Predicting Phosphorescence Energies and Inferring Wavefunction Localization with Machine Learning

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Phosphorescence is commonly utilized for applications including light-emitting diodes and photovoltaics. Machine learning (ML) approaches trained on ab-initio datasets of singlet-triplet energy gaps may expedite the discovery of phosphorescent compounds with the desired emission energies. However, we show that standard ML approaches for modeling potential energy surfaces inaccurately predict singlet-triplet energy gaps due to the failure to account for spatial localities of spin transitions. To solve this, we introduce localization layers in a neural network model that weight atomic contributions to the energy gap, thereby allowing the model to isolate the most determinative chemical environments. Trained on the singlet-triplet energy gaps of organic molecules, we apply our method to an out-of-sample test set of large phosphorescent compounds and demonstrate the substantial improvement that localization layers have on predicting their phosphorescence energies. Remarkably, the inferred localization weights have a strong relationship with the ab-initio spin density of the singlet-triplet transition, and thus infer localities of the molecule that determine the spin transition, despite the fact that no direct electronic information was provided during training. The use of localization layers is expected to improve the modeling of many localized, non-extensive phenomena and could be implemented in any atom-centered neural network model.
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Abstract

Phosphorescence is commonly utilized for applications including light-emitting diodes and photovoltaics. Machine learning (ML) approaches trained on ab-initio datasets of singlet-triplet energy gaps may expedite the discovery of phosphorescent compounds with the desired emission energies. However, we show that standard ML approaches for modeling potential energy surfaces inaccurately predict singlet-triplet energy gaps due to the failure to account for spatial localities of spin transitions. To solve this, we introduce localization layers in a neural network model that weight atomic contributions to the energy gap, thereby allowing the model to isolate the most determinative chemical environments. Trained on the singlet-triplet energy gaps of organic molecules, we apply our method to an out-of-sample test set of large phosphorescent compounds and demonstrate the substantial improvement that localization layers have on predicting their phosphorescence energies. Remarkably, the inferred localization weights have a strong relationship with the ab-initio spin density of the singlet-triplet transition, and thus infer localities of the molecule that determine the spin transition, despite the fact that no direct electronic information was provided during training. The use of localization layers is expected to improve the modeling of many localized, non-extensive phenomena and could be implemented in any atom-centered neural network model.
Keywords
Phosphorescence, machine learning, neural networks, localization, molecular properties, triplet states

Introduction

Molecules that are electronically excited by light or charge injection typically relax non-radiatively to their lowest-energy singlet or triplet excited states. Transitions between these singlet and triplet states (intersystem crossing) can be enabled by spin-orbit interactions. Subsequent radiative relaxation from excited-singlet to ground-singlet states leads to fluorescence, which occurs over nanosecond timescales. In contrast, radiative transitions from excited-triplet to ground-singlet states are forbidden on account of the difference in spin multiplicity. This radiative process, known as phosphorescence, occurs over much longer timescales, generally on the order of $10^{-3}$-100 s. The dynamics of low-energy singlet and triplet states form the basis for applications including light-emitting electrochemical cells, chemical sensors, organic light-emitting diodes (OLEDs), and
photovoltaics. For instance, a carefully designed thermally activated delayed fluorescence (TADF) process can be used to harvest energy from triplet to singlet states, raising the efficiency of an OLED to nearly 100%. As another example, simultaneous emission from triplet and singlet states in metal-organic polymers can be used to make white light LEDs. These examples illustrate the importance of a reliable prediction of triplet state emission energies across a large diversity of molecules capable of guiding experimental efforts toward future optoelectronic technologies. Computational screening using accurate ab initio calculations, such as density functional theory (DFT), can aid in molecular design. However, the computational costs of fully quantum mechanical approaches may restrict both the number and size of molecules that can be sampled efficiently. Machine learning (ML) has newfound relevance in quantum chemistry for accelerating simulations and providing predictions of ab initio quality.

Here, we leverage ML techniques and build an accurate and extensible ML model for phosphorescence energy that is enabled by its ability to account for electron localization associated with the spin transition.

ML research has led to predictive models of various molecular properties, among which are general interatomic potentials of ground state energies. Such models can be trained to large datasets (e.g., ~10^5-10^6 molecules) containing both equilibrium and off-equilibrium structures. This approach enables the construction of machine learned potential energy surfaces (PESs) for purposes such as dynamics and geometry optimization. Data curation and model training are computationally demanding tasks, but once trained, such models not only generate high-fidelity ab initio-quality predictions at low computational costs but also infer relationships within high-dimensional data and are transferable to molecules outside of the training dataset. ML for ground state chemistry has been explored at an appreciable depth, achieving models of high-accuracy theories and extremely large systems. However, its use for excited state processes such as phosphorescence is a new area of research.

The physics involved in describing an excited state transition is fundamentally different however from that of a ground state. For ground states, ML potentials incorporate the extensivity principle which defines the total energy of a molecule as a sum over individual atomic contributions. This assumption is physically motivated and has been
tested over a large chemical space, and provides the means for attaining transferable and extensible models.\textsuperscript{24,31,41} However, it breaks down in the case of electronic excitation energies, for which atoms may contribute to the transition energy in a disproportionate way. This disproportionality is evidenced by localized versus delocalized electronic transitions that are prevalent in chemical physics.\textsuperscript{42–45} In turn, the energy of an excitation does not scale strictly with the size of the molecule. Rather than using extensive predictions, it is reasonable to seek a method that can associate the energy of an excitation with specific regions of the molecule. Such an approach would have wide-ranging applicability since the notion of localization generalizes to many molecular phenomena and systems such as charged species and radicals.

In this work, we develop a model based on the Hierarchical Interacting Particle Neural Network (HIPNN)\textsuperscript{46} that accurately predicts the singlet-triplet energy gaps in a diverse chemical space of organic compounds at computational speeds that reach over one million times faster than the underlying \textit{ab-initio} method. HIPNN has previously shown excellent performance for ground state energies,\textsuperscript{46} partial atomic charges,\textsuperscript{47} and molecular dipole moments.\textsuperscript{48} We present new \textit{atomistic localization layers} that compute a weight for each atom corresponding to the atomic contribution to the molecule’s energy gap. The mathematics of these new layers can be likened to the statistical mechanics of a chemical potential, or to the technology of attention mechanisms in the neural network literature.\textsuperscript{49,50} The localization layers improve phosphorescence energy predictions on an out-of-sample test set of molecules that are larger than those found in the training set and that are known to be phosphorescent from experiment while qualitatively inferring the changes to the electron density due to the transition as shown by direct comparison to reference quantum mechanical spin density calculations. This result is remarkable given that DFT spin density was not provided as a target during training and highlights the added benefit that electronic information could have toward ML models of localized, non-extensive molecular phenomena.

\textbf{Methods}
We start with a brief review of how energy is computed with ML interatomic potentials, including the extensive HIPNN model,\textsuperscript{46} and describe the new methods in this work. The input descriptors of the molecules are atomic coordinates ($R_i$) and atomic numbers ($Z_i$), which together define the molecular geometry ($R$). In extensive HIPNN and several other atomistic neural networks,\textsuperscript{24,40,46} target energy for geometry $R$ is computed as a sum over atomic energy contributions,

$$E = \sum_{i=1}^{N} \varepsilon_i$$ \hspace{1cm} (1)

where $E$ is the energy of the molecule, $\varepsilon_i$ is the energy contribution of the $i$-th atom, and $i$ spans over the total number of atoms in the molecule $N$. Local atomic contributions are predicted as a linear combination of a high-dimensional learned feature vector $z_{i,a}$ using a vector of learned parameters $t_a$ and a bias $b$, where $a$ is a feature index:

$$\varepsilon_i = \sum_{a=1}^{N_{\text{features}}} t_a z_{i,a} + b$$ \hspace{1cm} (2)

Note that the $\varepsilon_i$ do not represent a direct physical quantity, but rather a factorization or ansatz form of the total energy $E$, representing the notion that the potential may be taken as a sum of contributions over latent variables $\varepsilon_i$ in the model, and it is a useful ansatz for an extensive total energy. For a single conformation of a system, many values of the $\varepsilon_i$ are compatible with the total energy. However, the machine learning algorithm learns a model of $\varepsilon_i$ so that $E$ will fit a large database of calculations simultaneously. The high-dimensional feature vector $z_{i,a}$ contains information collected from the local environment of that atom, and is also learned, but is less readily interpretable than $\varepsilon_i$.

This model can be applied in either the singlet ground state ($S_0$) or first triplet excited state ($T_1$). In addition to being trained to energy, our models are also trained to atomic forces. The inclusion of atomic forces as targets has been shown to improve energy predictions.\textsuperscript{51,52} Throughout the paper, we refer to the extensive HIPNN model that solely employs Eq. 1 to compute energy as HIPNN (Scheme 1a, left).
Scheme 1: (a) Traditional workflows for potentials with atomistic deep neural networks (DNNs) are based on an extensivity assumption (left) that predictions should be summed over all atoms in the system. With localization layers (right), atomistic neural networks can predict physical properties that are weighted by location and do not scale with the size of the molecule. This allows training to physical effects such as triplet excitations (which generally do not scale with molecule size), and identification of molecular regions that contribute to the investigated effect from a data-driven perspective. (b) Schematic of the $S_0$ and $T_1$ PESs depicted for reference DFT (black, solid
Transition energy relevant to phosphorescence ($\Delta E = E_{\text{phos}}$) is approximated as a difference between $T_1$ and $S_0$ energies with the $\Delta$SCF approach. This work introduces a localized variant of HIPNN, $\text{HIP-loc}$, to model $\Delta E$.

In HIPNN, singlet ($E_s$) and triplet ($E_T$) energies are determined from independent Self-Consistent Field (SCF) calculations, and both $E_s$ and $E_T$ are learned independently using separate linear prediction with the form of Eq. 1. Their difference,

$$\Delta E = E_T - E_S$$ (3)

is the singlet-triplet energy gap ($S_0$-$T_1$ gap) within the $\Delta$SCF method (Scheme 1b). For instance, near triplet state equilibrium, $\Delta E = E_{\text{phos}}$ represents the phosphorescence energy as calculated with $\Delta$SCF. We write the difference in Eq. 3 as a general $\Delta E$ to reflect that our method may be applicable to other localized, non-extensive properties, such as energies of anions, cations, or other excited states. The central motivation of our work is that Eq. 1, which is a sum over atom-centered energies, is inadequate in predicting $\Delta E$ (Eq. 3) for systems in which the electron density is spatially localized only on certain atoms. In other words, the extensivity approximation breaks down due to the absence of a well-defined scaling of $\Delta E$ with the number atoms (Fig. S1). The main contribution of our work is to develop a new approach to predict $\Delta E$ while accounting for this localization. This accomplishes two purposes: 1) The predicted $\Delta E$ will not scale intrinsically with the size of the system and 2) it gives rise to interpretable predictions regarding where in the molecule the singlet and triplet wave functions differ. The localized HIPNN model will be referred to as HIP-loc (Scheme 1a, right). We emphasize that the method developed here could also be applied to other atomistic neural networks that are trained using gradient methods.$^{24,53,54}$

We described how one could learn $E_S$ and $E_T$ and compute $\Delta E$ following their predictions (Eq. 3). This approach was carried out for the HIPNN model. Alternatively, one could learn $E_S$ and $\Delta E$, with $E_T$ defined as $E_T = E_S + \Delta E$. This definition represents $E_T$ as a sum of an extensive ($E_S$) and non-extensive ($\Delta E$) property, the latter of which
motivates the HIP-loc model. Atomic forces on the singlet state are the same as those used in the HIPNN model, $-\frac{dE_S}{dR_i} = F_{S,i}$ whereas the forces associated with $\Delta E$ are calculated as $-\frac{d\Delta E}{dR_i} = -\frac{dE_r}{dR_i} + \frac{dE_S}{dR_i} = \Delta F_i = F_{T,i} - F_{S,i}$. We now introduce the principal difference between HIPNN and HIP-loc (Scheme 1a). Instead of modeling $\Delta E$ as a simple sum over atom-centered energies (Eq. 1), we model it as a non-extensive quantity by weighting atomic energies by normalized weights $w_i$

$$\Delta E = \sum_{i=1}^{N} w_i \Delta \varepsilon_i$$

This form is physically motivated by the fact that the electron density may be localized on certain atoms. We show that the inclusion of these weights is instrumental in accurately predicting $\Delta E$, as opposed to Eq. 1, which assumes equal atomic contributions. We use a softmax function for $w_i$,

$$w_i = \frac{e^{a_i}}{\sum_{i=1}^{N} e^{a_i}}$$

where $a_i$, which we term the excitation propensity on the $i$-th atom, is a quantity learned in the training process. Eq. 5 ensures normalization of the weights, $\sum_{i=1}^{N} w_i = 1$. We predict both $\Delta \varepsilon_i$ and $a_i$ analogously to Eq. 2., with linear layers applied to the learned features. Because the weights sum to one, the predicted $\Delta E$ is bounded by the extrema of the $\Delta \varepsilon_i$, a local quantity that does not intrinsically scale with system size; Eq. 4 may be better thought of as a weighted average than as a sum.

The form of Eqs. 4 and 5 are similar to those of attention models and elementary statistical mechanical models. In a statistical mechanical analogy, the propensity $a_i$ plays the role of a (negative) chemical potential, whereas the weights $w_i$ are interpreted as a probability derived from the propensity using a Boltzmann weighting, and the excitation corresponds to an observable of the system. Such an analogy gives rise to intuition about the relationship between the propensity and the weights: if the
propensities are narrowly distributed, the weights will be roughly evenly distributed across the molecule. If a few propensities are larger than the rest, the weights will be concentrated on those few atoms. In our results, we show that these localization weights effectively infer the region of the triplet excitation, as determined by \textit{ab initio} spin density calculations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Sample set of the molecules used in this study. (Top panel) Select molecules from the train/test set (~702k structures in total). (Bottom panel) Select molecules from the phosphorescent test set (912 structures in total). The test set molecules are significantly larger (~2x larger on average) than the training set molecules and is often referred to as the phosphorescent extensibility set.}
\end{figure}

The molecules of the dataset were randomly sampled from the GDB13 dataset\cite{55} and contain C, H, N, O, S, and Cl atoms. \textit{Ab-initio} computations were performed using the \textit{ωb97x} density functional\cite{56} and 6-31g* basis set\cite{57} with Gaussian 16.\cite{58} All molecules were optimized in vacuum in the T$_1$ state. Thermal conformers ($T = 300$ K) near the minimum of T$_1$ were obtained with a normal mode sampling scheme.\cite{24} Doing so enables learning PESs at molecular conformations near points of stability (Scheme 1b). Subsequent single-point calculations of the entire dataset, including optimized and
thermal conformers, were carried out to determine $E_S$ and $E_T$. The entire dataset consisted of approximately ~702k structures with median molecule size of 8 heavy atoms (excluding H) and 16 total atoms with a maximum molecule size of 12 heavy atoms and 30 total atoms (Fig. S2). A more detailed breakdown of the dataset, including the number of molecules sampled from each GDB dataset, is available in Table S1.

The trained models were also tested on a challenging set of large aromatic molecules known to be phosphorescent from experiment with median molecule size of 17 heavy atoms (excluding H) and 27 total atoms with a maximum molecule size of 31 heavy atoms and 51 total atoms (Fig. S2). The compounds of this extensibility set were taken from Refs. 59–62 and make up 35 unique compounds and 912 thermal conformers. A sample set of the training and test set compounds is shown in Fig. 1. Further details regarding the neural network architecture and model training can be found in the Supporting Information under the section labeled Neural Network Architecture and Training Procedure.

**Results and Discussion**

Figure 2 presents the energy gaps that correspond to molecular geometries near the equilibrium of $T_1$. These geometries are relevant for phosphorescence and will be the focus of our discussion. HIPNN and HIP-loc achieve comparable prediction accuracies on the held-out test set (Figs. 2a and 2b). Both models exhibit root-mean-square errors (RMSEs) of ~4 kcal/mol and mean-absolute errors (MAEs) of ~2 kcal/mol (or ~0.1 eV), which are within the error of the DFT method when compared to experimental transition energies.$^{63}$ These predictions correspond to a median percent error of ~5% (Fig. S3). Thus, both HIPNN and HIP-loc attain experimentally informative predictions of $E_{phos}$ on the held-out test set. Training and testing results for all geometries sampled near the equilibria of $S_0$ and $T_1$ are shown in Figs. S4 and S5.
Figure 2: Parity plots of predicted versus true $\Delta E$ energy on the held-out test set using (a) HIPNN and (b) HIP-loc. (c) and (d) depict the same correlation as (a) and (b) but for the extensibility set. Results are for molecules sampled around the equilibrium of $T_1$. HIPNN and HIP-loc achieve comparable results on the held-out test set, but HIP-loc significantly outperforms HIPNN on the extensibility set compromising molecules that are on average ~2x larger than those found in the training set, highlighting the advantage that HIP-loc has for extended systems. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).

Despite HIPNN’s success of predicting $\Delta E$ for molecules with sizes comparable to those found in the training set, its performance substantially worsens for phosphorescent molecules of the extensibility set that consist of on average ~2x the number of atoms (Fig. S2). Yet we show that HIP-loc remedies this issue. HIPNN erroneously predicts negative $\Delta E$ energies (i.e., $T_1$ is lower in energy than $S_0$) for many molecules, contradicting reference results (Fig. 2c). This result is particularly troublesome given that the these are phosphorescent molecules for which DFT correctly predicts $T_1$ to be higher in energy than
Altogether, HIPNN’s performance on the extensibility set is quite poor with a RMSE of ~53 kcal/mol or ~2.3 eV, which is well outside the error commonly expected between \textit{ab initio} and experimental values.\textsuperscript{63} HIPNN’s predictions are especially poor for molecules composed of more than 35 atoms (Figs. S6 and S7). In contrast, Fig. 2d shows HIP-loc significantly outperforming HIPNN on the extensibility set. The RMSE of HIP-loc results on the extensibility set is ~13 kcal/mol, amounting to an ~4x improvement and median percent error of ~13\% (Fig. S3). The erroneous negative $\Delta E$ energies, predicted by HIPNN (Fig. 2c), are all but eliminated with HIP-loc (Fig. 2d and Fig. S8).

HIP-loc strongly outperforms HIPNN, and the only difference between the two models is the usage of localization layers to model the non-extensive part of $E_T$ (i.e., $\Delta E$) by weighting local atomic environments. The extensibility of the model is substantially improved, but relatively large disagreement between HIP-loc and DFT is observed for the largest molecules in the extensibility set comprising several bonded aromatic fragments (Fig. S9). Nevertheless, HIP-loc’s stronger performance demonstrates the importance of model engineering to account for the localized nature of spin transitions. Parity plots for all molecules of the extensibility set, categorized by chemical similarity, are shown in Figs. S9 through S14.

Additionally, we investigated whether the learned localization weights in HIP-loc have some physical significance. We compared the localization weights to DFT spin density differences between the $T_1$ and $S_0$ states. In order to compare the two methods, DFT spin density was approximated as an atom-centered quantity, which we obtained using the Hirshfeld charge partitioning scheme.\textsuperscript{64} Fig. 3a visualizes this comparison for a subset of representative molecules selected from a random sample of the held-out test set. Remarkably, there is qualitative agreement between HIP-loc and DFT for most molecules, suggesting that the HIP-loc localization weights provide physical insight. Moreover, the correspondence between the quantum mechanical and inferred localizations is somewhat correlated with the accuracy in predicted energies; the absolute error in $\Delta E$ for the last molecule shown in Fig. 3a is relatively high and, correspondingly, the atom-centered DFT spin density does not as strongly resemble the HIP-loc weights as compared to the other molecules shown. We also find a rough, yet highly significant correlation observed between these learned weights and the DFT spin densities (Fig. 3b).
It is important to note that the results of Figs. 3a and 3b are not meant to assert that learned weights are intrinsically related to spin densities in a rigorous way, especially since they are atom-centered quantities and charge partitioning is ambiguous, but rather that inferring localization through the use of energies and forces across a large dataset leads to similar assignments of localization.

We also analyzed the agreement between the ab initio and inferred localization over a large sample of the held-out test set. For this analysis, we made use of a localization metric $\eta$, defined as the ratio of the distance between the centers of localization computed using HIP-loc weights ($\vec{r}_{\text{HIP-loc}}$) and DFT spin density ($\vec{r}_{\text{DFT}}$) to the radius of gyration ($R_g$), which quantifies the spatial size of the molecule: $\eta = |\vec{r}_{\text{HIP-loc}} - \vec{r}_{\text{DFT}}| / R_g$. For $\eta \ll 1$, the centers of localizations are in close proximity to one another, whereas $\eta \sim 1$ signifies that the centers of localization differ by approximately the radius of the molecule and therefore there is very little or no agreement in the predicted localization. See Supporting Information under Localization Metric for more details. Fig. 3c shows a histogram of $\eta$ computed for our sample set. The distribution is concentrated at low $\eta$ (mean = 0.15), indicating that the center of HIP-loc’s inferred localization is in close proximity to that determined from DFT for the majority of compounds.
Figure 3: (a) Comparison of DFT spin density and HIP-loc localization weights for select molecules in the held-out test set. (b) Correlation between HIP-loc weights versus atom-centered DFT spin density. (c) Histogram of the localization metric $\eta$, which quantifies the agreement between the ab initio (DFT) and inferred (ML) centers of localization and where $\eta \ll 1$ signifies strong agreement. Energy $\Delta E$ is accurately predicted for the majority of molecules and jointly, HIP-loc weights closely resemble DFT spin density. For the final molecule with less accurate $\Delta E$, HIP-loc weights and DFT spin density are more dissimilar. Deviations are expressed in mean-absolute deviation (MAD) and root-mean-square deviation (RMSD).
This agreement is also observed for molecules of the phosphorescent extensibility set. Similar to Fig. 3a, Figure 4a visualizes the similarities between DFT and HIP-loc for two example molecules that perform particularly poorly with HIPNN. Additional visualizations of a similar nature are available in supplemental Figs. S15 through S18. The spatial localities associated with the singlet-triplet transitions in these molecules are confined to a relatively small number of atoms compared to the molecules’ total number of atoms. This result suggests, albeit not too surprisingly, that the advantages provided by HIP-loc are accentuated in the case of strongly localized transitions. In order to fully probe the improvement provided by HIP-loc for modeling localized versus delocalized transitions, we study the participation ratio (PR). The PR is described as follows: Given an $N$-body wavefunction expanded in terms of atom-localized states $|\psi\rangle = \sum_{i=1}^{N} c_i |\psi_i\rangle$ with expansion coefficients $c_i$, the PR is expressed as $(\sum_{i=1}^{N} |c_i|^2)^2 / \sum_{i=1}^{N} |c_i|^4$, ranging from 1 (fully localized to a single atom) to $N$ (equally delocalized across all atoms).42 Although we are not working with wavefunctions, we apply the concept of PR to estimate the number of atoms involved in the singlet-triplet transition based on the $ab$ initio (DFT) spin density and thereby quantify the degree of localization. The squares of the expansion coefficients are approximated from the atom-centered DFT spin density ($q_i$): $PR_{DFT} = (\sum_{i=1}^{N} q_i)^2 / \sum_{i=1}^{N} q_i^2$. The PR is complimentary to the previously utilized localization metric $\eta$. The latter quantifies the agreement in proximity of the $ab$ initio and ML-inferred centers of localization, whereas the former estimates the number of atoms involved in the transition and is therefore a more appropriate measure of quantifying the degree to which a transition is localized.

Fig. 4b shows the relationship between absolute error in $\Delta E$ and the degree of localization as computed by $PR/N$. For molecules in which the density is dispersed more homogeneously across the atoms (or larger $PR_{DFT}/N$ edging closer to $\sim 1$), energy is accurately predicted using Eq. 1 of HIPNN. In fact, HIPNN and HIP-loc achieve comparable performance in this regime. However, for molecules in which the density is strongly localized on only a small handful of atoms (or $PR_{DFT}/N$ closer to $\sim 1/N$), HIP-loc is superior. This result underscores the main motivation of our work in that HIPNN does not accurately predict the singlet-triplet energy gap for strongly localized transitions,
whereas HIP-loc’s localization weights allow the model to weight regions of the molecule that are attributed to the transition, resulting in better energy prediction.

Finally, in order to relate the agreement in the centers of localization to the accuracy in predicted energy, we also show absolute error in $\Delta E$ versus $\eta$ (Fig. 4c). The distribution is concentrated in the regime of low $\eta$ and low $\Delta E$ error, but in contrast to the held-out test set (Fig. 3c), there is also a significant number of molecules that lie in the regime of high $\eta$. The distribution of $\Delta E$ errors in this high $\eta$ regime is sporadic and extends to relatively high error. Altogether, these results suggest that robust energy prediction is generally improved when the inferred localization determined by the HIP-loc weights more closely resembles the localization determined by the quantum mechanical spin density.
Figure 4: (a) Comparison of DFT spin density and HIP-loc localization weights for select molecules of the phosphorescent extensibility set that perform poorly with HIPNN. Predominant regions of the molecules associated with the spin transitions are circled. Also shown are predicted absolute errors (abs. err.) in ΔE energies using HIPNN and HIP-loc. (b) Relationship between absolute error in ΔE energy and degree of localization for all molecules of the extensibility set as determined by the ratio of the reference DFT participation ratio divided by the total numbers of atoms in the molecule (PR_{DFT}/N). Results shown are those of HIPNN (top panel) and HIP-loc (bottom panel). HIPNN performs notably worse in the regime of strong localization (PR_{DFT}/N close to ~1/N) as compared to the regime of delocalized transitions (larger PR_{DFT}/N), whereas for HIP-loc, the ΔE prediction is less dependent on the degree of localization. Compared to HIPNN, HIP-loc is particularly more accurate in the regime of strong localization. (c) Relationship between HIP-loc’s error in ΔE versus localization metric η for all molecules of the extensibility set. Localities inferred by HIP-loc are in qualitative agreement with DFT and concomitantly the transition energy ΔE is predicted to better accuracy in the regime of low η.

To further demonstrate HIP-loc’s feature of localization without changing stoichiometry (and therefore drastically changing total molecular energy), we examined the predicted energy and concomitant variation in localization while scanning a single torsional angle. The set of molecules investigated consists of three to five six-membered aromatic rings and a central carbon-carbon single bond. A relaxed torsional scan over the dihedral angle around the carbon-carbon bond is performed and HIPNN and HIP-loc predictions are made for each conformation. The PR is calculated for both the DFT spin density and HIP-loc weights in order to compare the overall localization using both methods. The analogous form for PR_{HIP-loc} uses HIP-loc weights (w_i) in lieu of atom-centered spin density, that is, PR_{HIP-loc} = (\sum_{i=1}^{N} w_i)^2 / \sum_{i=1}^{N} w_i^2.

Our conformational analysis shows that when errors in ΔE predictions are relatively low across the conformational space, localization is accurately predicted by means of the PR. Rotating the molecule’s dihedral angle changes its aromaticity and shifts spatial localization of electron density. As a result, the S_0 and T_1 PESs, as well as the ΔE gap, vary with conformation. Fig. 5a shows absolute error in ΔE as a function of dihedral angle for a representative molecule containing three six-membered aromatic rings, computed
with HIPNN and HIP-loc. HIP-loc outperforms HIPNN for all scanned geometries. Additionally, there is qualitative agreement in the trends of the PRs computed using HIP-loc weights and DFT spin density (Fig. 5b). However, HIP-loc infers more delocalized transitions compared to DFT (PR of ~13 versus ~6), but in spite of that, for both methods the PR in the planar structure (dihedral of 0° and 180°) is delocalized across atoms on each ring, whereas the PR in the non-planar structure (dihedral of 90°) is localized to slightly more atoms exclusively on the larger ring. The net effect is an increase in PR for the non-planar conformation. An animation in Supporting Information showing a torsional scan of the molecule in Fig. 5 illustrates this point. Altogether, we find a correspondence between the accuracy of energy prediction and the progression in the degree of localization, quantified by PR. These observations are consistent for all the molecules studied (Figs. S19 through S23).
Figure 5: Conformational scan over the dihedral angle around the single carbon-carbon bond (blue arrow) in a representative molecule. (a) Absolute error (Abs. err.) in predicted $\Delta E$ energy gap computed with HIPNN and HIP-loc. (b) Participation ratio (PR) estimated using atom-centered DFT spin density (left axis) and HIP-loc weights (right axis) as a function of dihedral angle. HIP-loc significantly outperforms HIPNN in predicting $\Delta E$ for all scanned geometries. Qualitative agreement in the trends of PRs computed with DFT and HIP-loc is also observed.

Conclusions

In conclusion, machine learning (ML) is becoming an integral part of physical chemistry research and has already made substantial advances in the development of fast and transferable ML potentials for ground state dynamics. Ground state energy can be classified as an extensive property that is represented as a sum over individual atomic contributions whereas electronic excitation energies are best categorized as localized, non-extensive properties that depend on subsets of atoms. In this work, we utilized ML for advancing excited state electronic structure modeling by training a Hierarchical
Interacting Particle Neural Network (HIPNN) to predict phosphorescence energy, defined as the gap between the lowest energy triplet and singlet states, at computational speeds that reach over one million times faster than the underlying ab-initio method. Our work improves upon the original version of HIPNN that is based on the extensivity principle, particularly in the case of large aromatic compounds for which their singlet-triplet transition energies do not scale strongly with molecule size.

Our main contribution is a new set of localization layers for learning target excitation energies. These localization layers do not depend on the detailed structure of the underlying model and could be implemented in any atom-centered neural network. Combined with HIPNN, the new approach (denoted HIP-loc) defines energy as a weighted sum, where inferred localization weights assigned to the atoms determine the atoms’ contribution to the target energy (Eq. 4). This minor yet profound modification substantially improved prediction quality on a more challenging set of experimentally verified phosphorescent compounds that consist of, on average, ~2x more atoms than the molecules found in the training set. Extensibility is an important practical advantage of the model because it allows screening large molecules for which ab initio calculations are computationally prohibitive. Moreover, the superior energy prediction of HIP-loc over HIPNN was not readily visible on the held-out test set, but only the phosphorescent extensibility set in molecules with strongly localized transitions, showing that extensibility tests provide strong characterization of model performance. We achieve RMSEs of ~4 kcal/mol (~5% error) on the held-out test set and ~13 kcal/mol (~13% error) on the phosphorescent extensibility set (Fig. 2). The physical significance of HIP-loc’s localization weights, to our surprise, is that they qualitatively correlate to the quantum mechanical spin density (Figs. 3 and 4). Thus, the model inferred localities of the electron density associated with the singlet-triplet transition in order to make more accurate and transferable prediction of the singlet-triplet energy gap. This result is remarkable given that DFT spin density was not provided as a target during training. Instead, the neural network was provided with somewhat limited information, yet discovered this result nonetheless with a modest change in how target energy is calculated that effectively took into account the relative contribution of the atoms.
The results and performance of the new HIP-loc model leads us to conjecture that predictions for localized molecular properties are likely to improve if reference electronic properties (e.g., electron densities) are used explicitly as targets during training. This idea sets the stage for many interesting applications of ML in physical chemistry, where learned properties are dependent on, or correlated to, the spatial distribution of the many-electron wavefunction. We also envision applying localization layers to other localized molecular phenomena and systems such as anions, cations, radicals, or other excited states.

Supporting Information

Details regarding ML training procedures and localization metric $\eta$. \textit{Ab initio} energies $E_{S0}$, $E_{T1}$, and $\Delta E$ as a function of number of atoms, distributions of molecule size for the held-out and extensibility test sets, histograms of percentage error in $\Delta E$ prediction on $T_1$ thermal conformers in the held-out and extensibility test sets using HIPNN and HIP-loc, training and testing parity plots of predicted versus true $\Delta E$ on thermal conformers sampled around equilibria of $S_0$ and $T_1$ using HIPNN and HIP-loc, absolute errors in $\Delta E$ as a function of number of atoms, parity plots of predicted versus true $\Delta E$ for the extensibility set categorized by chemical similarity, localization of singlet-triplet transition for select molecules of the extensibility set computed from DFT spin density and HIP-loc weights, conformation-dependent localization of singlet-triplet transitions in molecules with a single torsional angle, and molecular animations of torsional scans including that of the molecule in Fig. 5.

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Supporting Information: Predicting Phosphorescence Energies and Inferring Wavefunction Localization with Machine Learning

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Neural Network Architecture and Training Procedure

The neural network architecture used in our work is HIPNN with tensor sensitivities. In particular, the network has 2 interaction blocks, each consisting of 1 interaction layer, followed by 3 on-site layers, and a linear layer to form a hierarchical contribution to target energy. In the HIP-loc model, localization weights are determined using linear layers in the same way as how atomic energy contributions are constructed. The target energy at each linear layer is computed as a sum over all atomic contributions.

The training procedure closely follows that described in Ref. 1. In addition to training the model to molecular energies, we also trained to atomic forces, as this has been shown to improve energy predictions. The cost function reflects this additional information and consists of the root-mean-square error (RMSE) and mean-absolute error (MAE) of the singlet ($S_0$) and triplet ($T_1$) state energies as well as the RMSEs and MAEs of the atomic forces:

$$\mathcal{L} = \mathcal{L}_2 + \mathcal{L}_R + \sum_{i=S_0,T_1} \lambda_E \left( \sqrt{\langle (E_i - E_i' \rangle^2 \rangle + \langle |E_i - E_i'| \rangle} \right) + \lambda_F \left( \frac{1}{3} \langle (\vec{F}_i - \vec{F}_i')^2 \rangle + \frac{1}{3} \langle |\vec{F}_i - \vec{F}_i'| \rangle \right)$$  (S1)

where angle brackets $\langle \cdots \rangle$ denote an average over the training batch, which was taken to be 512 structures. Primed versus unprimed represents ML versus reference quantum mechanical quantities and the scaling factors were set to $\lambda_E = 1/10$ and $\lambda_F = 1/30$. We
also included $L_{l2}$ regularization ($\lambda_{l2} = 10^{-6}$) and $L_{R}$ hierarchicality regularization ($\lambda_{R} = 10^{-1}$) to prevent overfitting. The factor of $1/3$ is a normalization that reflects the three degrees of freedom in an atomic force.

The dataset used to build and test the HIPNN and HIP-loc models was split using an 80-10-10 scheme, where 80% of the dataset was used for training, 10% for validation, and 10% for testing. Additional training parameters include minimum and maximum number of epochs of 10 and 500, $t_{\text{patience}} = 10$ epochs, and initial learning rate of $\eta = 10^{-3}$. See Ref. 1 for more details of the training procedure including the gradient-based optimization with the Adam optimizer and annealing/early stopping algorithm.

The cost function shown above was used to train both the HIPNN and HIP-loc models described in the main text. The only difference between the models is that HIPNN trains directly to the $S_0$ and $T_1$ state energies and atomic forces, whereas for HIP-loc, the triplet state energy is represented as the energy of the singlet plus the singlet-triplet energy gap, $E_T = E_S + \Delta E$, where now $\Delta E$ is computed as a weighted sum over atomic contributions. This feature of HIP-loc encompasses the novelty of the approach because unlike total energy, which is an extensive property that increases with system size, the energy gap is a non-extensive quantity that does not vary with molecule size in a clear way (Fig. S2). Furthermore, the singlet-triplet transition may be attributed to only a handful of atoms or localized regions of the molecule which, by way of the HIP-loc localization weights, can be accounted for by weighting atomic contributions disproportionately.

**Localization Metric**

To quantify the agreement in localization computed using HIP-loc and DFT, we introduce a localization metric, $\eta$, defined as the distance between the centers of localization computed using HIP-loc weights ($\tilde{r}_{\text{HIP-loc}}$) and DFT spin density ($\tilde{r}_{\text{DFT}}$) divided by the relative size of the molecule ($R$):

$$\eta = \frac{|\tilde{r}_{\text{HIP-loc}} - \tilde{r}_{\text{DFT}}|}{R} \quad (S2)$$

The center of localization is defined as

$$\tilde{r} = \frac{\sum_{i=1}^{N} \alpha_i \tilde{r}_i}{\sum_{i}^{N} \alpha_i} \quad (S3)$$

where the coefficient $\alpha_i$ is the “density” contribution on the $i$-th atom and $\tilde{r}_i$ is the position of the atom. For computing $\tilde{r}_{\text{DFT}}$, these coefficients are taken to be atom-centered.
densities \((q_i)\) approximated from Hirshfeld charge partitioning,\(^6\) while for \(\vec{r}_{\text{HIP-loc}}\), they are the localization weights \(w_i\). Finally, we quantify the relative size of the molecule \((R)\) with the radius of gyration \((R_g)\), assuming atoms are of equal mass,

\[
R_g = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\vec{r}_i - \vec{r}_{cm})^2}
\]  

(5.4)

where the center of mass or, more accurately, the center of atomic distribution is defined as

\[
\vec{r}_{cm} = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i
\]  

(5.5)

For \(\eta \ll 1\), the centers of localizations are in close proximity to one another, whereas \(\eta \sim 1\) or greater signifies that the centers of localization differ by approximately the radius of the molecule and therefore there is very little or no agreement in the predicted localization.

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Table S1: Number of molecules sampled from each GDB dataset. Here, GDB# means the sampled compounds are made up of # heavy atoms.
Figure S1: Energies as a function of number of atoms (including H) for all molecules in the dataset. (a) Triplet (E\textsubscript{T1}), (b) singlet (E\textsubscript{S0}), and (c) absolute |ΔE| energies are shown. Each box plot shows the median (orange line), first (Q1) to third (Q3) quartiles (blue box), and whiskers (black lines), capped at Q\textsubscript{1/2} ± 1.5(Q3 − Q1). Unlike E\textsubscript{T1} and E\textsubscript{S0} that decrease with molecule size, ΔE does not. The extensivity assumption of HIPNN does not apply for ΔE, prompting development of HIP-loc.
Figure S2: Distributions of molecule size for the dataset used to train the ML models as well as the extensibility test set with (top panel) and without (bottom panel) hydrogen included. Statistical values of the distributions including the minimum value, 25th percentile ($Q_1$), 50th percentile ($Q_2$), 75th percentile ($Q_3$), and maximum value are shown to the right of the corresponding panel.
Figure S3: Histograms of percentage error in ΔE energy. Data are of thermal conformers sampled around the triplet equilibria of molecules in the held-out test set (left panels) and the extensibility set (right panels) using HIPNN (top panels) and HIP-loc (bottom panels). In each panel, the first ($Q_1$) to third ($Q_3$) quartiles (orange shaded regime) and median ($Q_2$) (black dashed line) are labeled and whose values are explicitly shown. HIP-loc outperforms HIPNN, especially on the extensibility set.
Figure S4: Parity plots of predicted versus true $\Delta E$ energy on thermal conformers sampled around the singlet-optimized (left panels) and triplet-optimized (right panels) geometries of the full dataset using HIPNN (top panels) and HIP-loc (bottom panels). Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S5: Parity plots of predicted versus true $\Delta E$ energy on thermal conformers sampled around the singlet-optimized (left panels) and triplet-optimized (right panels) geometries of the held-out test set using HIPNN (top panels) and HIP-loc (bottom panels). Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S6: Absolute error in $\Delta E$ energy as a function of molecule size (including H). Data are of thermal conformers sampled around the singlet-optimized (left panels) and triplet-optimized (right panels) geometries of the extensibility set using HIPNN (top panels) and HIP-loc (bottom panels). Each box plot shows the median (orange line), first ($Q_1$) to third ($Q_3$) quartiles (blue box), and whiskers (black lines), capped at $Q_{1/3} \pm 1.5(Q_3 - Q_1)$. Perfect agreement between ML and reference DFT is labeled with a red dashed line. HIP-loc outperforms HIPNN, especially as molecule size increases.
Figure S7: Percentage error in $\Delta E$ energy as a function of molecule size (including H). Data are of thermal conformers sampled around the singlet-optimized (left panels) and triplet-optimized (right panels) geometries of the extensibility set using HIPNN (top panels) and HIP-loc (bottom panels). Each box plot shows the median (orange line), first ($Q_1$) to third ($Q_3$) quartiles (blue box), and whiskers (black lines), capped at $Q_{1/3} \pm 1.5(Q_3 - Q_1)$. Perfect agreement between ML and reference DFT is labeled with a red dashed line. HIP-loc outperforms HIPNN, especially as molecule size increases.
Figure S8: Parity plots of predicted versus true $\Delta E$ energy on thermal conformers sampled around the singlet-optimized (left panels) and triplet-optimized (right panels) geometries of the extensibility set using HIPNN (top panels) and HIP-loc (bottom panels). Predicted $\Delta E$ energies are significantly improved with HIP-loc. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S9: Parity plots of predicted versus true $\Delta E$ energy for a group of chemically similar molecules of the extensibility set, each overlaid with the results of all molecules in the extensibility set. The optimized structure is labeled with a red square and thermal conformers are labeled with blue circles. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S10: Parity plots of predicted versus true ΔE energy for a group of chemically similar molecules of the extensibility set, each overlaid with the results of all molecules in the extensibility set. The optimized structure is labeled with a red square and thermal conformers are labeled with blue circles. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S11: Parity plots of predicted versus true $\Delta E$ energy for a group of chemically similar molecules of the extensibility set, each overlaid with the results of all molecules in the extensibility set. The optimized structure is labeled with a red square and thermal conformers are labeled with blue circles. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S12: Parity plots of predicted versus true $\Delta E$ energy for a group of chemically similar molecules of the extensibility set, each overlaid with the results of all molecules in the extensibility set. The optimized structure is labeled with a red square and thermal conformers are labeled with blue circles. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S13: Parity plots of predicted versus true $\Delta E$ energy for a group of chemically similar molecules of the extensibility set, each overlaid with the results of all molecules in the extensibility set. The optimized structure is labeled with a red square and thermal conformers are labeled with blue circles. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S1: Parity plots of predicted versus true $\Delta E$ energy for a group of chemically similar molecules of the extensibility set, each overlaid with the results of all molecules in the extensibility set. The optimized structure is labeled with a red square and thermal conformers are labeled with blue circles. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).

Figure S14: Parity plots of predicted versus true $\Delta E$ energy for a group of chemically similar molecules of the extensibility set, each overlaid with the results of all molecules in the extensibility set. The optimized structure is labeled with a red square and thermal conformers are labeled with blue circles. Prediction errors are expressed in root-mean-square error (RMSE) and mean-absolute error (MAE).
Figure S15: A comparison of DFT spin density and HIP-loc localization weights for a select molecule of the extensibility set. Conformers with the best and worst predicted $\Delta E$ energy, measured in absolute error (Abs. err.), are shown. Predominant localities associated with the spin transitions are circled. Localities inferred by HIP-loc weights are in qualitative agreement with reference DFT spin densities for the best performing conformer. The root-mean-square error (RMSE) and mean-absolute error (MAE) over all 27 conformers are also shown.
Figure S16: A comparison of DFT spin density and HIP-loc localization weights for a select molecule of the extensibility set. Conformers with the best and worst predicted $\Delta E$ energy, measured in absolute error (Abs. err.), are shown. Predominant localities associated with the spin transitions are circled. Localities inferred by HIP-loc weights are in qualitative agreement with reference DFT spin densities for the best performing conformer. The root-mean-square error (RMSE) and mean-absolute error (MAE) over all 27 conformers are also shown.
Figure S17: A comparison of DFT spin density and HIP-loc localization weights for a select molecule of the extensibility set. Conformers with the best and worst predicted $\Delta E$ energy, measured in absolute error (Abs. err.), are shown. Predominant localities associated with the spin transitions are circled. Localities inferred by HIP-loc weights are in qualitative agreement with reference DFT spin densities for the best performing conformer. The root-mean-square error (RMSE) and mean-absolute error (MAE) over all 27 conformers are also shown.
Figure S18: A comparison of DFT spin density and HIP-loc localization weights for a select molecule of the extensibility set. Conformers with the best and worst predicted $\Delta E$ energy, measured in absolute error (Abs. err.), are shown. Predominant localities associated with the spin transitions are circled. Localities inferred by HIP-loc weights are in qualitative agreement with reference DFT spin densities for the best performing conformer. The root-mean-square error (RMSE) and mean-absolute error (MAE) over all 27 conformers are also shown.
Figure S19: Dihedral scans of molecules with a single torsional angle. Absolute error (Abs. err.) in $\Delta E$ computed with HIPNN and HIP-loc (left panels). Participation ratio (PR) estimated using atom-centered DFT spin density (right panels, left axis) and HIP-loc localization weights (right panels, right axis) as a function of dihedral angle. HIP-loc outperforms HIPNN in predicting $\Delta E$ for all molecules. For the top two molecules with relatively low $\Delta E$ errors, the trend in the PRs computed with DFT and HIP-loc qualitatively agree with one another. By contrast, the trends in PR differ significantly between DFT and HIP-loc for the bottom two molecules and coincidentally the errors in $\Delta E$ are relatively large for HIP-loc, albeit considerably lower than the errors without accounting for localization (HIPNN).
Figure S20: Scan of the central dihedral angle in a representative molecule in Fig. 4 of the main text. Participation ratios (PRs) are computed using atom-centered DFT density (top panel) and HIP-loc localization weights (bottom panel) as a function of dihedral angle. For both DFT and HIP-loc, the PR in the planar structure (dihedral of 0° and 180°) is delocalized across atoms on each ring, whereas the PR in the non-planar structure (dihedral of 90°) is localized to more atoms exclusively on the larger ring. The net effect is an increase in PR for the non-planar conformation. Compared to DFT, HIP-loc infers more delocalized transitions, but qualitative agreement between the methods' PRs is observed. An animated figure covering all molecular conformations can be found in the ESI.
Figure S21: Scan of the central dihedral angle in a representative molecule in Fig. S19 of the main text. Participation ratios (PRs) are computed using atom-centered DFT density (top panel) and HIP-loc localization weights (bottom panel) as a function of dihedral angle. An animated figure covering all molecular conformations can be found in the ESI.
Figure S2: Scan of the central dihedral angle in a representative molecule in Fig. S19 of the main text. Participation ratios (PRs) are computed using atom-centered DFT density (top panel) and HIP-loc localization weights (bottom panel) as a function of dihedral angle. An animated figure covering all molecular conformations can be found in the ESI.
Figure S23: Scan of the central dihedral angle in a representative molecule in Fig. S19 of the main text. Participation ratios (PRs) are computed using atom-centered DFT density (top panel) and HIP-loc localization weights (bottom panel) as a function of dihedral angle. An animated figure covering all molecular conformations can be found in the ESI.
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