

Equivariant message passing for the prediction of tensorial properties and molecular spectra

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Message passing neural networks have become a method of choice for learning on graphs, in particular the prediction of chemical properties and the acceleration of molecular dynamics studies. While they readily scale to large training data sets, previous approaches have proven to be less data efficient than kernel methods. We identify limitations of invariant representations as a major reason and extend the message passing formulation to rotationally equivariant representations. On this basis, we propose the *polarizable atom interaction neural network* (PAINN) and improve on common molecule benchmarks over previous networks, while reducing model size and inference time. We leverage the equivariant atomwise representations obtained by PAINN for the prediction of tensorial properties. Finally, we apply this to the simulation of molecular spectra, achieving speedups of 4-5 orders of magnitude compared to the electronic structure reference.

I. INTRODUCTION

Studying dynamics of chemical systems allows insight into processes such as reactions or the folding of proteins, and constitutes a fundamental challenge in computational chemistry. Since the motion of atoms is governed by the laws of quantum mechanics, accurate *ab initio* molecular dynamics (MD) simulations may require solving the Schrödinger equation for millions of time steps. While the exact solution is infeasible to compute for all but the smallest systems, even fast approximations such as density functional theory quickly become prohibitive for large systems and the prediction of accurate spectra.

Recently, machine learning potentials¹⁻³ have gained popularity for studying systems ranging from small molecules at high levels of theory^{4,5} to systems with thousands or millions of atoms⁶⁻⁸. In particular, message-passing neural networks⁹ (MPNNs) yield accurate predictions for chemical properties across chemical compound space and can handle large amounts of training data. Albeit MPNNs have significantly increased in accuracy over the years (as well as in computational cost), kernel methods with manually crafted features¹⁰⁻¹² have still proven to perform better when only small training sets are available.

While molecules are often represented as graphs, they are in fact interacting particles in a continuous 3d space. Consequently, SchNet¹³ modeled message passes as continuous-filter convolutions over that space, albeit with rotationally invariant filters. As Miller *et al.*¹⁴ pointed out, this leads to a loss of relevant directional, equivariant information. Klicpera, Groß, and Günnemann¹⁵ have introduced directional message-passing, the angular information here is restricted to the messages while

the representation of nodes (atoms) remains rotationally invariant. While equivariant convolutions have been successfully applied in computer vision¹⁶⁻¹⁸, previous approaches to molecular prediction^{19,20} have not reached the accuracy of their rotationally invariant counterparts.

In this work, we propose rotationally equivariant message passing and the *polarizable atom interaction neural network* (PAINN) architecture as one instance of it. We examine the limited capability of rotation-invariant representations to propagate directional information and show that equivariant representations do not suffer from this issue. PAINN outperforms invariant message passing networks on common molecular benchmarks and performs at small sample sizes on par with kernel methods that have been deemed to be more data-efficient than neural networks. Beyond that, the rotationally equivariant representation of PAINN enables the prediction of tensorial properties which we apply to the ring-polymer MD simulation of infrared and Raman spectra. By an acceleration of 4-5 orders of magnitude, PAINN makes the simulation of these spectra feasible, reducing the runtime in one case from projected 25 years to one hour.

II. RELATED WORK

Behler and Parrinello²¹ introduced neural network potentials taking atom-centered symmetry functions based on distances and angles as features. Graph neural networks²² for molecular graphs^{23,24} and 3d geometries^{9,25-28} do not require such manually crafted features, but learn embeddings of atom types and use graph convolutions or, more general, message passing⁹, to model atom interactions based on interatomic distances. Klicpera, Groß, and Günnemann¹⁵ introduced directional message passing by including additional angular information in the message.

Steerable CNNs^{16,29} allow to build equivariant filter

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banks according to known symmetries of associated feature types. While these approaches work on grids, architectures such as Tensor Field Networks¹⁹, Cormorant²⁰ and NEQUIP³⁰ use equivariant convolutions based on spherical harmonics (SH) and Clebsch-Gordon (CG) transforms for point clouds. Kondor and Trivedi³¹ have described a general framework on equivariance and convolutions in neural networks focusing on irreducible representations. In contrast, PAINN models equivariant interactions in Cartesian space which is conceptually simpler and does not require tensor contractions with CG coefficients. A similar approach was proposed by Jing *et al.*³² with the GVP-GNN. Both approaches are designed for distinct applications resulting in crucial differences in the design of the neural network architectures, most notably the message functions. The GVP-GNN has been designed for single-point protein sequence predictions, e.g., allowing the use of non-smooth components. In contrast, PAINN is designed for simulations with millions of inference steps, requiring a fast message function and a smoothly differentiable model.

III. EQUIVARIANT MESSAGE PASSING

a. Notation. To clearly distinguish between the two concepts, we write feature vectors as $\mathbf{x} \in \mathbb{R}^{F \times 1}$ and vectors in 3d coordinate space as $\vec{r} \in \mathbb{R}^{1 \times 3}$. Vectorial features will be written as $\vec{\mathbf{x}} \in \mathbb{R}^{F \times 3}$. Norms $\|\cdot\|$, scalar products $\langle \cdot, \cdot \rangle$ and tensor products \otimes are calculated along the spatial dimension. All other operations are calculated along the feature dimension, if not stated otherwise. We write the Hadamard product as \circ .

A. Message passing for 3d-embedded graphs

MPNNs build complex representations of nodes within their local neighborhood in a graph through a repeated exchange of *messages* followed by *updates* of node features. Here, we consider graphs embedded in 3d Euclidean space, where edges are specified by the relative positions $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ of nodes i, j within a local neighborhood $\mathcal{N}(i) = \{j \mid \|\vec{r}_{ij}\| \leq r_{\text{cut}}\}$. In a chemistry context, this agrees with the fact that a large part of the energy variations can be attributed to local interactions, often conceptualized as bond lengths and angles. Thus, only nodes within that range can interact directly, so the number of messages does not scale quadratically with the number of the nodes. A general MPNN for embedded graphs can be written as

$$\mathbf{m}_i^{t+1} = \sum_{j \in \mathcal{N}(i)} \mathbf{M}_t(\mathbf{s}_i^t, \mathbf{s}_j^t, \vec{r}_{ij}) \quad (1)$$

$$\mathbf{s}_i^{t+1} = \mathbf{U}_t(\mathbf{s}_i^t, \mathbf{m}_i^{t+1}). \quad (2)$$

with the update and message functions \mathbf{U}_t and \mathbf{M}_t , respectively⁹. Many neural network potentials and even

conventional CNNs can be cast in this general framework. Rotational invariance of the representation can be ensured by choosing rotationally invariant message and update functions, which by definition need to fulfill

$$\mathbf{f}(\vec{\mathbf{x}}) = \mathbf{f}(R\vec{\mathbf{x}}), \quad (3)$$

for any rotation matrix $R \in \mathbb{R}^{3 \times 3}$.

B. Building equivariant MPNNs

To obtain more expressive representations of local environments, neurons do not have to be scalar, but can be geometric objects such as vectors and tensors^{16,19,20,33}. For the purpose of this work, we restrict ourselves to scalar and vectorial representations \mathbf{s}_i^t and $\vec{\mathbf{v}}_i^t$, respectively, such that a corresponding message pass can be written as

$$\vec{\mathbf{m}}_i^{v,t+1} = \sum_{j \in \mathcal{N}(i)} \vec{\mathbf{M}}_t(\mathbf{s}_i^t, \mathbf{s}_j^t, \vec{\mathbf{v}}_i^t, \vec{\mathbf{v}}_j^t, \vec{r}_{ij}) \quad (4)$$

Message and update functions for scalar features can be defined analogously. Rotational equivariance of vector features $\vec{\mathbf{v}}_i^{t+1}$ can be ensured by employing rotationally equivariant functions $\vec{\mathbf{U}}_t$ and $\vec{\mathbf{M}}_t$, fulfilling

$$R\vec{\mathbf{f}}(\vec{\mathbf{x}}) = \vec{\mathbf{f}}(R\vec{\mathbf{x}}) \quad (5)$$

for any rotation matrix $R \in \mathbb{R}^{3 \times 3}$, where the matrix-vector product is applied over the spatial dimension. This constitutes essentially a linearity constraint for directional information. Therefore, any nonlinearities of the model need to be applied to scalar features. In particular, equivariant MPNNs may use the following operations:

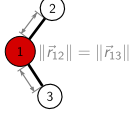
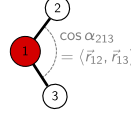
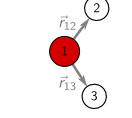
- Any (nonlinear) function of scalars: $\mathbf{f}(\mathbf{s})$
- Scaling of vectors: $\mathbf{s} \circ \vec{\mathbf{v}}$
- Linear combinations of equivariant vectors: $\mathbf{W}\vec{\mathbf{v}}$
- Scalar products: $\mathbf{s} = \|\vec{\mathbf{v}}\|^2$, $\mathbf{s} = \langle \vec{\mathbf{v}}_1, \vec{\mathbf{v}}_2 \rangle$
- Vector products: $\vec{\mathbf{v}}_1 \times \vec{\mathbf{v}}_2$

Thus, directional information is preserved during message passing while invariant representations can be recovered from scalar products to obtain rotationally invariant predictions.

C. Limits of rotationally invariant representations

In the following, we examine the expressiveness of invariant and equivariant representations at the example of simple 2d molecular structures. To ensure rotational invariance of a predicted property, the message function is often restricted to depend only on rotationally invariant inputs such as distances^{25,28} or angles^{15,34}. While a

TABLE I: Comparison of expressiveness and computational complexity of distances, angles and directions for a simple message function of the oxygen atom of a water molecule.

Features	Distances	Angles	Directions
H_2O			
Message M at atom i	$\sum_{j \in \mathcal{N}_i} \ \vec{r}_{ij}\ $	$\sum_{j \in \mathcal{N}_i} \sum_{k \in \mathcal{N}_i} \alpha_{jik}$	$\sum_{j \in \mathcal{N}_i} \frac{\vec{r}_{ij}}{\ \vec{r}_{ij}\ }$
Scaling with neighbors	$\mathcal{O}(\mathcal{N})$	$\mathcal{O}(\mathcal{N} ^2)$	$\mathcal{O}(\mathcal{N})$
Resolve change of $\ \vec{r}_{1j}\ $	yes	no	no
Resolve change of α_{213}	no	yes	yes

single pass is limited to interactions within a local environment, successive message passes are supposed to construct more complex representations and propagate local information beyond the neighborhood. This raises the question whether rotationally invariant representations of atomic environments \mathbf{h}_i are sufficient here.

Tab. I compares three simplified message functions for the example of a water molecule. Using a distance-based message function, the representation of the atom 1 (oxygen) is able to resolve changing bond lengths to atoms 2 and 3 (hydrogens), however it is not sensitive to changes of the bond angle. On the other hand, using the angle directly as part of the message function can not resolve the distances. Therefore, a combination of distances and angles is required to obtain a more expressive message function¹⁵. Unfortunately, including angles in the messages scales $\mathcal{O}(|\mathcal{N}|^2)$ with the number of neighbors. Alternatively, directions to neighboring atoms may be used as messages $\vec{M}_t(\vec{r}_{ij}) = \vec{r}_{ij}/\|\vec{r}_{ij}\|$. Employing the update function $U_t(m) = \|m\|^2$, this is related to angles as follows:

$$\left\| \sum_{j=1}^N \frac{\vec{r}_{ij}}{\|\vec{r}_{ij}\|} \right\|^2 = \sum_{j,k} \left\langle \frac{\vec{r}_{ij}}{\|\vec{r}_{ij}\|}, \frac{\vec{r}_{ik}}{\|\vec{r}_{ik}\|} \right\rangle = \sum_{j=1}^N \sum_{k=1}^N \cos \alpha_{jik}.$$

Thus, using equivariant messages, the runtime complexity remains $\mathcal{O}(|\mathcal{N}|)$ while angular information can be resolved. Note that this update function contracts the equivariant messages to a rotationally invariant representation.

Beyond the computational benefits, equivariant representations allow to propagate directional information beyond the neighborhood which is *not* possible in the invariant case. Fig. 1 illustrates this at a minimal example, where four atoms are arranged in an equidistant chain

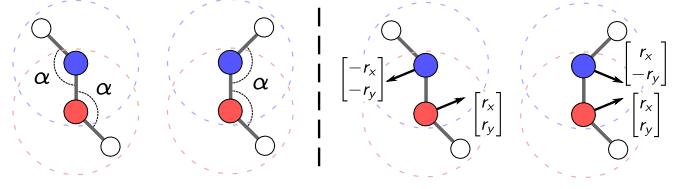


FIG. 1: Illustration of message passing using angles and directions for two structures. All edges within the cutoff range (dashed lines) have equal length. The representations of the blue and red node are the same using angles (left), while directions allow to distinguish both structures (right).

with the cutoff chosen such that only neighboring atoms are within range. We observe that for the two arrangements the angles are equal as well (Fig. 1, left). Therefore, they are indistinguishable for invariant message passing with distances and angles. In contrast, the equivariant representations differ in sign of their components (Fig. 1, right). When contracting them to invariant representations, as in the previous example, this information is lost. However, we may instead retain equivariance in the representation and design a message function \vec{M}_t that does not only propagate directions to neighboring atoms, but those of equivariant representations as well. This enables the efficient propagation of directional information by scaling linearly with the number of neighbors and keeping the required cutoff small.

Note that neither many-body representations, using angles, dihedral angles etc., nor equivariant representations corresponding to a multipole expansion are complete. It has been shown that even when including up to 4-body invariants, there are structures with as few as eight atoms which cannot be distinguished³⁵ and that a many-body expansion up to n -body contributions is necessary to guarantee convergence for a system consisting of n atoms³⁶. The same holds for multipole expansions, where scalars and vectors correspond to the 0th and 1st order. Thus, even spherical harmonics expansions with less than infinite degree are unable to represent arbitrary equivariant n -body functions. Instead, a practically sufficient and computationally efficient approach for the problem at hand is desirable.

In the following, we propose a neural network architecture that takes advantage of these properties. It overcomes the limitations of invariant representations discussed above, which we will demonstrate at the example of an organometallic compound in Section VC 2.

IV. POLARIZABLE ATOM INTERACTION NEURAL NETWORK (PAINN)

The potential energy surface $E(Z_1, \dots, Z_N, \vec{r}_1, \dots, \vec{r}_N)$, with nuclear charges $Z_i \in \mathbb{N}$ and atom positions $\vec{r}_i \in \mathbb{R}^3$ exhibits certain symmetries. Generally, they include in-

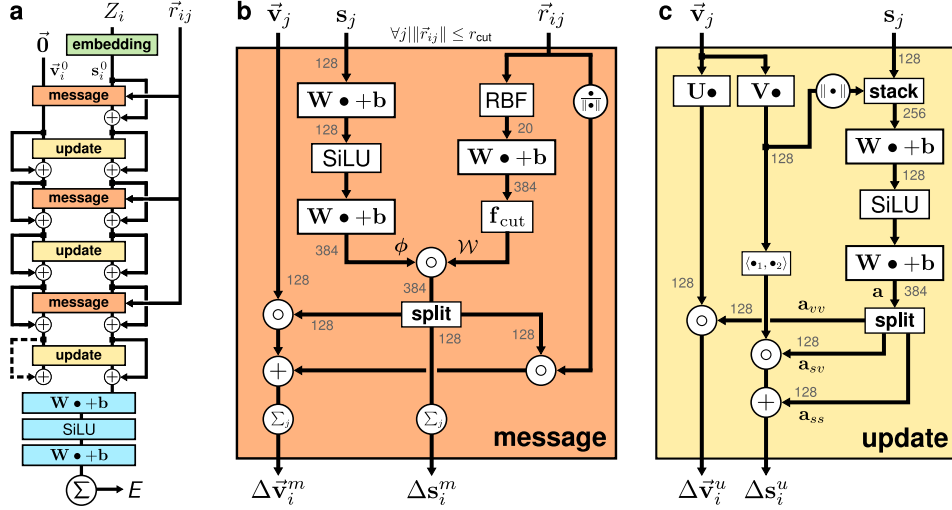


FIG. 2: The architecture of PAINN with the full architecture (a) as well as the message (b) and update blocks (c) of the equivariant message passing. In all experiments, we use 128 features for s_i and \vec{v}_i throughout the architecture. Other layer sizes are annotated in grey.

variance of the energy towards the permutation of atom indices i , as well as rotations and translations of the molecule. A neural network potential should encode these constraints to ensure the symmetries of the predicted energy surface and increase data efficiency. A common inductive bias of the neural network potential is a decomposition of the energy into atomwise contributions $E = \sum_{i=1}^N \epsilon(s_i)$, where an output network ϵ predicts energy contributions from atoms embedded within their chemical environment, represented by $s_i \in \mathbb{R}^{F \times 21}$.

While properties of chemical compounds may be such rotationally invariant scalars, they can also be equivariant tensorial properties, e.g. the multipole expansion of the electron density

$$n(\vec{r}) = q + \vec{\mu}^\top \vec{r} + \vec{r}^\top Q \vec{r} + \dots, \quad (6)$$

with charge q , dipole $\vec{\mu}$, quadrupole Q and so on. Similarly, one can interpret invariant and equivariant atomwise representations as local charges and dipole moments of atom-centered multipole expansions³⁸. We leverage this in Section IV B to predict tensorial molecular properties. We coin our proposed architecture *polarizable atom interaction neural network* (PAINN).

A. Representation

The inputs to PAINN are the nuclear charges $Z_i \in \mathbb{N}$ and positions $\vec{r}_i \in \mathbb{R}^3$ for each atom i . Similar to previous approaches, the invariant atom representations are initialized to learned embeddings of the atom type $s_i^0 = \mathbf{a}_{Z_i} \in \mathbb{R}^{F \times 1}$. We keep the number of features F constant throughout the network. The equivariant representations are set to $\vec{v}_i^0 = \vec{0} \in \mathbb{R}^{F \times 3}$, since there is no directional information available initially.

Next, we define message and update functions as introduced in Sec. III. We use a residual structure of interchanging message and update blocks (Fig. 2a), resulting in coupled scalar and vectorial representations. For the residual of the scalar message function, we adopt the feature-wise, continuous-filter convolutions introduced by Schütt *et al.*¹³

$$\begin{aligned} \Delta s_i^m &= (\phi_s(s) * \mathcal{W}_s)_i \\ &= \sum_j \phi_s(s_j) \circ \mathcal{W}_s(\|\vec{r}_{ij}\|), \end{aligned} \quad (7)$$

where ϕ_s consists of atomwise layers as shown in Fig. 2b. The rotationally-invariant filters \mathcal{W}_s are linear combinations of radial basis functions $\sin(\frac{n\pi}{r_{\text{cut}}}\|\vec{r}_{ij}\|)/\|\vec{r}_{ij}\|$ as proposed by Klicpera, Groß, and Günnemann¹⁵ with $1 \leq n \leq 20$. Additionally, we apply a cosine cutoff to the filters³⁹.

Analogously, we use continuous-filter convolutions for the residual of the equivariant message function

$$\begin{aligned} \Delta \vec{v}_i^m &= \sum_j \vec{v}_j \circ \phi_{vv}(s_j) \circ \mathcal{W}_{vv}(\|\vec{r}_{ij}\|) \\ &\quad + \sum_j \phi_{vs}(s_j) \circ \mathcal{W}'_{vs}(\|\vec{r}_{ij}\|) \frac{\vec{r}_{ij}}{\|\vec{r}_{ij}\|}, \end{aligned} \quad (8)$$

where the first term is a convolution of an invariant filter with scaled, equivariant features $\sum_j \vec{v}_j \circ \phi_s(s_j)$, related to the gating proposed by Weiler *et al.*²⁹ as an equivariant nonlinearity. This propagates directional information obtained in previous message passes to neighboring atoms. The second term is a convolution of invariant features with an equivariant filter. This can be derived as the gradient of an invariant filter

$$\nabla \mathcal{W}_{vs}(\|\vec{r}_{ij}\|) = \mathcal{W}'_{vs}(\|\vec{r}_{ij}\|) \frac{\vec{r}_{ij}}{\|\vec{r}_{ij}\|}.$$

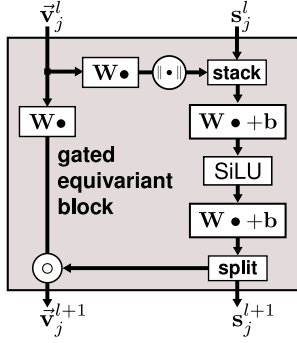


FIG. 3: Gated equivariant block.

Since $\mathcal{W}'_{vs}(\|\vec{r}_{ij}\|)$ is another invariant filter, we can model it directly without taking the derivative. Furthermore, we use a shared network ϕ to perform the transform of all message functions and split the features afterwards (see Fig. 2b).

After the features-wise message blocks, the update blocks are applied atomwise across features. The residual of the scalar update function is given by

$$\Delta \mathbf{s}_i^u = \mathbf{a}_{ss}(\mathbf{s}_i, \|\mathbf{V}\vec{\mathbf{v}}_i\|) + \mathbf{a}_{sv}(\mathbf{s}_i, \|\mathbf{V}\vec{\mathbf{v}}_i\|) \langle \mathbf{U}\vec{\mathbf{v}}_i, \mathbf{V}\vec{\mathbf{v}}_i \rangle. \quad (9)$$

Again, we use a scaling functions computed by a shared network $\mathbf{a}(\mathbf{s}_i, \|\mathbf{V}\vec{\mathbf{v}}_i\|)$ as nonlinearity. In this case, the norm of a linear combination of features is also used to obtain the scaling, thus, coupling the scalar representations with contracted equivariant features. In a second term, we use the scalar product of two linear combinations of equivariant features. Similarly, we define the residual for the equivariant features

$$\Delta \vec{\mathbf{v}}_i^u = \mathbf{a}_{vv}(\mathbf{s}_i, \|\mathbf{V}\vec{\mathbf{v}}_i\|) \mathbf{U}\vec{\mathbf{v}}_i, \quad (10)$$

which is again a nonlinear scaling of linearly combined equivariant features.

B. Prediction of tensorial properties

PAINN is able to predict scalar properties using atomwise output layers of rotationally invariant representations \mathbf{s}_i , in the same manner as previous approaches^{25,27}. Beyond that, the additional equivariant representations enable the prediction of equivariant tensors of order M that can be constructed using a rank-1 tensor decomposition

$$T = \sum_{i=1}^N \sum_{k=1}^R \lambda(\mathbf{s}_i) \vec{\nu}(\vec{\mathbf{v}}_i)_{k,1} \otimes \cdots \otimes \vec{\nu}(\vec{\mathbf{v}}_i)_{k,M}. \quad (11)$$

The scalar and vectorial components of this decomposition can be obtained from an output network of *gated equivariant blocks*, as shown in Fig. 3. These components again make use gated equivariant nonlinearities¹⁷ and show similarities to geometric vector perceptrons (GVP)³². However, while GVP blocks are used as message functions,

PAINN keeps the pairwise message functions comparatively lightweight. Instead complex transformations are restricted to the atomwise update function and tensor output network.

Depending on the chemical property of interest, one may want to include additional constraints or replace $\vec{\nu}_{k,m}$ with the atom positions to include the global molecular geometry. In the following, we demonstrate how this can be employed for two tensorial properties that are important for the simulation of molecular spectra.

The molecular dipole moment $\vec{\mu}$ is the response of the molecular energy to an electric field $\nabla_{\vec{r}} E$ and, at the same time, the first moment of the electron density (see Eq. 6). It is often predicted using latent atomic charges⁴⁰:

$$\vec{\mu} = \sum_{i=1}^N q_{\text{atom}}(\mathbf{s}_i) \vec{r}_i. \quad (12)$$

This assumes the center of mass at $\vec{r} = \vec{0}$ for brevity. While this only leverages invariant representations, we can take advantage of the equivariant features of PAINN. In this picture, the molecular dipole is constructed from polarized atoms, i.e. both atomic dipoles and charges⁴¹, yielding

$$\vec{\mu} = \sum_{i=1}^N \vec{\mu}_{\text{atom}}(\vec{\mathbf{v}}_i) + q_{\text{atom}}(\mathbf{s}_i) \vec{r}_i. \quad (13)$$

In terms of Eq. 11, this is a simple case with $M = 1$, $R = 2$, where the first term predicts the latent local dipoles and the second term computes the dipole generated by the local charges.

As an example with order $M = 2$, we consider the polarizability tensor, which describes the response of the molecular dipole to an electric field $J_{\vec{r}}(\vec{\mu}) = H_{\vec{r}}(E)$. We construct polarizability tensors using

$$\boldsymbol{\alpha} = \sum_{i=1}^N \alpha_0(\mathbf{s}_i) I_3 + \vec{\nu}(\vec{\mathbf{v}}_i) \otimes \vec{r}_i + \vec{r}_i \otimes \vec{\nu}(\vec{\mathbf{v}}_i), \quad (14)$$

where the first term of the sum models isotropic, atomwise polarizabilities. The other two terms add the anisotropic components of the polarizability tensor. Similar to the charges in Eq. 13, here the atom positions are used to incorporate the global structure of the molecule.

V. RESULTS

PAINN has been implemented using PYTORCH⁴² and SCHNETPACK⁴³. All models use $F = 128$ and two output layers as shown in Fig. 2 (blue) with the type of output layers depending on the property of interest. They were trained using the Adam optimizer⁴⁴, the squared loss and weight decay $\lambda = 0.01^?$, if not stated otherwise. We decay the learning rate by a factor of 0.5 if the validation loss plateaus. We apply exponential smoothing with factor 0.9

to the validation loss to reduce the impact of fluctuations which are particularly common when training with both energies and forces. Please refer to the supplement for further details on training parameters.

A. Chemical compound space

We use the QM9 dataset of ≈ 130 k small organic molecules⁴⁵ with up to nine heavy atoms to evaluate the performance of PAiNN for the prediction of scalar properties across chemical compound space. We predict the magnitude of the dipole moment using Eq. 13 and the electronic spatial extent by

$$\langle R^2 \rangle = \sum_{i=1}^N q_{\text{atom}}(\mathbf{s}_i) \|\vec{r}_i\|^2,$$

as implemented by SCHNETPACK. The remaining properties are predicted as sums over atomic contributions. PAiNN is trained on 110k examples while 10k molecules are used as a validation set for decaying the learning rate and early stopping. The remaining data is used as test set and results are averaged over three random splits. For the isotropic polarizability α , we first observed validation MAEs of $0.054 a_0$. Upon closer inspection, we notice that for this property both the squared loss as well as the MAE can be reduced when minimizing the MAE directly (as done by Klicpera, Groß, and Günnemann³⁴). This yields both validation and test MAEs of $0.045 a_0$ that are comparable to those of DIMENET++.

Tab. II shows the mean absolute error (MAE) of PAiNN for 12 target properties of QM9 in comparison with previous approaches. SCHNET¹³ and PHYSNET²⁷ are MPNNs with distance-based interactions, DIMENET++³⁴ includes additional angular information and is an improved variant of DIMENET¹⁵. L1NET¹⁴ and CORMORANT²⁰ are equivariant neural networks based on spherical harmonics and Clebsch-Gordon coefficients.

PAiNN achieves state-of-the-art results in six target properties and yields comparable results to DIMENET++ on another two targets. On the remaining properties, PAiNN achieves the second best results after DIMENET++. Note that PAiNN using about 600k parameters is significantly smaller than DIMENET++ with about 1.8M parameters. For random batches of 50 molecules from QM9, the inference time is reduced from 45 ms to 13 ms, i.e. an improvement of more than 70%, when comparing PAiNN to the reference implementation of DIMENET++⁴⁶ using an NVIDIA V100.

B. Molecular dynamics trajectories

We evaluate the ability to predict combined energies and forces on the MD17 benchmark¹⁰ including molecular dynamics trajectories of small organic molecules. While

the atomic forces could be predicted directly from vectorial features, we employ the gradients of the energy model $\vec{F}_i = -\partial E / \partial \vec{r}_i$ to ensure conservation of energy. This property is crucial to run stable molecular dynamics simulations. To demonstrate the data efficiency of PAiNN, we use the more challenging setting with 1k known structures of which we use 950 for training and 50 for validation, where a separate model is trained for each trajectory. Tab. 5 shows the comparison with sGDML⁴ and NEQUIP³⁰, which were trained on forces only, as well as SCHNET, PHYSNET, DIMENET and FCHL19¹¹, that were trained on a combined loss of energies and forces. Christensen and von Lilienfeld⁴⁷ have found that the energies of MD17 are noisy. Thus, depending on the molecule and chosen tradeoff, using energies for training is not always beneficial. For this reason, we train two PAiNN models per trajectory: only on forces and on a combined loss including energy with a force error weight of $\rho = 0.95$. PAiNN achieves the lowest mean absolute errors for 12 out of 14 targets on models trained only on forces and exhibits errors in a similar range as Gaussian regression with the FCHL19 kernel. Overall, PAiNN performs best or equal to FCHL19 on 9 out of 14 targets. This demonstrates that equivariant neural networks approaches such as PAiNN are able to compete with kernel methods in the small data regime, while being able to scale to large data sets at the same time.

C. Advantages of equivariant features

1. Ablation studies

We evaluate the impact of equivariant vector features at the example of the aspirin MD trajectory from the previous section. Compared to the full model, we remove the scalar product of vector features in Eq. 9 from the update block and the convolution over vector features in Eq. 8 (i.e., $\mathcal{W}_{vv} = 0$). Table IV show the results for the various ablations. The number of parameters is kept approximately constant by raising the number of node features F accordingly. We observe that all ablated components contribute to the final accuracy of the model, where the convolution over equivariant features in the message function has a slightly larger impact. This component also enables the propagation of directional information, which will be examined in Sec. V C 2. Finally, we remove all vector features from the model, resulting in an invariant model. Despite keeping the number of parameters constant by increasing the number of atoms features to $F = 174$, the mean absolute error of the forces increases beyond 1 kcal/mol/Å.

TABLE II: Mean absolute errors on QM9 dataset for various chemical properties. Results for PaiNN are averaged over three random splits. Best in **bold**.

Target	Unit	SchNet	PhysNet	DimeNet++	Cormorant	L1Net	PaiNN
μ	D	0.033	0.053	0.030	0.038	0.043	0.012
α	\AA^3	0.235	0.062	0.044	0.085	0.088	0.045
ϵ_{HOMO}	meV	41	32.9	24.6	34	46.0	27.6
ϵ_{LUMO}	meV	34	24.7	19.5	38	34.6	20.4
$\Delta\epsilon$	meV	63	42.5	32.6	38	67.5	45.7
$\langle R^2 \rangle$	\AA^2	0.073	0.765	0.331	0.961	0.354	0.066
ZPVE	meV	1.7	1.39	1.21	2.03	1.56	1.28
U_0	meV	14	8.15	6.32	22	13.46	5.85
U	meV	19	8.34	6.28	21	13.83	5.83
H	meV	14	8.42	6.53	21	14.36	5.98
G	meV	14	9.40	7.56	20	13.99	7.35
c_v	$\frac{\text{cal}}{\text{mol K}}$	0.033	0.028	0.023	0.026	0.031	0.024

TABLE III: Mean absolute errors on MD17 dataset for energy and force predictions in kcal/mol and kcal/mol/ \AA , respectively. Batzner *et al.*³⁰ only reported force errors for NEQUIP. Results for PaiNN are averaged over three random splits. Best in **bold**.

		sGDML NequIP PaiNN <i>trained on forces only</i>			SchNet PhysNet DimeNet FCHL19 PaiNN <i>trained on energies & forces</i>				
Aspirin	<i>energy</i>	0.19	–	0.167	0.37	0.230	0.204	0.182	0.159
	<i>forces</i>	0.68	0.348	0.338	1.35	0.605	0.499	0.478	0.371
Ethanol	<i>energy</i>	0.07	–	0.064	0.08	0.059	0.064	0.054	0.063
	<i>forces</i>	0.33	0.208	0.224	0.39	0.160	0.230	0.136	0.230
Malondialdehyde	<i>energy</i>	0.10	–	0.100	0.13	0.094	0.104	0.081	0.091
	<i>forces</i>	0.41	0.337	0.344	0.66	0.319	0.383	0.245	0.319
Naphthalene	<i>energy</i>	0.12	–	0.116	0.16	0.142	0.122	0.117	0.117
	<i>forces</i>	0.11	0.096	0.077	0.58	0.310	0.215	0.151	0.083
Salicylic Acid	<i>energy</i>	0.12	–	0.116	0.20	0.126	0.134	0.114	0.114
	<i>forces</i>	0.28	0.238	0.195	0.85	0.337	0.374	0.221	0.209
Toluene	<i>energy</i>	0.10	–	0.095	0.12	0.100	0.102	0.098	0.097
	<i>forces</i>	0.14	0.101	0.094	0.57	0.191	0.216	0.203	0.102
Uracil	<i>energy</i>	0.11	–	0.106	0.14	0.108	0.115	0.104	0.104
	<i>forces</i>	0.24	0.172	0.139	0.56	0.218	0.301	0.105	0.140

TABLE IV: Ablation study for the prediction of energies [kcal/mol] and forces [kcal/mol/ \AA] for aspirin trajectories from MD17.

Ablation	# params	F	energy MAE	force MAE
no ablation	588.3k	128	0.159	0.371
no scalar product of vector features in Eq. 8	589.1k	134	0.173	0.420
no vector propagation ($\mathcal{W}_{vv} = 0$ in Eq. 7)	589.2k	135	0.183	0.441
remove both	590.1k	142	0.200	0.507
no vector features	590.3k	174	0.449	1.194

2. Propagation of directional information in substituted ferrocene

To demonstrate the advantages of equivariant over invariant representations in practice, we consider a ferrocene derivative where one hydrogen atom in each cyclopentadienyl ring is substituted by fluorine (see Fig. 4). This molecule has been chosen as it features small energy fluctuations (<1 kcal/mol) when the rings rotate relative to each other. Since the torsional energy profile depends mainly on the orientation of the distant fluorine atoms (measured by the rotation angle θ), it is a challenging prediction target for models without equivariant representations. Fig. 4 shows the predicted energy profiles for a full rotation of the cyclopentadienyl ring using cut-offs $r_{\text{cut}} \in \{2.5, 3.0, 4.0\}$ \AA . All models are trained on energies of 10k structures sampling thermal fluctuations (300 K) and ring rotations of substituted ferrocene. An-

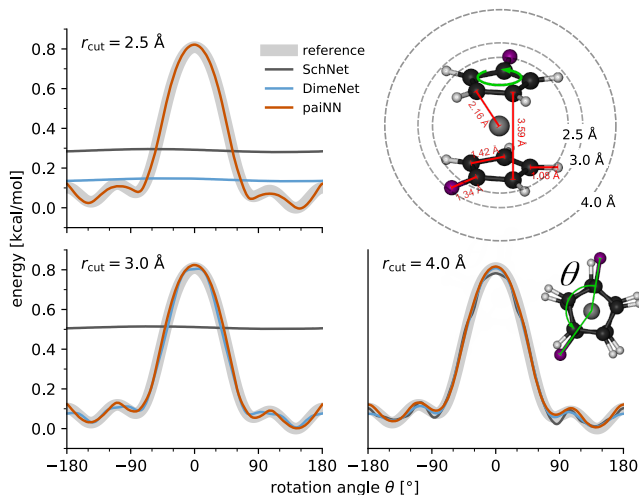


FIG. 4: Rotational energy profile of substituted ferrocene obtained by varying the rotation angle θ while keeping all bond distances fixed at their equilibrium values (H: white, C: black, F: purple, Fe: grey). For small cutoff r_{cut} (dashed grey circles), MPNNs with scalar feature representations are unable to represent information about the rotation angle θ .

other 1k structures are used for validation. SchNet¹³, which uses scalar features, predicts a flat energy profile for $r_{\text{cut}} \leq 3.0$ Å, because it is unable to resolve θ . Although it is possible to encode the relevant information when using a larger cutoff, the learned representation seems to be susceptible to noise, as indicated by the deviations of the predicted energy profile. Since DimeNet¹⁵ includes terms that explicitly depend on angles between triplets of atoms, θ can be resolved for smaller cutoffs, but still fails for $r_{\text{cut}} = 2.5$ Å. In contrast, the equivariant environment representation of PAiNN allows to faithfully reproduce the torsional energy profile even for very small cutoffs.

D. Molecular Spectra

We apply PAiNN to the efficient computation of infrared and Raman spectra of ethanol and aspirin. Although these spectra can in principle be obtained from a single molecular structure via the harmonic oscillator approximation, such an approach tends to neglect important effects, e.g. different molecular conformations⁴⁸. In order to obtain high quality spectra, molecular dynamics simulations have to be performed, requiring the prediction of forces at each time step. Additionally, one needs to compute dipole moments and polarizabilities along the generated trajectory. The infrared and Raman spectra are obtained as the Fourier transform of the time autocorrelation functions of the respective property. Using electronic structure methods, such simulations become prohibitively expensive due to the large number of suc-

cessive computations required. Since nuclear quantum effects (NQE) need to be considered to obtain high quality spectra⁴⁹, ring-polymer molecular dynamics (RPMD) simulations need to be performed, which treat multiple copies of a molecule simultaneously and further increase computational cost.

We train a joined model for energies, forces, dipole moments and polarizability tensors on 8k ethanol conformations using additional 1k molecules each as validation and test set. A second model is trained for aspirin with 16k training examples and 2k molecules for validation and testing. Energies and forces are predicted as described above for MD17. The dipole moments and polarizability tensors are obtained as described in Section IV B, employing two gated equivariant blocks each yielding atomwise scalars and vectors, that are used to compute the outputs as described in Eqs. 13 and 14. The joined model exhibits accurate predictions for energy, forces, dipole moments and polarizabilities, as shown in the inset table of Fig 5. To evaluate the importance of equivariant features for the dipole prediction, we have trained an alternative model using only latent partial charges, but no local dipoles. The results show that predicting molecular dipoles using vector features (Eq. 13) reduces the mean abs. error by more than 50%, reaching 0.009 D compared to 0.020 D using only scalars and positions (Eq. 12). Simulated infrared and Raman spectra using classical MD and RPMD with 64 replicas and the respective PAiNN models are shown for both molecules in Fig. 5, alongside harmonic spectra obtained with the electronic structure reference and, for ethanol, experimental spectra recorded in the gas phase^{50,51}.

The peak positions and intensities of ethanol infrared spectra (Fig. 5a, top) computed with classical MD and PAiNN agree closely with the static electronic structure reference, e.g. in the C-H and O-H stretching regions at 3000 cm^{-1} and 3900 cm^{-1} . This indicates, that PAiNN faithfully reproduces the original electronic structure method in general. However, when compared to experiment, both spectra are shifted towards higher frequencies. The PAiNN RPMD spectrum, on the other hand shows excellent agreement with experiment, illustrating the importance of NQEs. Similar observations can be made for the ethanol Raman spectrum (Fig. 5a, bottom), where the PAiNN RMPD spectrum once again offers the most faithful reproduction of the experiment. We observe similar trends for aspirin (Fig. 5b). RPMD spectra are once again shifted to lower frequencies while the classical MD closely resembles the static electronic structure spectrum.

PAiNN reduces the time required to obtain these spectra by several orders of magnitude. For ethanol, an individual reference computation takes ≈ 140 seconds compared to 14 ms for a PAiNN evaluation on a V100 GPU. This corresponds to a reduction of the overall simulation time from 400 days to approximately one hour. The speedup offered by PAiNN is even more pronounced for aspirin, where a simulation that would have taken 25

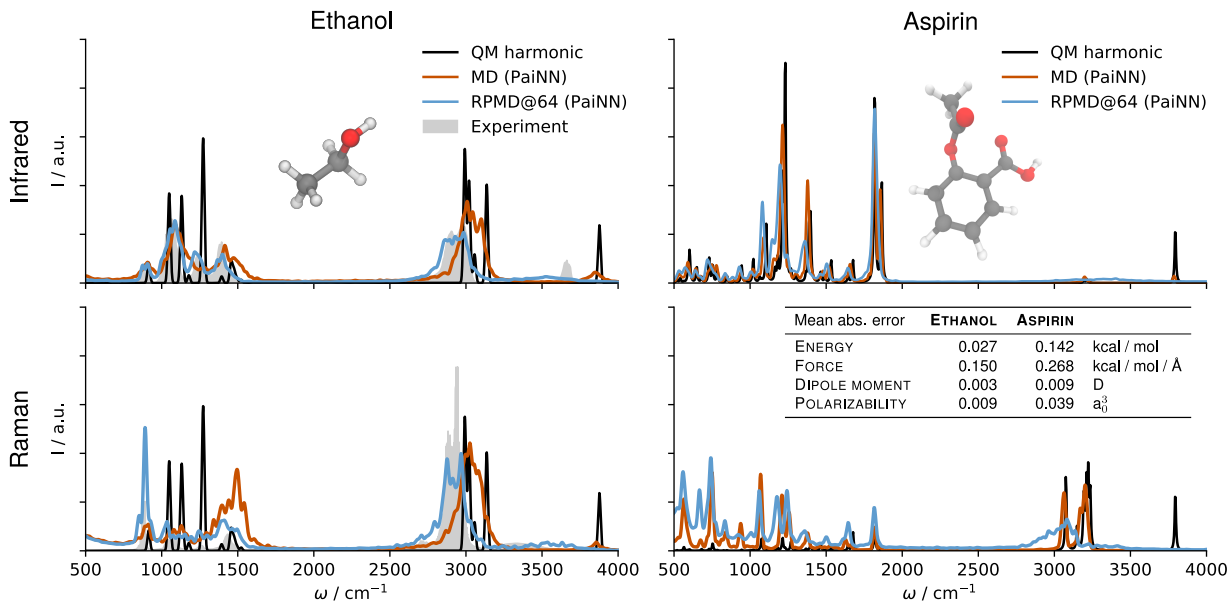


FIG. 5: IR (top) and Raman (bottom) spectra of ethanol and aspirin. Spectra calculated with the reference method using the harmonic oscillator approximation are shown in black (QM harmonic). The inset table shows the mean absolute errors on the respective test set.

years (3140 seconds / step) now takes one hour (15 ms / step).

VI. CONCLUSIONS

We have given general guidelines to design equivariant MPNNs and discussed the advantages of equivariant representations over angular features in terms of computational efficiency as well as their ability to propagate directional information. On this basis, we have proposed PAiNN that yields fast and accurate predictions of scalar and tensorial molecular properties. Thereby, equivariant message passing allows us to significantly reduce both model size and inference time compared to directional message-passing while retaining accuracy. Finally, we have demonstrated that PAiNN can be applied to the prediction of tensorial properties, which we leverage to accelerate the simulation of molecular spectra by 4-5 orders of magnitude – from years to hours.

In future work, the equivariant representation of PAiNN as well as the ability to predict tensorial properties may be leveraged in generative models of 3d geometries^{52–54} or the prediction of wavefunctions^{55–57}. We see further applications of equivariant message passing in 3d shape recognition and graph embedding⁵⁸.

Many challenges remain for the fast and accurate prediction of molecular properties, e.g. modeling of enzymatic active sites or surface reactions. To describe such phenomena, highly accurate reference methods are required. Due to their computational cost, reference data generation can become a bottleneck, making data-efficient MPNNs such as PAiNN invaluable for future chemistry research.

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Appendix A: Data

1. Reference data for substituted ferrocene

Reference computations for substituted ferrocene were carried out with the semi-empirical GFN2-xTB method⁵⁹ using the `xtb` package⁶⁰). Training structures were generated by normal mode sampling⁶¹ at 300 K starting from the global minimum structure and randomly rotating the cyclopentadienyl (Cp) moieties relative to each other around the Cp-Fe-Cp axis by angles uniformly sampled from $[0, 2\pi]$. The rotational potential energy profile was generated by sampling a full rotation around the Cp-Fe-Cp axis using 1k steps, starting from the global minimum structure and keeping all other degrees of freedom fixed at their equilibrium positions.

2. Reference data for infrared and Raman spectra

Electronic structure reference computations for aspirin were carried out at the PBE0/def2-TZVP^{62,63} level of theory using the ORCA quantum chemistry package⁶⁴. SCF convergence was set to tight and integration grid levels of 4 and 5 were employed during SCF iterations and the final computation of properties, respectively. Computations were accelerated using the RIJK approximation⁶⁵. The reference data for aspirin was generated by selecting 20 000 random configurations from the MD17 database¹⁰ and recomputing them at the above level of theory. Reference data for the ethanol molecule was taken from reference³⁸, which employed the same level of theory bar the RIJK approximation.

Appendix B: Training details

All models were trained using the Adam optimizer⁴⁴. The learning rate is decayed by a factor of 0.5 if the validation loss plateaus, starting with the largest learning rate that does not diverge in steps 1e-4, 5e-4, 1e-3, etc. We apply exponential smoothing with factor 0.9 to the validation loss to reduce the impact of fluctuations which are particularly common when training with both energies and forces. We use smaller batches for datasets where we train on both energies and forces, since it is commonly observed that larger batch sizes converge to larger errors in this setting.

Appendix C: Computation of infrared and Raman spectra

All simulations were carried out with the molecular dynamics module implemented in SchNetPack²⁶. Classical molecular dynamics simulations for ethanol and aspirin were carried out for 50 ps at a temperature of 300 K controlled via Nose-Hoover chain⁶⁶ thermostat with a chain length of 3 and time constant of 100 fs. The first 10 ps of these trajectories were then discarded. Ring polymer molecular dynamics using 64 replicas were performed using the same simulation and equilibration periods and temperature, but employed a specially adapted global Nose-Hoover chain as introduced in Ref.⁶⁷ for thermostatting instead. The overall chain settings were kept the same as above. In all cases, the velocity Verlet algorithm and a time step of 0.2 fs were used to integrate the equations of motion. Infrared and Raman spectra were computed from the time-autocorrelation functions of the dipole moment and polarizability time derivatives (see Ref.⁴⁸). All autocorrelation functions were computed with the Wiener-Khinchin theorem⁶⁸, using an autocorrelation depth of 2048 fs. A Hann window function⁶⁹ and zero-padding were applied to the autocorrelation functions in order to enhance the spectra. Raman spectra were calculated using a laser frequency of 514 nm and temperature of 300 K.

Supplementary Table 5: Training parameters for all experiments.

DATA SET	BATCH SIZE	LEARNING RATE	DECAY PATIENCE	STOPPING PATIENCE	r_{CUT} [Å]
QM9	100	$5 \cdot 10^{-4}$	5	30	5.0
MD17	10	$1 \cdot 10^{-3}$	50	150	5.0
FERROCENE	10	$1 \cdot 10^{-3}$	10	30	2.5-4.0
SPECTRA	10	$5 \cdot 10^{-4}$	15	50	2.7