Efficient Quantum-Mechanics-Based Molecular Dynamics Through Machine Learning-Driven Density Functional Theory Hamiltonian

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***Abstract*—Ab-initio molecular dynamics (AIMD) is widely adopted for its high accuracy in semiconductor device and materials modeling, as it captures atomistic defect dynamics, interface phenomena, and thermo-mechanical behavior. However, its substantial computational cost hinders its application to large-scale or long-timescale simulations. To overcome this limitation, we present Neural Network Hamiltonian Molecular Dynamics, which employs a graph neural network to model the density functional theory Hamiltonian and updates atomic positions via forces from energy gradients. For copper and palladium systems, our method demonstrates good agreement with AIMD in temperature evolution, mean squared displacements, radial distribution functions, angular distribution functions, and density of states, while achieving faster performance. Our framework not only enables large-scale molecular dynamics simulations, but also establishes a novel approach to atomistic modeling by incorporating neural network-derived Hamiltonians.**

***Index Terms*—molecular dynamics, density functional theory, Hamiltonian, and machine learning**

I. INTRODUCTION

Molecular dynamics (MD) simulations play a pivotal role in advancing research across a wide range of scientific disciplines, including chemistry, physics, and materials science. In particular, their utility has become increasingly important in device modeling, where atomistic insights into amorphous structures, interfacial phenomena, and thermal evolution are essential for accurately capturing the behavior of materials at the nanoscale [1]–[3]. While ab initio MD methods offer high predictive accuracy by explicitly solving for the electronic structure, their significant computational cost poses a major limitation for large-scale or long-time simulations, especially when compared to classical MD approaches [4]. To address this issue, tight-binding molecular dynamics (TBMD) has been proposed as a compromise, offering reduced computational demands [5]. However, TBMD suffers from inherent limitations in terms of accuracy and transferability, particularly for systems with complex bonding environments or varying chemical compositions.

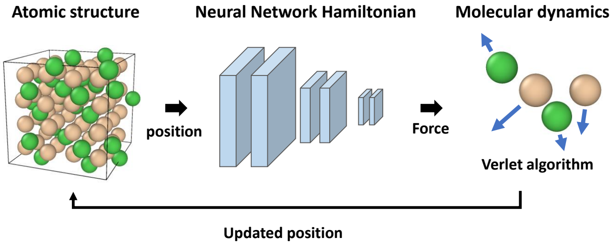

Fig. 1. The overall structure of our method. Atomic coordinates are fed into a neural network that computes forces, and these computed forces are then used by the Verlet algorithm to calculate subsequent atomic positions.

In recent years, the application of graph neural networks in materials science has progressed considerably, providing effective tools for addressing diverse challenges in computational materials research [6]. Among these efforts, modeling density functional theory (DFT) Hamiltonians with neural networks has shown potential for maintaining reasonable accuracy while reducing computational cost [7]–[9]. In this study, we introduce a neural network Hamiltonian molecular dynamics (NNH-MD) framework that enables computationally efficient MD simulations by learning the DFT Hamiltonian and computing atomic forces as energy gradients. The proposed approach allows for the propagation of atomic trajectories with accuracy comparable to ab-initio MD, while offering a substantial reduction in computational overhead. Benchmark results demonstrate that NNH-MD yields reliable physical predictions across key descriptors, including temperature evolution, radial distribution functions (RDFs), angular distribution functions (ADFs), mean squared displacements (MSDs), and electronic density of states (DOS), indicating its effectiveness for large-scale atomistic simulations.

II. METHOD

A. Neural Netwrok Hamiltonian

Message-passing neural networks (MPNNs) provide a robust framework for representing molecules and materials as graphs, enabling effective modeling of complex interatomic

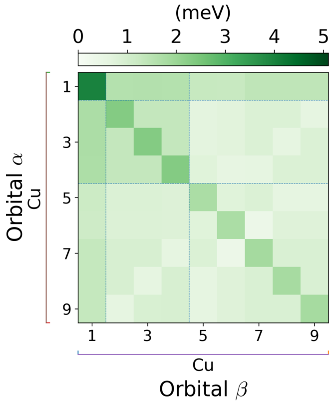

Fig. 2. Element-wise error between DFT Hamiltonian and neural network Hamiltonian matrix elements, evaluated over 150 configurations for copper (left) and 100 configurations for palladium (right). Each panel shows the absolute error between corresponding matrix elements, with orbital indices labeled on both axes. The MAE for both cases is approximately 1 meV.

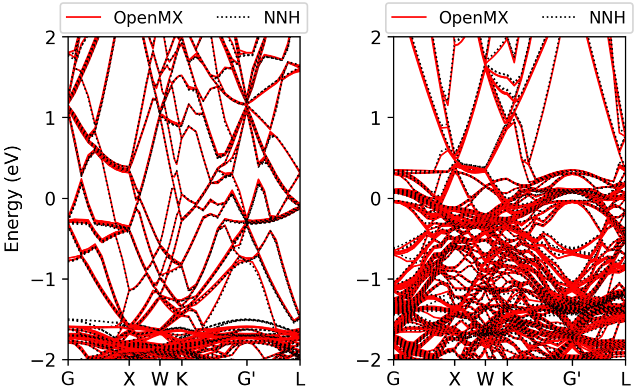

Fig. 3. Comparison of band structures obtained from OpenMX and NNH for 64-atom systems. Results for both cases are shown, with OpenMX depicted as a solid red line and NNH as a dashed black line. (Left) Band structure for copper; (right) band structure for palladium.

interactions. We use DeepH-E3 [10], a state-of-the-art MPNN-based model, to learn the DFT Hamiltonian. To enhance the physical consistency of the model and improve the reliability of atomic force predictions, we introduce a composite loss function that includes both the Hamiltonian and atomic forces during training. Specifically, the total loss is formulated as a weighted sum of the Hamiltonian loss and the force loss, expressed as:

$$\mathcal{L}_{\text{total}} = \alpha \cdot \mathcal{L}_{\text{H}} + \beta \cdot \mathcal{L}_{\text{F}}, \tag{1}$$

where $\mathcal{L}_{\text{H}}$ and $\mathcal{L}_{\text{F}}$ denote the losses associated with the Hamiltonian and atomic forces, respectively, and α and β are weighting factors that balance their contributions during optimization.

The atomic forces are computed as the negative gradients of the total energy with respect to atomic positions:

$$\mathbf{F} = -\frac{\partial E}{\partial \mathbf{R}} = -\frac{\partial}{\partial \mathbf{R}} \sum_i f_i \epsilon_i, \tag{2}$$

where f_i is the Fermi–Dirac occupation for the ith eigenvalue ϵ_i of the predicted Hamiltonian, and $\mathbf{R}$ denotes the atomic positions. In practice, this differentiation is performed using the PyTorch autograd framework [11], ensuring consistency between the learned Hamiltonian and the computed forces.

B. Molecular dynamics

Atomic forces, once obtained from the neural network Hamiltonian, are used to advance the atomic positions at each timestep (Δt) according to the Verlet integration scheme combined with the Nosé–Hoover thermostat (Fig. 1), as follows:

$$\mathbf{R}(t+\Delta t) = 2\mathbf{R}(t)\beta - \mathbf{R}(t-\Delta t)\alpha\beta + \frac{\mathbf{F}(t)}{m}(\Delta t)^2\beta, \tag{3}$$

where

$$\alpha = 1 - 0.5\,\xi(t)\,\Delta t, \tag{4}$$

$$\beta = \frac{1}{1 + 0.5\,\xi(t)\,\Delta t}, \tag{5}$$

and $\xi(t)$ is the friction coefficient determined by the Nosé–Hoover thermostat. The friction coefficient is then updated as

$$\xi(t) = \frac{3\eta(t) - 4\eta(t-\Delta t) + \eta(t-2\Delta t)}{2\Delta t}. \tag{6}$$

The time evolution of the Nosé–Hoover thermostat variable $\eta(t)$ is given by

$$\eta(t+\Delta t) = 2\eta(t) - \eta(t-\Delta t) + \frac{2}{Q}\left[K(t) - K_0\right](\Delta t)^2, \tag{7}$$

where Q is the thermostat mass, $K(t)$ is the instantaneous kinetic energy, and K_0 is the target kinetic energy corresponding to the desired temperature. Initial velocities are sampled from the Maxwell–Boltzmann distribution at the target temperature, and thermal equilibration is maintained by the thermostat throughout the simulation.

III. RESULTS

A total of 750 configurations for copper and 600 for palladium, each with 64 atoms, were generated by applying random displacements of up to 25% and 20% of the lattice constant, respectively. DFT calculations were performed using OpenMX [12], which employs norm-conserving pseudopotentials [13], the generalized gradient approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [14]. Based on this dataset, an NNH model was trained and validated, demonstrating reliable reproduction of the DFT Hamiltonian elements and corresponding band structures. For both copper and palladium, the mean absolute error (MAE) of the Hamiltonian elements predicted by the NNH model with respect to the DFT reference remains below 5 meV for all orbital pairs. (Fig. 2) The electronic band structures computed using the NNH Hamiltonian closely match the DFT results, with MAE of 12.0 meV for copper and 14.3 meV for palladium. (Fig. 3).

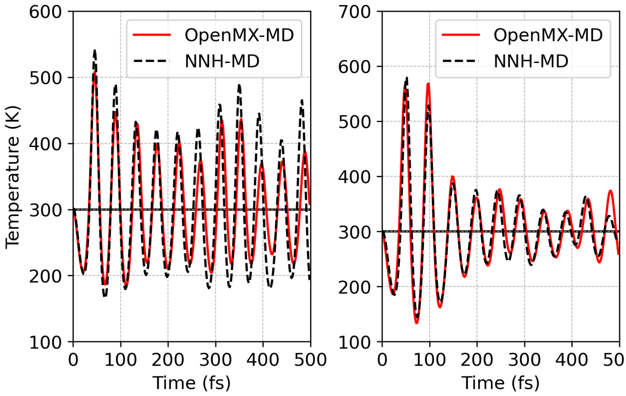

Fig. 4. Comparison of temperature evolution obtained from OpenMX-MD (solid red line) and NNH-MD (dashed black line) for 64-atom systems at 300 K. (Left) Results for copper; (right) results for palladium.

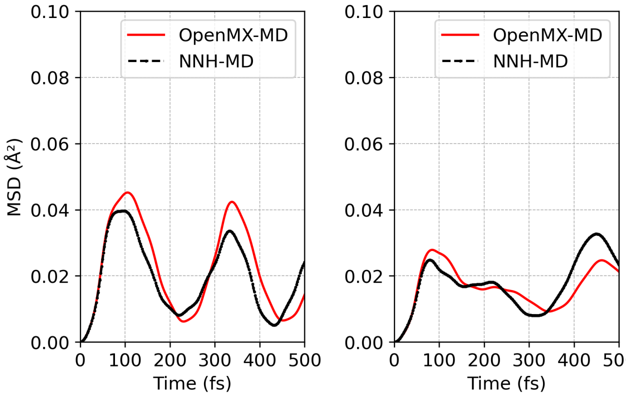

Fig. 5. Time evolution of the mean squared displacement (MSD) at 300 K, comparing OpenMX-MD (solid red line) and NNH-MD (dashed black line). (Left) Results for 64-atom copper; (right) results for 216-atom palladium.

We performed simulations at 300 K for copper using a 64-atom supercell, which matches the system size used during training NNH, and for palladium using a larger 216-atom supercell to evaluate scalability. The results for palladium were specifically analyzed to assess the applicability of NNH-MD to larger systems. For validation, these results were compared with ab-initio MD simulations carried out using OpenMX and a 3×3×3 k-point grid. Temperature evolution, which directly reflects energy conservation and system equilibration, was first examined. As shown in Fig. 4, the results from NNH-MD similarly followed those from ab-initio MD, demonstrating that both methods yield consistent kinetic energy evolution under the same simulation conditions. This consistency establishes a reliable foundation for subsequent analyses of structural and dynamical properties, including RDFs, ADFs, and MSDs.

The MSD, which quantifies how far atoms deviate from their original positions over time, exhibited an oscillatory behavior in both approaches, indicating that the atomic motions and vibrational amplitudes are in good agreement at 300 K (Fig. 5). The initial fluctuations in temperature observed in both simulations gradually diminished, ultimately resulting in steady-state dynamics characteristic of the solid phase.

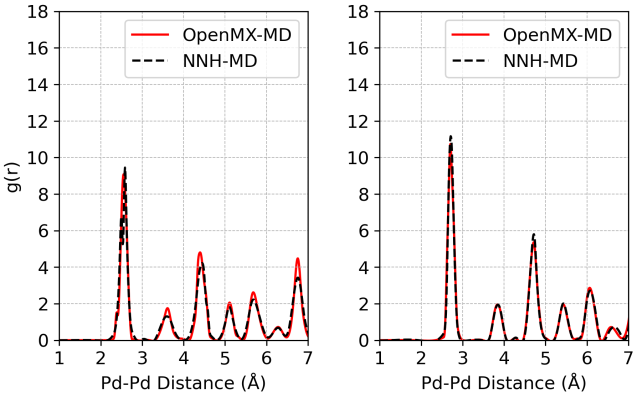

Fig. 6. RDFs at 500 fs obtained from OpenMX-MD (solid red line) and NNH-MD (dashed black line), showing how particle density varies as a function of distance from a reference particle. (Left) Comparison for a system of 64 Cu atoms. (Right) Comparison for a system of 216 Pd atoms.

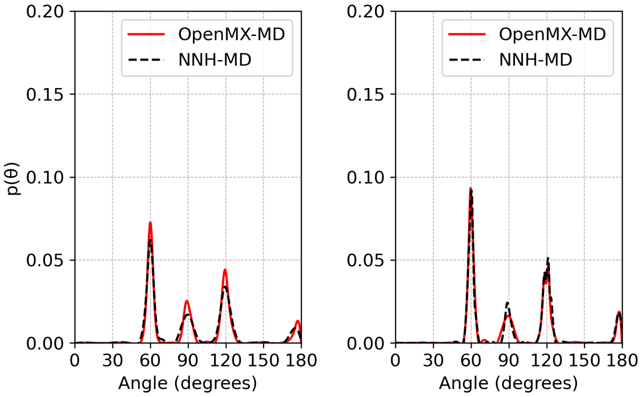

Fig. 7. ADFs at 500 fs obtained from OpenMX-MD (solid red line) and NNH-MD (dashed black line), showing the distribution of bond angles formed between neighboring atoms. (Left) Comparison for a system of 64 copper atoms. (Right) Comparison for a system of 216 palladium atoms.

Analysis of the RDF revealed that NNH-MD captures the main features of atomic arrangement observed in ab-initio MD, as evidenced by nearly coinciding peak positions and intensities (Fig. 6). Furthermore, the ADF measurements showed that the bond angle environments generated by NNH-MD align well with those obtained from ab-initio MD, suggesting that the key aspects of local bonding structures are maintained (Fig. 7). Taken together, these findings suggest that, while some quantitative differences remain, NNH-MD is generally able to construct spatial atomic configurations that are in reasonable agreement with those generated by ab-initio MD, supporting its potential for qualitatively capturing the key structural features of the system.

The DOS obtained from NNH-MD shows a good overall match with that from ab-initio MD, indicating that the NNH accurately reproduces the electronic structure of the system.

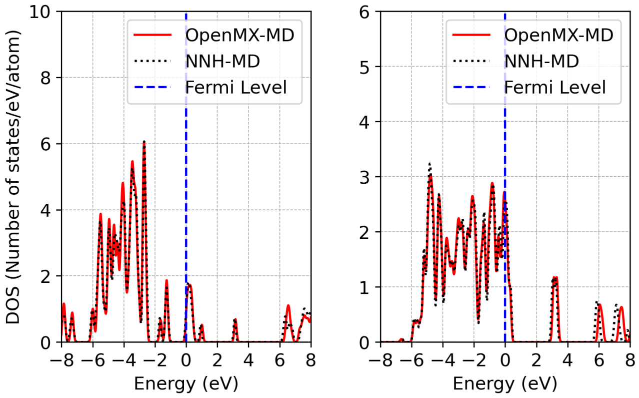

Fig. 8. Density of states (DOS) at 500 fs computed at the Γ-point with OpenMX-MD (solid red line) and NNH-MD (dashed black line), the latter based on NN-driven MD trajectories and a Hamiltonian predicted by the neural network. (Left) 64 copper atoms. (Right) 216 palladium atoms.

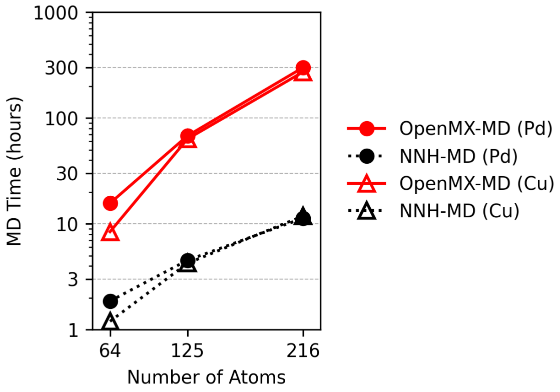

Fig. 9. Calculation times for MD simulations of palladium and copper systems with 64, 125, and 216 atoms. Results for OpenMX-MD (solid red lines) and NNH-MD (dashed black lines) are shown, with circles representing palladium and triangles representing copper. OpenMX-MD calculations were performed on an Intel Xeon E5-2660 CPU, while NNH-MD utilized an NVIDIA RTX 3090 GPU. For the 216-atom case, OpenMX-MD simulations were conducted with reduced accuracy due to time and memory constraints, resulting in an effective underestimation of the required computational time.

This agreement further supports the reliability of NNH-MD in predicting both structural and electronic properties (Fig. 8), underscoring its suitability for charge transport and other semiconductor device simulations.

NNH-MD demonstrates more than a tenfold speedup compared to ab-initio MD for both Pd and Cu systems with 216 atoms, as shown in Fig. 9. Notably, ab-initio MD computation time tends to increase roughly quadratically with the number of atoms, whereas NNH-MD shows a near-linear scaling behavior. This indicates that NNH-MD can serve as a significantly more efficient tool for simulations involving larger atomic systems.

IV. CONCLUSION

We have presented a neural network Hamiltonian molecular dynamics (NNH-MD) framework that efficiently learns the DFT Hamiltonian using a graph neural network and computes atomic forces via autograd differentiation. Validation on copper and palladium systems demonstrates that NNH-MD reliably reproduces key structural and electronic properties including temperature evolution, RDFs, ADFs, MSDs, and DOS with accuracy comparable to conventional ab-initio MD. Importantly, NNH-MD achieves more than an order of magnitude speedup for systems of several hundred atoms, with near-linear scaling in computational cost compared to the quadratic scaling observed in ab-initio MD. These advantages position NNH-MD as a promising tool for large-scale atomistic simulations and device-scale semiconductor modeling, enabling exploration of complex material behaviors beyond the reach of traditional methods.

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