude of E_m in these systems. The mean magnitude for V_{mn} is only 14.7 meV and 8.8 meV for the monolayer and amorphous systems, respectively, while the mean magnitude of E_m is about 2960 meV and 3120 meV, respectively. Thus, the

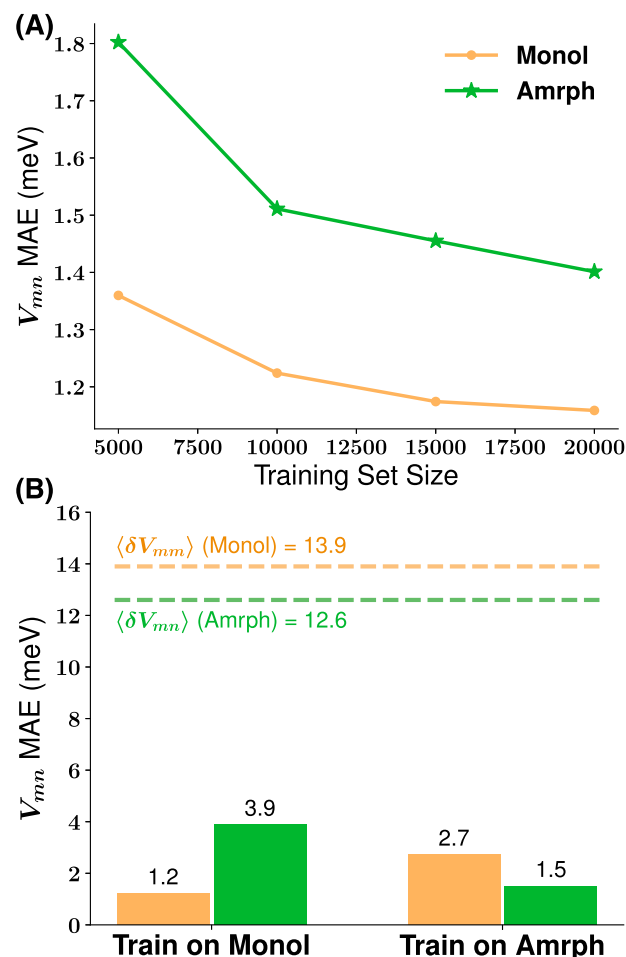


FIG. 4. V_{mn} prediction performance using the direct model. (a) Mean absolute error in PPP/CIS V_{mn} predictions vs the number of one-molecule PPP/CIS excited-state calculations used to generate the training set. (b) Cross-morphology error analysis on the predictions of V_{mn} using 10 000 ES calculations = 260 000 coupling training sets.

% error is much larger than what we had for E_m even when training with only 1000 examples. Perhaps more importantly, the errors are a large proportion of the fluctuations in V_{mn} , and the cross-morphology error is very significant. The latter suggests that even if we accept the lower accuracy to training size trade-off of this coupling ML model, for every different morphology that one might want to simulate, one would need to do tens of thousands of additional ES calculations, significantly hampering the efficiency bonus of using ML.

We believe that the poor performance of the direct V_{mn} model can be attributed to the very large bimolecular conformational space, which requires significantly more data to properly sample than those of the unimolecular space for E_m . The unimolecular conformational space only includes small perturbations of the nuclear positions due the vibrations and intermolecular forces, whereas bimolecular conformational space contains the same small perturbations as well as the myriad of different ways the two molecules (and constituent segments/rings) may be oriented with respect to each other. Clearly, sampling such a space thoroughly would require much more data. Even with the ratio of the naturally higher ES calculation to the number of datapoints (1:1 for E_m vs 1:26 for V_{mn}), the amount of ES calculations required to train a V_{mn} model from bimolecular data far exceeds the number of calculations required to train an equivalent accuracy E_m model from unimolecular data. Motivated by this difficulty, we sought to find a ML approach whereby we could predict V_{mn} from unimolecular features, which leads to our transition charge model.

VI. INDIRECT ML MODEL FOR COUPLINGS VIA TRANSITION DENSITIES

A. Coupling calculation benchmarking

In this section, we benchmark several methods of calculating the excitonic coupling. We begin by comparing couplings calculated via PPP/CIS to the exact couplings calculated via TDDFT [Fig. 5(a)]. The PPP/CIS couplings tend to significantly underestimate the TDDFT couplings for larger values. The decreased couplings of PPP/CIS would result in lower exciton transport rates when compared to TDDFT, highlighting the importance of the ML approach for allowing us to use higher levels of theory when parameterizing V_{mn} . However, given the very low computational cost and severe simplifications of PPP/CIS, we are encouraged by how well the PPP/CIS and TDDFT couplings are correlated.

There appears to be no clear consensus in the literature about whether exchange (Dexter transfer) is physically significant when considering the excitonic couplings in small-molecule organic semiconductors; hence, here, we benchmark the error when neglecting exchange. In Fig. 5(b), we illustrate that the exchange contribution to coupling is completely negligible in the monolayer system, with an average difference of 0.03 meV from using exchange or not. This result is somewhat surprising as T6 molecules come in very close proximity to each other during the MD simulation, with the minimum center of geometry distance between two T6 molecules being as small as 3.5 Å. Examining the LUMO of a

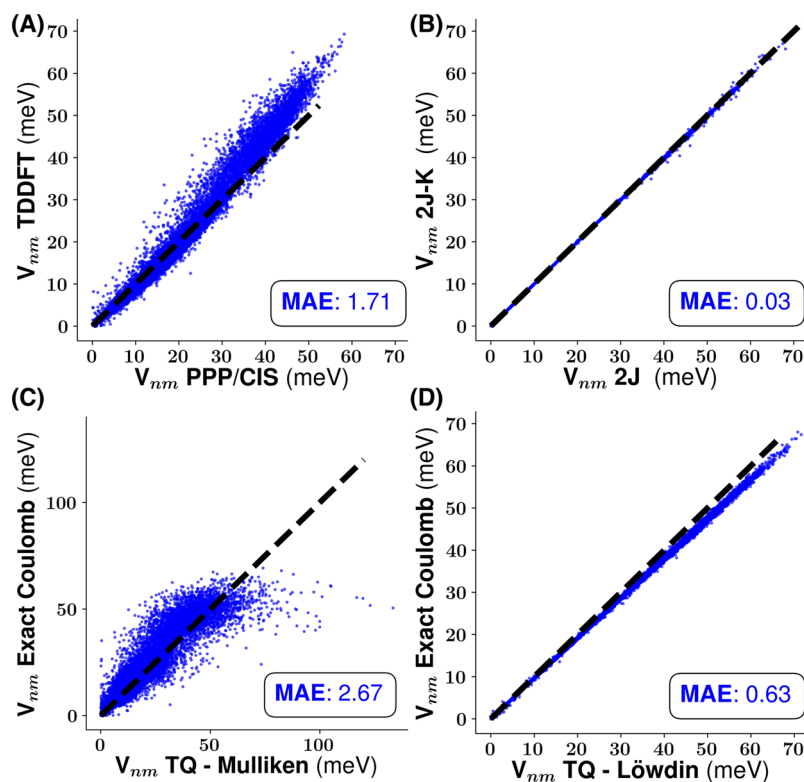


FIG. 5. Parity plots for benchmarking coupling calculations. All values are from monolayer simulation. (a) Exact PPP/CIS vs TDDFT couplings. (b) TDDFT couplings with and without exchange. (c) TDDFT Coulomb couplings from Mulliken transition charges. (d) TDDFT Coulomb couplings from Löwdin transition charges.

typical T6 from the monolayer simulation (Fig. S4 of the [supplementary material](#)), it appears tightly bound to the molecule, supporting the low-exchange interactions from our calculations. However, such tight-binding orbitals may be just an artifact of the Frenkel exciton model's use of independent single-molecule calculations. We speculate that outside the Frenkel exciton model, in real systems, the electronic polarization due to the neighboring T6 molecules may lead to more delocalized molecular orbitals, thus more spatial overlap and strong exchange.

Now that we have established that Coulomb couplings are sufficient when computing couplings in T6, we test whether they can be reproduced using a set of transition charges localized on each atom as in Eq. (4) (Fig. 6). Both Mulliken and Löwdin population analyses were tested. The Mulliken-charge based couplings show a significant deviation from the exact Coulomb couplings due to the significant overestimation of the charge on the central atoms of T6 [Fig. 4(b)]. Mulliken population analysis is well known to be highly basis set dependent;⁷³ in the limit where a complete basis set is localized on a single atom, Mulliken analysis will assign the entire transition density to that atom. In T6, the high overlap between the atomic basis functions of the carbons on the central rings with the surrounding atomic orbitals can lead to an artificial concentration of charge on a few carbon atoms. This concentration of charge leads to couplings that are highly dependent on the positions of these carbons, i.e., if the central carbons are too close together, Mulliken charges can give up to double the actual coupling. Although it is well-known that Löwdin analysis may also show a significant basis set dependence, in T6, the Löwdin orbital orthogonalization procedure leads to charges that are more evenly spread across the atoms, giving a better representation of the actual charge density and thus better couplings. The Löwdin charges do an excellent job at reproducing the Coulomb couplings,

with an average difference of only 0.6 meV from the exact Coulomb integral calculations.

One may think that given the high predictive performance of the Löwdin transition charges, it may be possible to calculate the couplings using a single-set of transition charges, similar to how interactions between molecules are calculated in molecular dynamics. This approach would side-step the need for high dimensional regression algorithms such as NN and KRR; however, in Fig. S5 of the [supplementary material](#), we show that such an approach leads to an enormous increase in error, with an MAE of 1.74 meV.

We also explored charge embedding based on the natural atomic orbitals as opposed to the Löwdin orbitals (the so-called natural population analysis), and found that the results were essentially equivalent to the Löwdin analysis (Fig. S4 of the [supplementary material](#)), and therefore proceed with using the Löwdin charges for the remainder of this study.

We would also like to emphasize that the transition charge method is effective not only because it gives us another avenue for machine learning the couplings but also because it is significantly less computationally demanding than calculating the couplings exactly. In Table SI of the [supplementary material](#), we show that computing the exact Coulomb coupling calculation takes 8300 CPU h for the monolayer system. Meanwhile, the cost of the Löwdin transition charge couplings is only 22 CPU h. While, as shown in Fig. 5(c), the Löwdin transition charge method produces some systematic error for molecules very close together, we believe that this degree of error is acceptable in light of the enormous improvement in computational efficiency.

B. Machine learning model

In Sec. VI A, we described how Löwdin transition charges can effectively reproduce the excitonic coupling V_{mn} ; in this section, we proceed with describing a ML model for V_{mn} by predicting the Löwdin transition charge on each atom from molecular conformations. Our strategy is generally the same as our model for E_m : a KRR model with Coulomb matrix features. However, here, we train an individual KRR model per transition charge. This approach is similar to the one described by Brockherde *et al.*,⁷¹ as a way of predicting the ground-state one-electron density.

Even using the same model and features, the percent mean absolute error (%MAE) when predicting individual transition charges is higher than the %MAE when predicting the excitation energies (Table SII of the [supplementary material](#)). This increase is to be expected however; both the transition density and transition charges vary greatly with small perturbations in the positions of the nuclei. Fortunately, the prediction quality when calculating the couplings from the transition charges improves dramatically due to how this approach captures the $\frac{1}{r}$ dependence of the Coulomb interaction between charge densities exactly, as opposed to relying on the ML algorithm to determine this dependence on its own. The performance of this transition charge ML model for predicting V_{mn} is significantly better than the performance of the direct model. In Fig. 7(a), we see that the error convergence is much improved, almost on par with the energy calculations, and the increase in error from cross-morphology predictions is negligible. Overall, when training with 10 000 examples, the

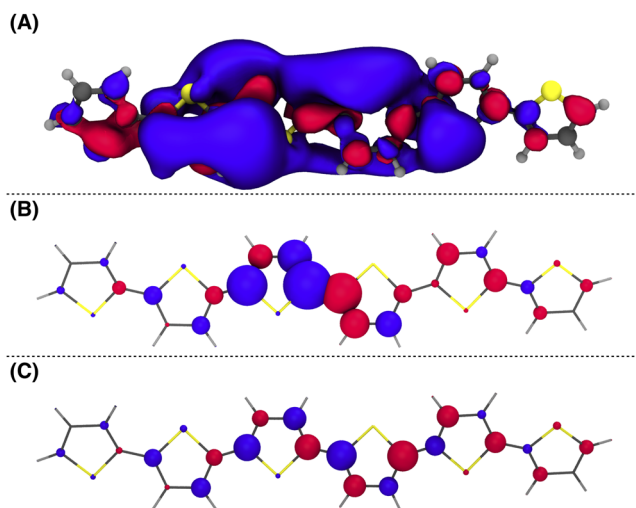


FIG. 6. Charges and density visualizations for a typical molecule taken from monolayer simulation. (a) Isosurface of transition density using a value of 0.07: violet lobes are positive, and red lobes are negative. (b) Mulliken charges, the size of each sphere indicates the magnitude of the assigned charge. (c) Löwdin charges.

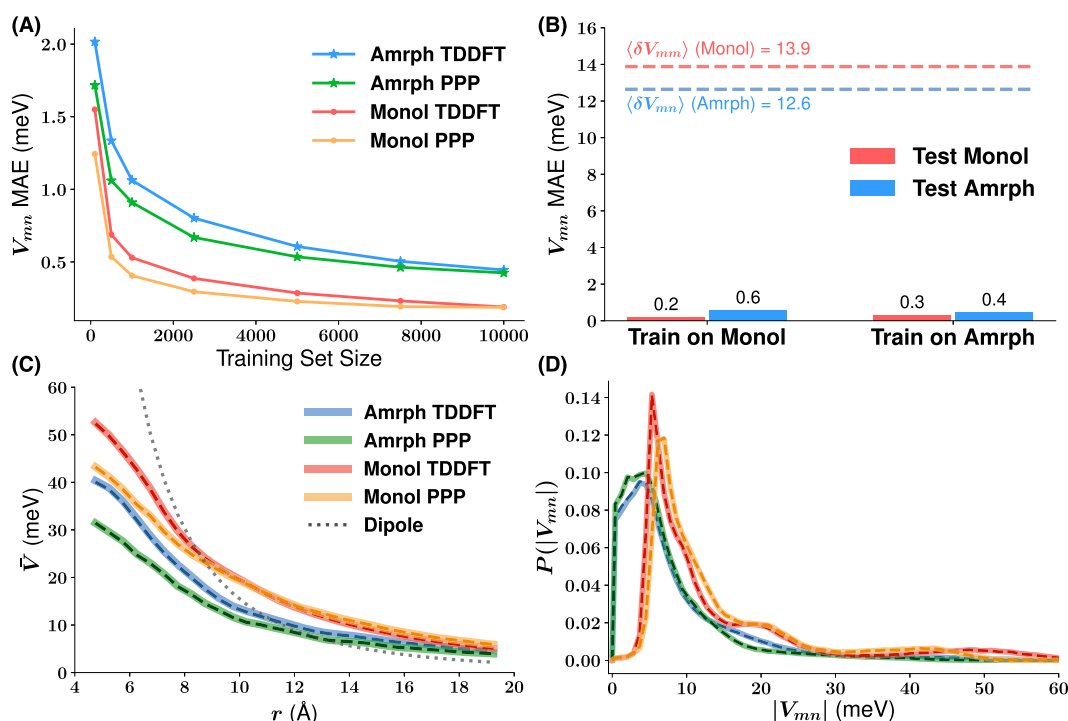


FIG. 7. Comparing the error between actual transition charge couplings and machine-learned transition charge couplings. (a) Mean absolute error in V_{mn} predictions vs training set size used. (b) Cross-morphology error analysis with TDDFT data. (c) Average coupling vs center of geometry distance: solid lines are from the exact transition charges, and dashed lines are from ML predicted charges. (d) Coupling distributions.

MAE is only a small fraction of the fluctuations in V_{mn} and roughly the same as the degree of intrinsic error from the Löwdin charge embedding. Thus, in stark contrast to the direct V_{mn} model, the transition charge V_{mn} model satisfies all of our ML performance criteria.

To further illustrate the high performance of this transition charge model, we analyzed the performance of the model at predicting the average distance dependence of V_{mn} as well as the probability distribution of Figs. 7(c) and 7(d). In both cases, the agreement between ML results and actual values is almost exact due to how the ML errors are largely random and these random errors are effectively averaged out. Such high accuracy is a very desirable property, as these distributions are an important visual tool for giving mechanistic insight into exciton transport and assessing why exciton diffusion rates differ between systems.

It is worth noting that the error analysis shown in Fig. 7 focuses on differences between the ML predictions and the actual transition charge coupling from Eq. (4), not the exact couplings from Eq. (3). Thus, in Fig. 8, we compare the MAE of the ML predicted couplings to the exact Coulomb couplings in the monolayer morphology. The error between the ML predicted transition charge couplings and exact Coulomb couplings is only 0.03 meV greater than the error induced by the charge monopole approximation itself [Fig. 5(d)]. This result once again indicates the efficacy of the ML approach, as it highlights how the errors induced by the ML (when trained with sufficient data) are insignificant

compared to the standard approximations already necessary for computing the electronic structure of the extended condensed phase systems.

C. Trajectory analysis

Now that we have described ML models capable of reproducing E_m and V_{mn} at high accuracy, we turn to using the said models in tandem to predict a time-series of Frenkel Hamiltonians. As proof that our ML models can give accurate dynamics, we compare exciton trajectory statistics from the ML predicted Hamiltonians (using 10 000 training examples) to those directly from PPP/CIS calculations. In order to assess the transferability of the ML models, we only include only conformations from the monolayer simulation in the training data. We do not test TDDFT here since the large time interval makes it difficult to accurately assess dynamics.

Exciton dynamics are propagated using a discrete set of time-ordered propagators calculated at 10 fs intervals from MD conformations,

$$|\Psi(n\Delta t)\rangle = \left[\prod_{j=0}^n \exp(-iH_j\Delta t/\hbar) \right] |\Psi(0)\rangle, \quad (7)$$

where $\Psi(t)$ denotes the time-dependent exciton wavefunction, Δt is the time step interval, and H_j represents the j th Frenkel Hamiltonian. We study two experimentally observable statistics of

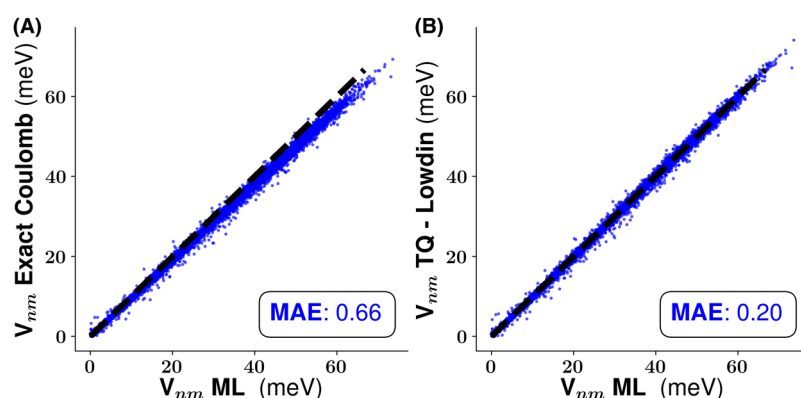


FIG. 8. Parity plots for comparing accuracy of ML predictions to (a) the exact values, and (b) the values computed with TDDFT Coulomb couplings from Löwdin transition charges. All values are from monolayer simulation. The ML model was trained using 10 000 molecular conformations.

interest: the exciton mean-square displacement (MSD) and the lowest energy eigenvalue (LEE) of the Frenkel Hamiltonian. The MSD is defined as

$$MSD(t) = \left\langle \sum_n |\mathbf{r}_n(t) - \mathbf{r}_n(0)|^2 |c_n(t)|^2 \right\rangle_m, \quad (8)$$

where $\mathbf{r}_n(t)$ is the center of the mass position of molecule n at time t , and $|c_n(t)|^2$ is the probability of finding the exciton on molecule n at time t . The angled brackets indicate an average over an ensemble of trajectories with the exciton initially localized on each different molecule. Without exciton delocalization, this MSD is equivalent to the usual MSD for particles.

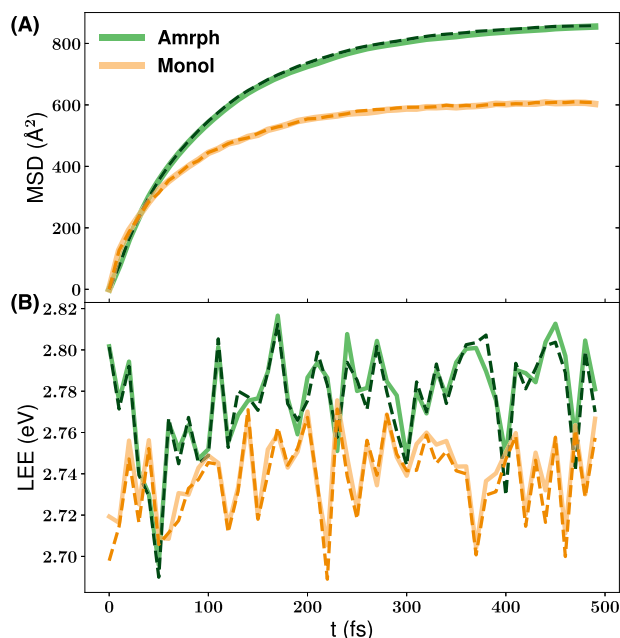


FIG. 9. PPP/CIS trajectory statistics from monolayer and amorphous simulations. Solid lines are using exact calculations, and dashed lines are using the ML model trained with 10 000 training examples selected only from the monolayer simulation. (a) Mean-square displacement. (b) Lowest energy eigenvalue.

In both cases, the predictions from the ML model match the exact PPP/CIS results very well (Fig. 9). There is virtually no difference in the MSD, as the ML predictions do not produce systematic errors, and the random errors are washed out when averaging over many trajectories. The agreement for the LEE is not as quantitative as the MSD, particularly for the amorphous system, but still quite strong as the PPP/CIS and ML lines are very well correlated. We believe that the close fit between actual MSD/LEE and the ML predictions illustrates that our model can not only predict individual E_m and V_{mn} elements accurately but also give very good predictions for the Frenkel Hamiltonian as a whole.

VII. CONCLUSIONS

In this paper, we presented a novel ML strategy for generating Frenkel Hamiltonian trajectories from MD conformations. We built separate models for the diagonal excitation energies, E_m , and off-diagonal couplings, V_{mn} , and tested the ML models against a set of four rigorous criteria: (1) applicability across electronic-structure methods, (2) lower errors than intrinsic uncertainty in the electronic-structure method, (3) lower errors than fluctuations from the MD bath, and (4) transferability across morphologies. We showed that a simple KRR model with Coulomb matrix features is capable of satisfying all four criteria when predicting E_m . We then attempted to build a ML model to directly predict V_{mn} from two-molecule features but illustrated that such an approach failed the performance criteria, likely due to the much larger size of the bimolecular conformational space. The failure of this approach motivated us to pursue building an ML model for V_{mn} from unimolecular features by predicting a set of atom-centered transition charges. We demonstrated that these transition charges reproduce the coupling quite poorly when assigned with Mulliken population analysis but do much better when assigned with Löwdin population analysis. We then built another ML model, completely analogous to the E_m model, but for predicting each individual transition-charge independently. We demonstrated that like the E_m model, it satisfied the performance criteria. While regression algorithms other than KRR may be proposed and utilized in the future, we hope that the insight into the relative ease of predicting a vectorial unimolecular quantity vs a scalar bimolecular quantity will prove to be generally helpful to the broader

community interested in combining machine learning and quantum chemistry.

The strong performance of both our E_m and transition charge V_{mn} models with 10 000 training examples suggests that an even smaller training set may be employed if necessary. However, 10 000 ES calculations are still orders of magnitude less than the number of calculations necessary to produce a single Frenkel Hamiltonian trajectory in many systems. In the future, it would be interesting to expand the models built here using “active learning” methods,^{74,75} where the ML algorithm retrains itself when encountering datapoints far outside the training set.

While we studied the application of our model only in T6 systems, we believe that it may be applied in across a variety of systems where the Frenkel–Davydov model is appropriate. Of course, care must be taken in systems such as polymers, where individual fragments may have a significant wavefunction overlap and exchange coupling is not negligible, as our transition charge V_{mn} model breaks down with significant exchange. However, it may be possible to build a very similar unimolecular V_{mn} model by predicting the entire transition density matrix using features taken from lower level electronic-structure data, such as overlap and Fock matrices. We believe that this is another exciting area for future development. It is also worth noting that it is dubious whether the assumptions made in the standard Frenkel–Davydov model are appropriate in strong-coupling situations where exchange is significant.

Finally, we note that parameterizing Frenkel Hamiltonians directly from MD conformations does neglect the backaction of the exciton on the nuclear bath. However, we hope that with the improved efficiency of our ML-Frenkel model, we may begin to address this limitation by introducing corrections to the MD forces based on the state of the exciton. We hope to further develop this ML-Frenkel protocol and, after careful validation against experiment, employ it to understand the effects of molecular morphology and correlated environmental noise on exciton diffusion in organic semiconductors and guide organic semiconductor design.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional error analysis of ML methods and charge monopole approximation.

ACKNOWLEDGMENTS

A.F. and A.P.W. were supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-SC0019441. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We would like to thank Amr Dodin and Maria Alejandra Castellanos for helpful discussions on exciton dynamics. Ardavan Farahvash acknowledges support from the National Science Foundation Graduate Research Fellowship Program.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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