Deep Neural Network Representation of Density Functional Theory Hamiltonian

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The marriage of density functional theory (DFT) and deep learning methods has the potential to revolutionize modern research of material science. Here we study the crucial problem of representing DFT Hamiltonian for crystalline materials of arbitrary configurations via deep neural network. A general framework is proposed to deal with the infinite dimensionality and covariance transformation of DFT Hamiltonian matrix in virtue of locality and use message passing neural network together with graph representation for deep learning. Our example study on graphene-based systems demonstrates that high accuracy (∼meV) and good transferability can be obtained for DFT Hamiltonian, ensuring accurate predictions of materials properties without DFT. The Deep Hamiltonian method provides a solution to the accuracy-efficiency dilemma of DFT and opens new opportunities to explore large-scale materials and physics.

One of the most fundamental problems in quantum physics is to solve the Schrödinger equation \( \hat{H}|\psi\rangle = E|\psi\rangle \) for interacting electrons of matter, so as to predict material properties from first principles. Density functional theory (DFT) [1, 2] has been highly recognized for the purpose, which replaces the complicated many-body problem by a simpler auxiliary one \( \hat{H}_{\text{DFT}}|\psi\rangle = E|\psi\rangle \) describing non-interacting electrons with interacting density [3]. Nowadays, \textit{ab initio} calculation based on DFT is becoming more and more indispensable to scientific research ranging from physics, chemistry to biology [4]. However, the approach is computationally rather demanding and hardly applicable to over thousands of atoms for routine calculations, which limits the exploration of important systems including defects, disorders, interfaces, heterostructures, quasi-crystals, etc. Tremendous effort has been devoted to developing efficient algorithms, for instance, the linear-scaling methods [5]. While the computational cost could be moderately reduced, these techniques usually rely on approximate construction of DFT Hamiltonian at the expense of losing accuracy and transferability. The accuracy-efficiency dilemma of DFT hinders the investigation of materials and physics phenomena at large-scale.

Recently, deep learning methods based on neural network have revolutionized many disciplines ranging from computer vision, natural language processing to scientific discovery [6–8]. Neural network is able to learn complicated functions by composing simple but nonlinear transformations [9], whose remarkable expressive power gained by multilayer perceptron has been utilized to predict materials properties (e.g., total energy, force, band structure, charge density) [10–18]. The primary problem is to represent the mapping from material structures to DFT Hamiltonians by neural network for systems of arbitrary size, so that various kinds of physical properties can be predicted simultaneously via the trained DFT Hamiltonians (Fig. 1 (a)). The problem is quite challenging, because the Hamiltonian matrix has dimensions varying with system size and more critically it transforms covariantly under changes of coordinate, basis and gauge, which is much more complicated to deal with than scalar quantities. Schütz et al. considered a similar problem for small individual molecules with varying atomic struc-

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tures [19]. Gu et al. used neural network to learn energy eigenvalues instead of Hamiltonian matrix for one-dimensional chains [18]. The important problem of learning DFT Hamiltonian for infinitely large systems with arbitrary atomic configurations remains illusive.

In this Letter, a general theoretical framework is proposed to represent DFT Hamiltonians of crystalline materials by deep neural network, so as to predict material properties from given atomic structures without DFT computations. The major difficulties of learning Hamiltonian matrix caused by infinite dimensionality and covariant transformation are overcome by utilizing localized orbital functions together with local coordinate systems. Then an architecture and workflow of neural network in combination with graph representation are developed for training and learning DFT Hamiltonian matrix, whose capability is demonstrated by example studies of graphene-based systems. Our method is expected to be universal and could find useful applications in studying large periodic or non-periodic systems.

As suggested by Kohn and Sham [2], the complicated many-body problem of interacting electrons is mapped to an auxiliary problem of non-interacting electrons described by \( \hat{H}_{\text{DFT}} = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{KS}} \). In the DFT Hamiltonian, the exchange-correlation effect is considered by the Kohn-Sham potential \( V_{\text{KS}} \). Typically \( \hat{H}_{\text{DFT}} \) is obtained via self-consistent field (SCF) calculations for a given material structure (\( \{ R \} \) describing atomic types and positions) and then the electronic structure is studied by solving the effective single-particle problem (Fig. 1 (a)). However, the SCF computation of \( \hat{H}_{\text{DFT}} \) demands much computational resource that grows considerably with system size, forbidding the study of large-scale systems. According to the Hohenberg-Kohn theorem [1], there is a one-to-one correspondence between external field (determined by \( \{ R \} \)) and \( \hat{H}_{\text{DFT}} \). Thus the construction of \( \hat{H}_{\text{DFT}} \) is essentially to obtain a mapping function: \( \{ R \} \mapsto \hat{H}_{\text{DFT}}(\{ R \}) \). The generic form of \( \hat{H}_{\text{DFT}}(\{ R \}) \), however, is too complicated to be expressed analytically, because \( \hat{H}_{\text{DFT}} \) depends sensitively on atomic details. We suggest to train and learn \( \hat{H}_{\text{DFT}}(\{ R \}) \) through deep neural network, which is named Deep Hamiltonian (DeepH) method.

In general, non-periodic structures containing nearly infinite number of atoms will be considered. Learning \( \hat{H}_{\text{DFT}}(\{ R \}) \) for such kind of systems seems to be a formidable task due to the following difficulties. Firstly, \( \hat{H}_{\text{DFT}} \) has an infinite number of independent variables in \( \{ R \} \). Secondly, the DFT Hamiltonian matrix is basis-dependent and its dimension could be infinitely large. Thirdly, the Hamiltonian matrix should satisfy certain physical and gauge symmetry requirements, such as invariance under atom permutation and translation, covariance under rotations and gauge transformations. The covariant condition demands transformations of the entire Hamiltonian matrix under changes of coordinate, basis function, gauge, etc., which is much more difficult to implement than invariant ones. Obviously, one must significantly reduce these difficulties to make DeepH method workable.

As revealed by W. Kohn and others, local electronic properties do not respond to changes of the effective external potential at a distant due to destructive interferences between many-particle eigenstates [20, 21]. This implies a widely applicable principle of locality or “nearsightedness” for electronic matter, which plays an essential role in our investigation. Consequently, there is no need to consider the entire system at once. Instead only information of neighborhood within a finite distance \( R_N \) is relevant for studying local electronic properties (Fig. 1 (b)).

A proper selection of basis set is critical to our study. DFT calculations usually use plane waves or localized orbitals as basis functions. The localized basis is compatible with the locality and non-periodicity nature of the system, and thus will be employed. With this choice, \( \hat{H}_{\text{DFT}} \) can be expressed as a sparse matrix benefiting from the local or semilocal property of the Kohn-Sham potential. The matrix element \( H_{\alpha i,j\beta} \) (\( \alpha, \beta \) refer to localized orbitals centered at atoms \( i, j \)) vanishes when the distance between atoms \( i \) and \( j \) is larger than a cutoff radius \( R_C \) (Fig. 1 (b)). \( R_C \) is determined by the spread of localized orbitals, which is on the order of angstrom, much smaller than \( R_N \). We suggest using non-orthogonal atomic-like orbitals. They are typically more localized than orthogonal ones due to the conflicting requirement of localization and orthogonalization [22]. Moreover, their gauge is system-independent and the rotation transformation is well described by the spherical harmonics. In contrast, the widely used Wannier functions do not possess such kind of advantages. By taking advantages of the sparseness and the nearsightedness, only Hamiltonian matrix blocks \( H_{ij} \) between neighboring atoms (within \( R_C \)) have to be learned, and only information of neighborhood of atom \( i \) or \( j \) (within \( R_N \), denoted by \( \{ R \}_N \)) is needed for learning \( H_{ij} \). In this sense, complexity of the learning problem is reduced from infinite to finite.

A tricky issue is to deal with covariant transformations of the Hamiltonian matrix. Because the Hamiltonian matrix is not physically observable, it will change when globally or locally varying coordinate, basis or gauge. The local transformation is less obvious. As shown in Fig. 1 (c), the atom pairs \( AB, AC \) and \( AD \) share the same local chemical environment, but give different Hamiltonian matrix blocks, which are related by a local transformation. Under a clockwise rotation of basis functions by 120 (240) degrees for \( AC \) (AD), the transformed Hamiltonian matrix block \( H_{AC} \) (\( H_{AD} \)) coincides with \( H_{AB} \). In practice, we may encounter atom pairs with nearly infinite number of possible orientations. Thus it is difficult (if not impossible) to learn the covariant requirement automatically by neural network via data augmentation [19].
We propose a strategy to help DeepH method work efficiently and accurately via local coordinate (details described in the Supplemental Material [23]), in which the locally transformed Hamiltonian matrix blocks $H'_{ij}$ are invariant under translation and rotation (Fig. 1 (c)). Consequently, covariant transformations are reduced to invariant ones and individual blocks $H'_{ij}(\{R\}_N)$ could be treated separately.

Next we present a deep neural network representation of DFT Hamiltonian based on message passing neural network (MPNN) [24] in combination of graph representation that are widely applied for materials studies [11, 25–28]. Rules of constructing graphs and MPNN are illustrated in Fig. 2(a). Each atom is represented by a vertex and atom pairs (with distance smaller than $R_C$) by edges. MPNN will use edge embeddings to represent $H'_{ij}$. Self-loop edges are added in the graph to consider intra-site couplings. Let $v_i$ and $e_{ij}$ denote the vertex feature of atom $i$ and edge feature of atom pair $ij$, respectively. The initial vertex features are the embeddings of atomic number $Z_i$, and the initial edge features are the interatomic distance $|r_{ij}|$ expanded with Gaussian basis centered at different points $r_n$,

$$v_i^{(0)} = \text{Embedding}(Z_i),$$
$$e_{ij}^{(0)} = \exp(-(|r_{ij}| - r_n)^2/\sigma^2).$$

The architecture and workflow of MPNN are presented in Fig. 2(b). In a message passing (MP) layer, the vertex and edge features are updated successively as follows:

$$v_i^{(l)} = \text{LayerNorm} \left( \sum_{k \in N_i} \Phi_v^{(l)}(z_{ik}^{(l-1)}) + v_i^{(l-1)} \right),$$
$$e_{ij}^{(l)} = \Phi_e^{(l)} \left( v_i^{(l)} \parallel v_j^{(l)} \parallel e_{ij}^{(l-1)} \right),$$

where $N_i$ is a set containing neighbors vertices with edge connection to vertex $i$, $\parallel$ denotes concatenation of feature vectors, the superscript $l$ refers to the $l$-th MP layer, $z_{ik}^{(l-1)} \equiv v_i^{(l-1)} \parallel v_k^{(l-1)} \parallel e_{ik}^{(l-1)}$ is the concatenation of vertex and edge features of neighborhood, and layer normalization [29] is employed to improve training efficiency. The neural network of vertex $\Phi_v^{(l)}(x) = \sigma(xW_1^{(l)} + b_1^{(l)}) \circ g(xW_2^{(l)} + b_2^{(l)})$, where the input $x \in \mathbb{R}^{n_{in}}$, the weight $W \in \mathbb{R}^{n_{in} \times n_{out}}$, the bias $b \in \mathbb{R}^{n_{out}}$, $\circ$ denotes element-wise multiplication, $\sigma$ denotes the sigmoid function, and $g$ denotes the softplus function [26]. The neural network of edge $\Phi_e^{(l)}(x) = \text{ReLU}(xW_3^{(l)} + b_3^{(l)})W_4^{(l)} + b_4^{(l)}$, which is a fully connected neural network with a hidden layer and a ReLU activation function. The local chemical environment of neighborhood within $R_C$ will be aggregated in a MP layer. As MP layers are stacked, more and more information of distant chemical environment will be aggregated into the features, enabling the learning of $H'_{ij}(\{R\}_N)$.

A problem about local coordinate system should be remarked. Since a local coordinate is defined for each edge according to its local chemical environment, sometimes minor modifications of local structures could change the coordinate axes, making the transformed $H'_{ij}$ considerably different and thus leading to inaccuracy of deep learning [23]. We find that the problem is solvable by introducing one local coordinate message passing (LCMP) layer after several MP layers [23]. In the LCMP layer, orientation information $(\phi_{ik}^{pq} \parallel \theta_{ik}^{pq})$ of bond $ik$ relative to a local coordinate defined for edge $pq$ is added into initial edge features. $\theta_{ik}^{pq}$ and $\phi_{ik}^{pq}$ are the corresponding polar and azimuthal angles, respectively. The vertex and edge features defined for the local coordinate system are updated

![FIG. 2.](image-url)
The DeepH method is applied to study realistic material systems of graphene for demonstrating its capability. Random atomic structures of graphene are generated by ab initio molecular dynamics (AIMD) calculations done by the Vienna ab initio simulation package [30] with a 6×6 supercell. The corresponding DFT Hamiltonian is computed via the localized-orbital-based OpenMX package [31, 32] using 13 non-orthogonal atomic-like basis functions for carbon and the Perdew-Burke-Ernzerhof exchange correlation functional. Then the MPNN model including five MP layers followed by one LCMP layer is trained by minimizing the loss function defined as the mean squared errors of $H'_{\alpha\alpha',\beta\beta'}$. To test the performance of DFT Hamiltonian, linear and nonlinear optical responses are studied using the methods we developed recently [22, 33]. More details of methods are described in the SM [23].

The training of neural network generally demands a large amount of data. In our study, 5,000 configurations of the graphene supercell are generated by AIMD at a temperature of 300 K, giving 14,400,000 nonzero Hamiltonian matrix blocks. 270 configurations are used for training, 90 configurations for hyperparameter optimization and the remaining for test. The mean absolute error (MAE) of $H'_{\alpha\alpha',\beta\beta'}$ for the test set is shown for every orbital combination in Fig. 3(a). The MAE value averaged over all the $13 \times 13$ orbital combinations is 2.1 meV, with individual values distributed between 0.4 meV and 8.5 meV. Such a MAE is quite small considering that the Hamiltonian matrix element is typically on the order of eV. For instance, $H'_{\alpha\alpha',\beta\beta'}$ for the first orbital and the nearest neighbor obtained from DFT calculations has a mean value of -10.1 eV and a standard deviation (SD) of 315 meV (Fig. 3(b)), whereas the corresponding MAE of DeepH is 6.6 meV, corresponding to a high coefficient of determination $r^2 = 0.9994$. For another 2,000 new configurations of graphene supercell sampled by AIMD from 100 K to 400 K, the generalization MAE of $H'_{\alpha\alpha',\beta\beta'}$ is as small as 1.9 meV on average, in analogy to the previous test. High accuracy of the predicted DFT Hamiltonian is thus demonstrated.

A great advantage of DeepH method is that once the function $\hat{H}_{\text{DFT}}(\{\mathcal{R}\})$ is learned by neural network, various kinds of physical properties, such as the band structure, the Berry phase, and physical responses to external field, can be predicted in no need of doing DFT calculations. To check the reliability of our method, we study eigen-energy-based quantities (density of states (DOS) or bands) as well as wavefunction-related properties (optical transition and shift current). Shift current is of particular interest as an important photovoltaic effect generated by nonlinear optical progress and closely related to topological quantities (e.g., Berry phase and curvature) [22, 33, 34].
slightly deviate from each other even for the latter case.

Furthermore we test the transferability of our method by making predictions on new materials (unseen in the training set). Carbon nanotubes (CNTs) are selected for the purpose, which have curved quasi-one-dimensional atomic structures, significantly distinct from graphene. Two types of CNTs are considered, including armchair and zigzag ones. Overall, the averaged MAE of DFT Hamiltonian matrix is insensitive to nanotube chirality and monotonically decreases with increasing nanotube diameter ($d$), which reduces to below 3.5 meV for $d > 2$ nm (Fig. 4(a)). For a zigzag (25, 0) CNT ($d \sim 2$ nm), the predicted band structure (Fig. 4(b)) and electric susceptibility as a function of frequency (Fig. 4(c), corresponding to inter-band transitions) can well reproduce DFT calculation results. More comparisons are contained in the SM [23]. Remarkably, properties of large-diameter CNTs can be accurately predicted by DeepH method at very low computational expense.

In summary, we have proposed a general framework to represent DFT Hamiltonian by deep neural network, which builds a mapping from materials structures to physical properties for nearly arbitrary atomic configurations. As demonstrated for graphene and CNTs, the DeepH method is not restricted by system size or periodic requirement and is able to properly deal with global or local transformations, enabling study of large-size material systems with high accuracy and efficiency. The method greatly extends the scope of first-principles research and opens new opportunities to investigate fundamental physics (disorder, defect or interface effects, quantum transport, electron-lattice coupling, etc.) and realistic systems (biological materials, twisted van der Waals materials, etc.), which is useful for materials research and device design.

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