

Mapping Electronic Structure to Coarse-Grained Degrees of Freedom via Supervised Machine Learning

Nicholas Jackson^{1,2}, Lucas Antony², Alec Bowen², Daniel Reid², Juan de Pablo^{1,2}

jackson@anl.gov

1. Materials Science Division, Argonne National Laboratory, Lemont, IL 60434 USA

2. Institute of Molecular Engineering, University of Chicago, Chicago, IL 60615 USA



Introduction

The modeling of photoactive soft materials involves the union of classical and quantum mechanical simulation protocols to capture the impact of nuclear degrees of freedom on the electronic structure of the material. A common workflow consists of:

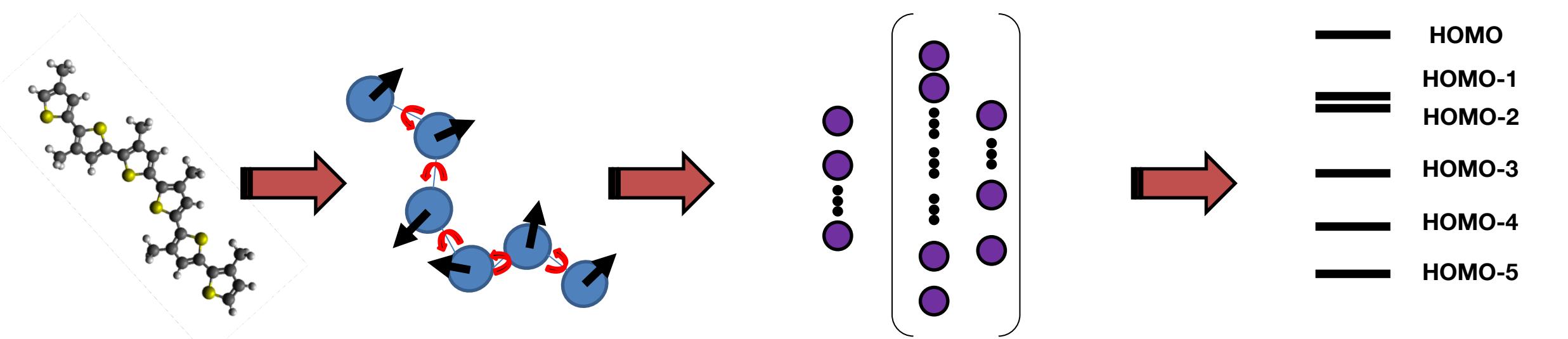
1. Sample long length and timescales with a coarse-grained model.
2. Backmap atomistic representation, relaxing local configurations.
3. Perform quantum-chemical analysis of atomistic representation.
4. Parameterize rate theories and compute carrier mobilities.

We outline a simulation approach for mapping configuration-dependent electronic structure directly to coarse-grained, nuclear degrees of freedom that both accelerates the above workflow and provides insights into effective coarse-grained degrees of freedom useful for classical simulation.

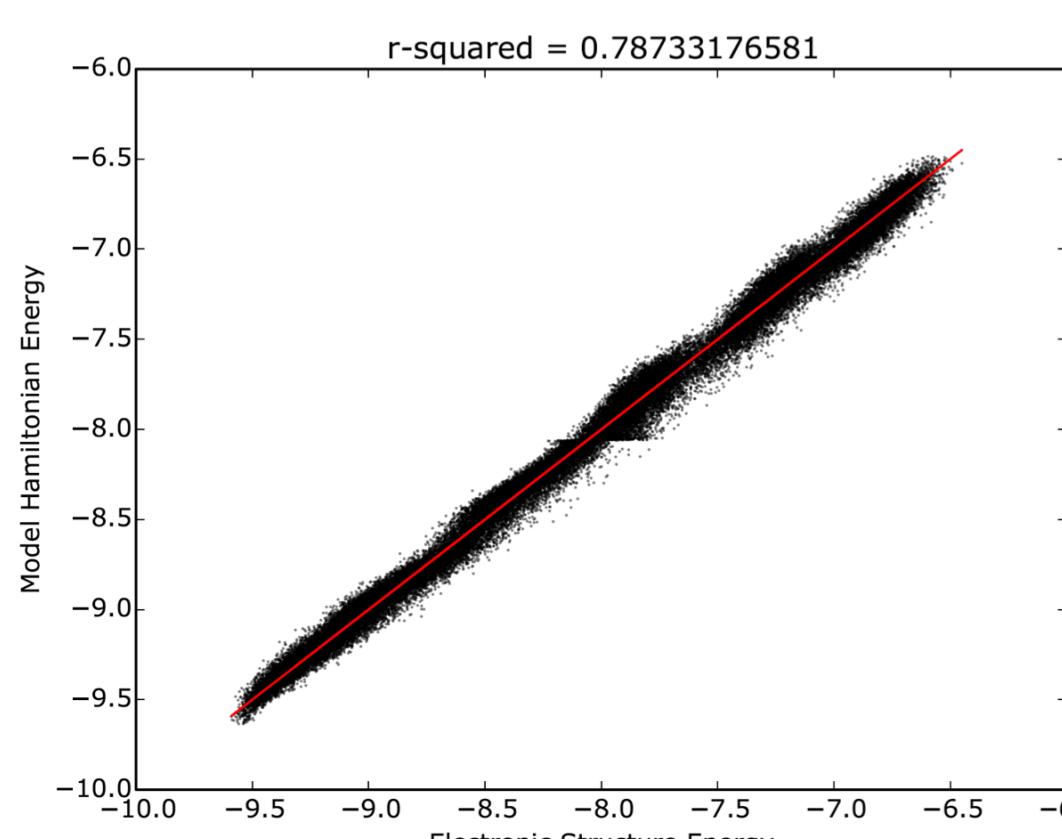
Further details may be found in the upcoming manuscript Jackson, N.E.; Antony, L.A.; Bowen, A.; Reid, D.R.; Vishwanath, V.; de Pablo, J.J. "Mapping Electronic Structure to Coarse-Grained Degrees of Freedom via Supervised Machine Learning", *In Preparation*

Learning Configurational Energetics

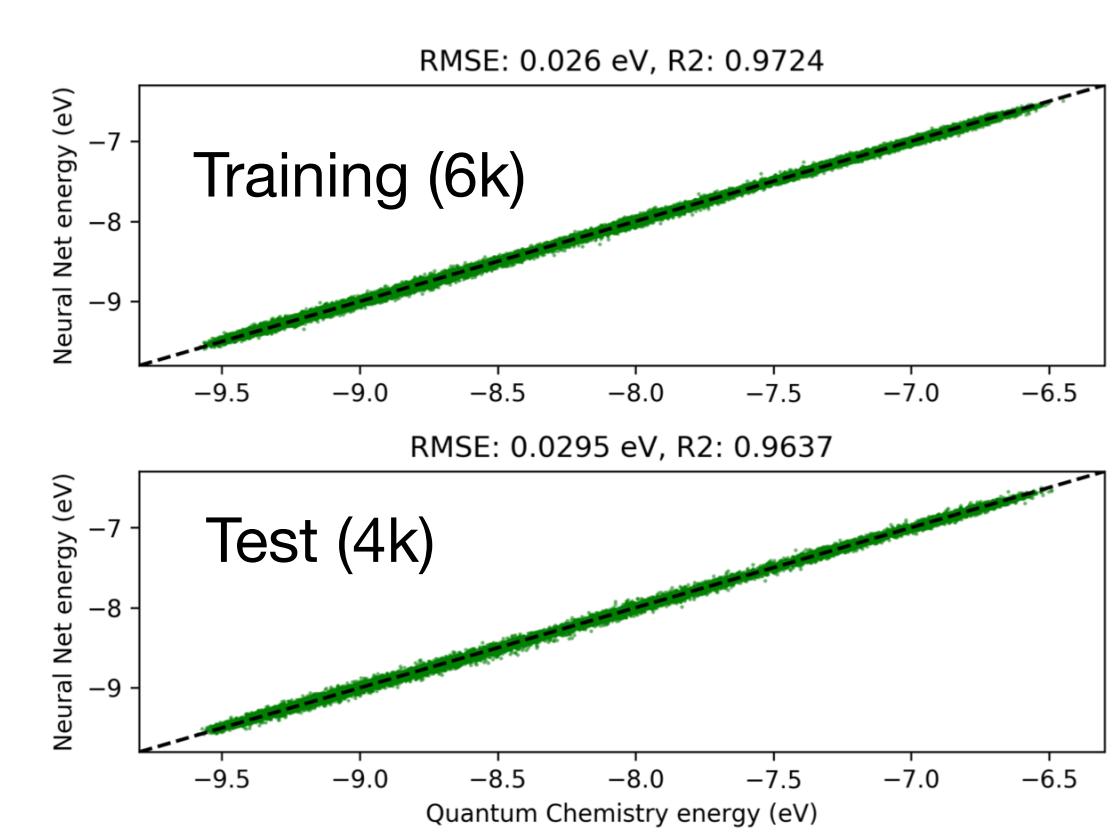
Utilizing deep artificial neural networks (ANN), we map the configurational dependence of the valence orbitals of a thiophene oligomer at 500K to a coarse-grained model, eliminating the need to backmap an atomistic representation for quantum-chemical analysis.



Tight-Binding Model



ANN Model



Performance

- ANN**
- RMSE = 0.03 eV
 - R² = 0.96

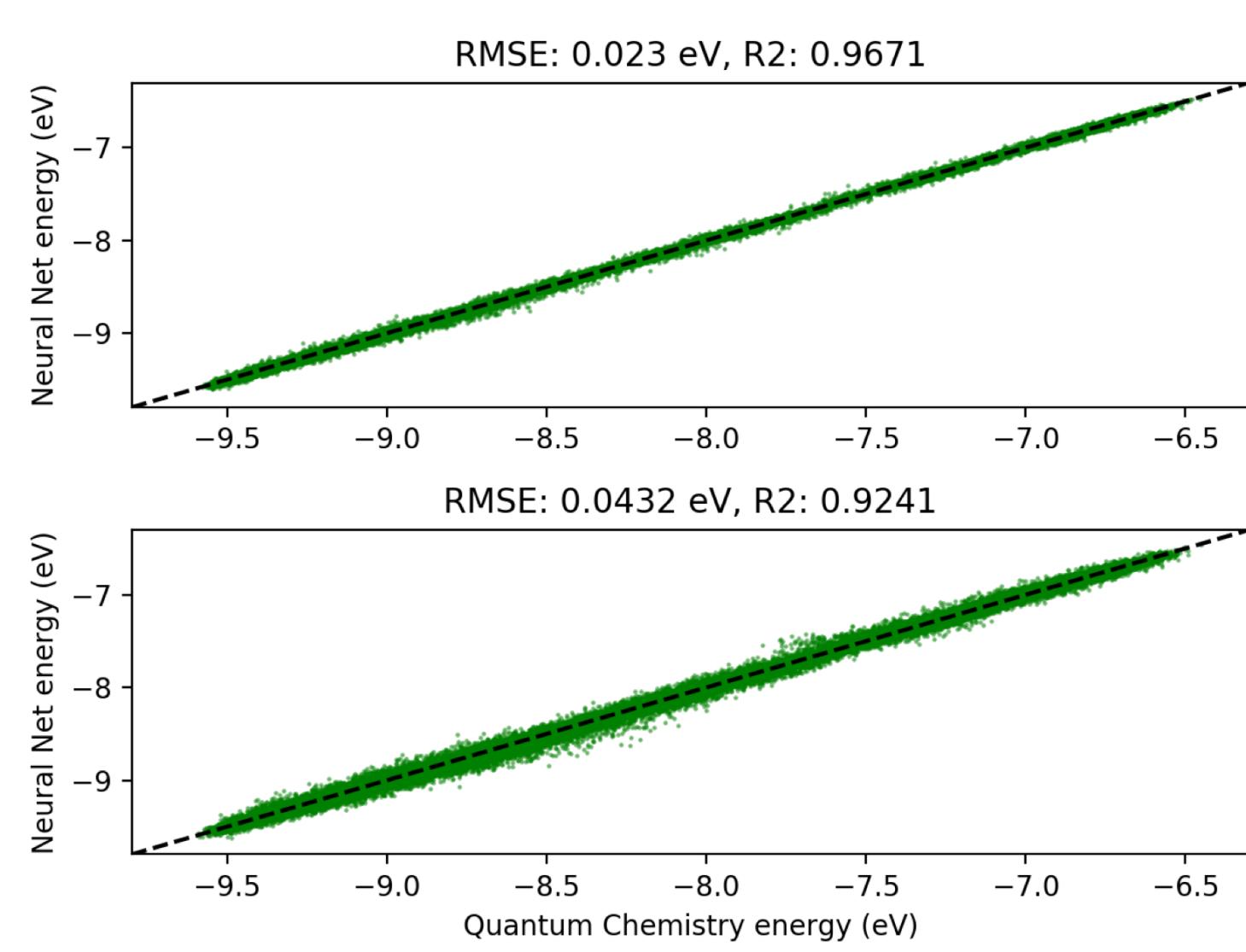
TB Model

- TB Model**
- RMSE = 0.15 eV
 - R² = 0.79

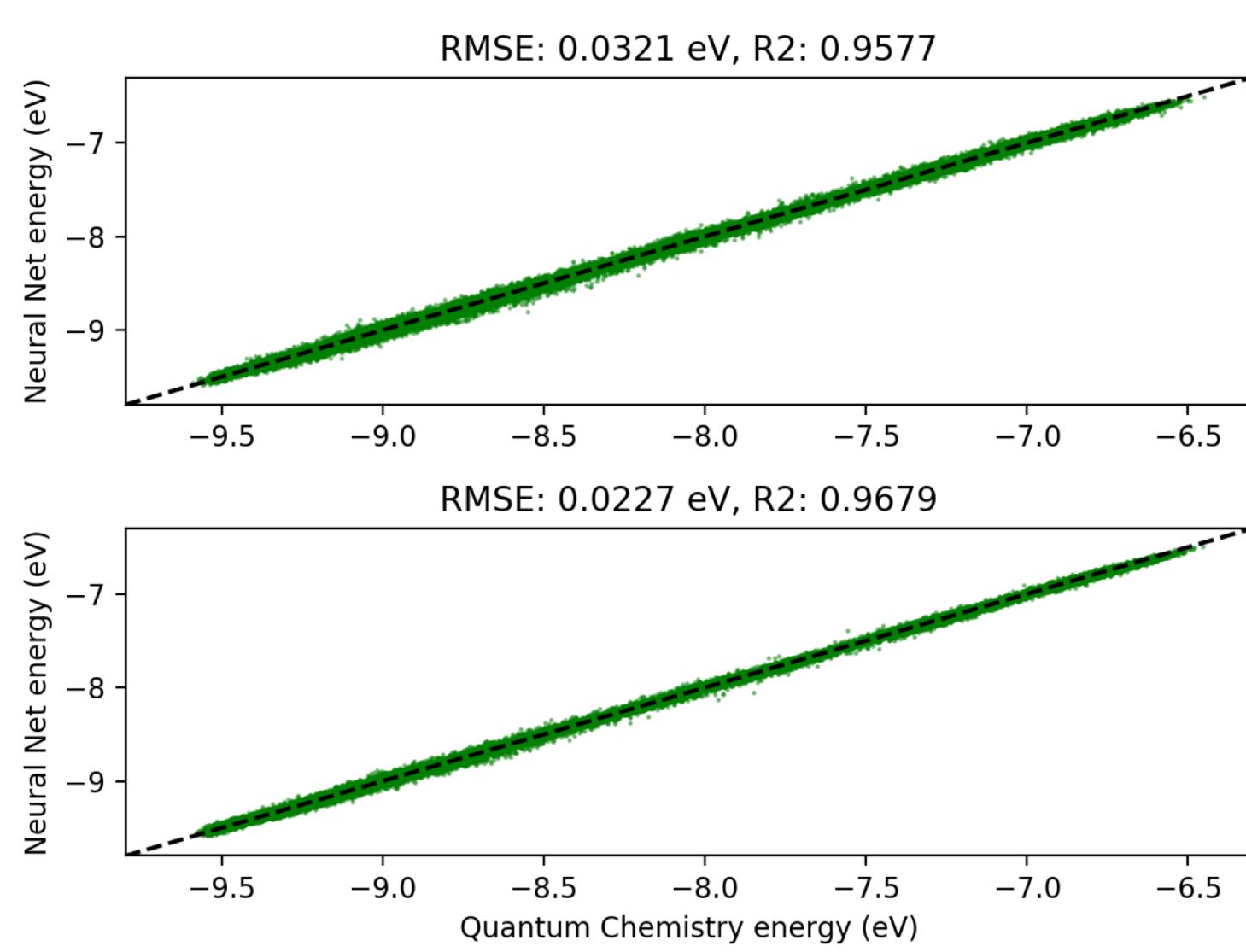
Temperature Transferability of ANN Model

Data is generated using a NVT MD simulation. How temperature transferrable is our ANN?

Trained at 300K Applied at 500K



Trained at 500K Applied at 300K

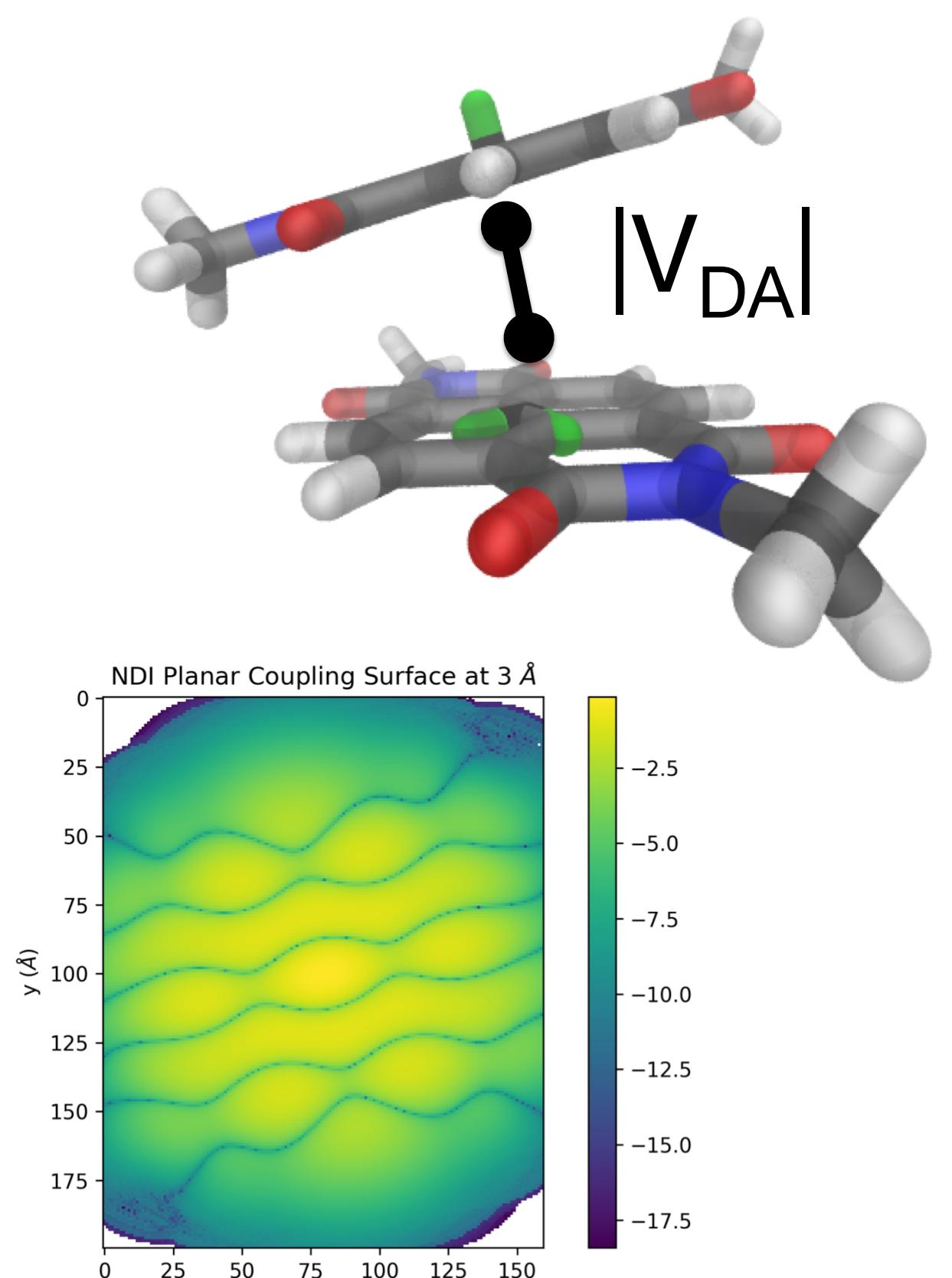
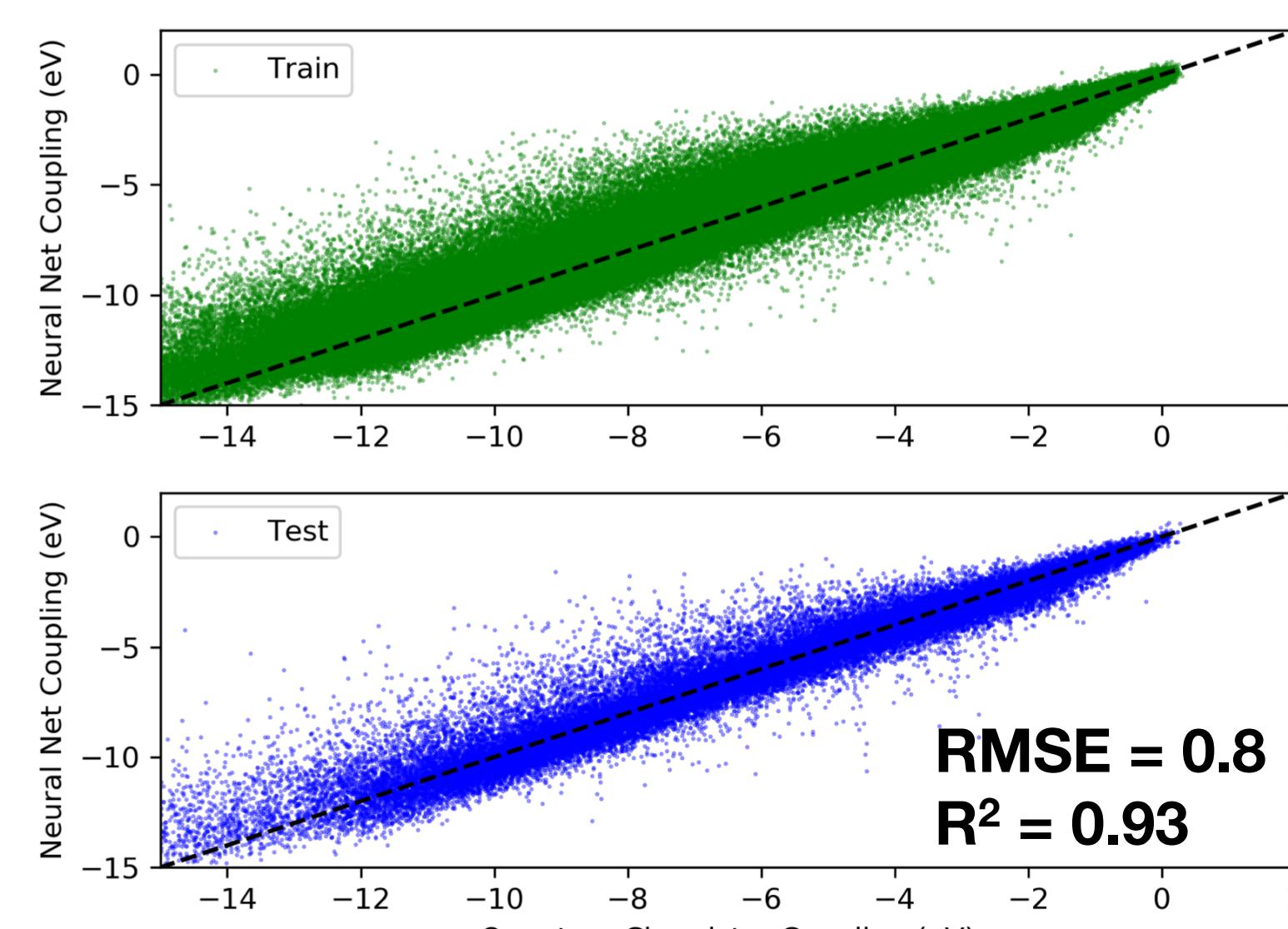


ANN is partially transferrable. A range of temperature data must be sampled to create a temperature transferrable ANN model.

Learning Dimer Electronic Couplings

As a step up in complexity, we learn the configurational dependence of the intermolecular LUMO-LUMO transfer integral between two naphthalenediimide (NDI) molecules.

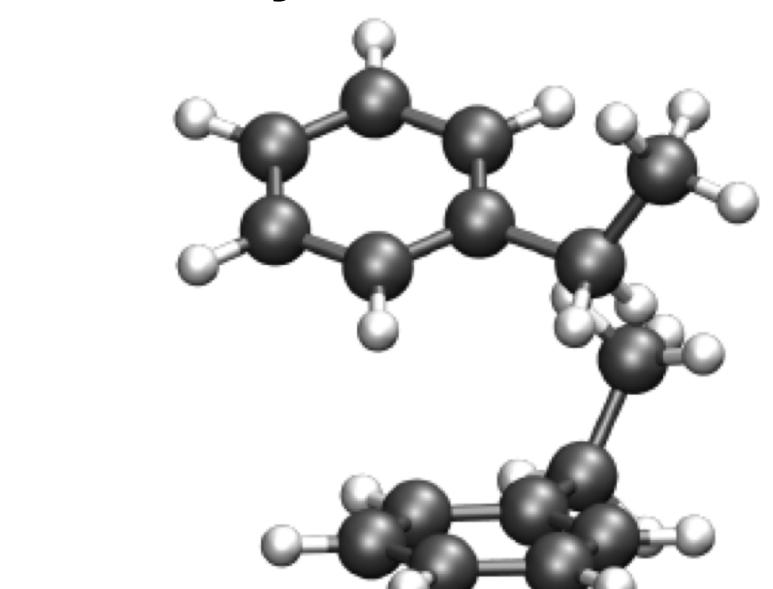
$$k = \sqrt{\frac{4\pi^3}{h^2 \lambda k_B T}} |V_{DA}|^2 \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right)$$



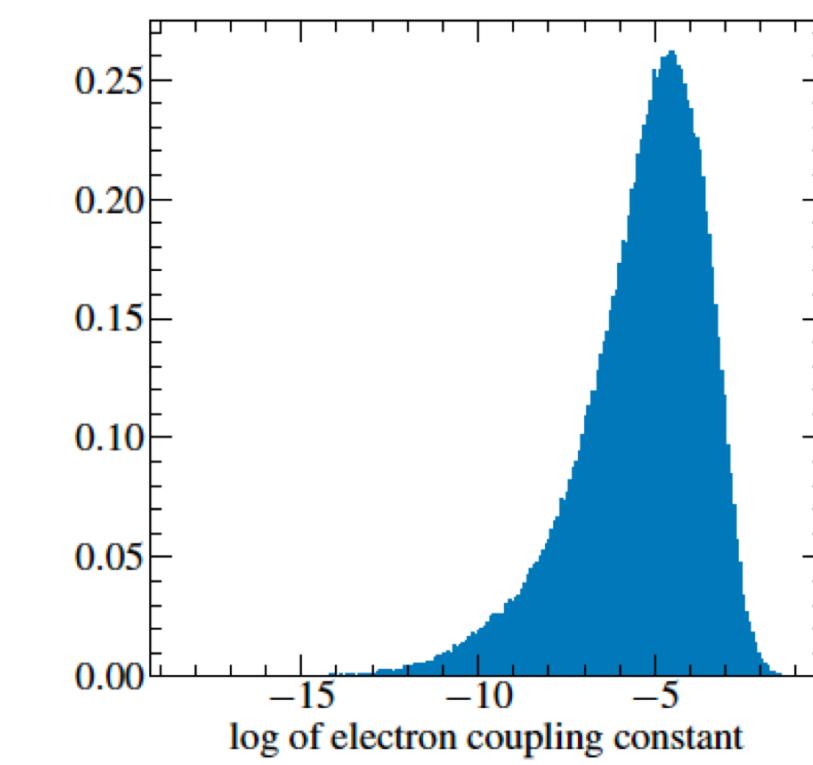
Learning Couplings on Flexible Molecules

All previous simulations utilized rigid monomers. We next release the rigidity constraint and attempt to learn the HOMO-HOMO couplings of a vapor-deposited glass of flexible ethylbenzene molecules.

Ethylbenzene Dimer



Log Distribution of Couplings



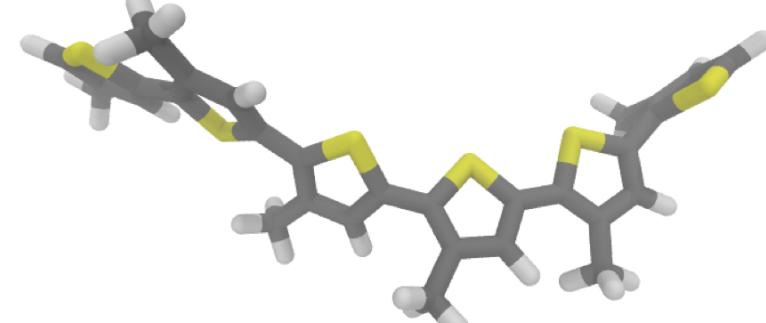
- Feature set includes the full atomic Coulomb Matrix, and a set of CG descriptors.
- ANN performance is strongly limited by molecular flexibility.

Informing Coarse-Grained Models

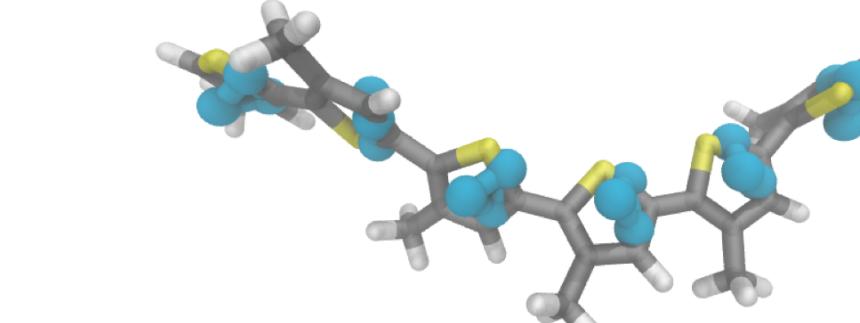
Training data using a more abstract feature set (rigid body geometries) and a deep NN always outperforms computed geometric features (bond lengths, angles, dihedrals).

This suggests the simple idea that extra CG beads, or orientational vectors, can be included in the CG description to characterize 3D orientations, allowing for mapping electronic structure to CG degrees of freedom, critically accelerating the overall workflow.

Atomistic Rep



Coarse-Grained Rep



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