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Field theoretic atomistics: Learning thermodynamic and variational surrogate to density functional theory

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Abstract

The Hohenberg-Kohn (HK) theorem—the bedrock of density functional theory (DFT)—establishes a universal map from the external potential to the energy. It also relates the electron density and atomic forces to the variation of the energy with the external potential. But the HK map is rarely utilized in atomistics, where inter-atomic potentials are defined using the molecular or crystal structure rather than the external potential. Beyond the lack of attention to the HK theorem in atomistics, a more severe difficulty is that the HK map applies only to the electronic energy, which is not thermodynamically well-defined, as the electronic energy per atom diverges in the thermodynamic limit. We alleviate this difficulty by deriving an HK-like theorem for the total energy—comprising both electronic energy and nuclear-nuclear repulsion—in terms of auxiliary fields. We refer to this reformulation as the *field theoretic atomistics* (FTA) map. We machine learn the FTA map using an equivariant architecture. We

obtain both forces and electron density from the variation of the FTA map with respect to the auxiliary fields, that are exact relations. Our models attain good accuracy across diverse benchmarks and compete with state-of-the-art machine learned interatomic potentials (MLIPs). Notably, through electron density, we predict accurate dipole and quadrupole moments, otherwise nontrivial for interatomic potentials. Our formulation paves the way for a scalable electronic structure surrogate to DFT.

1 Introduction

Density functional theory (DFT) [1, 2, 3, 4] and interatomic potentials (IP) [5, 6, 7, 8, 9, 10, 11] have long remained indispensable tools in computational chemistry and materials science. Although both are intricately tied to the principles of quantum mechanics, DFT and IPs have evolved as two disparate methods. DFT is applied to understand the electron-electron and electron-nuclear interactions and IPs are used to define the potential energy surface (PES) for the atoms in terms of the molecular or crystal structure. Thus, while DFT is an inherently electronic structure method, the IPs are considered to be atomistic models without any knowledge or predictability of the electronic structure. This distinction, however, is artificial, as theoretically both DFT and IPs are conjoined by the Hohenberg-Kohn (HK) theorem [1]. The HK theorem establishes the groundstate electronic energy (E_e) as a universal functional of the external potential, denoted as $v_{\text{ext}}(\mathbf{r})$. That is, as per the HK theorem, $E_e \equiv E_e[v_{\text{ext}}]$. The external potential can represent the nuclear potential and/or any externally applied potential. The PES (E) can be obtained by adding the nuclear-nuclear repulsion energy (E_{ZZ}) to E_e . The HK theorem also proves a one-to-one map between the groundstate electron density ($\rho_g(\mathbf{r})$) and the external potential, given as $\rho_g(\mathbf{r}) = \frac{\delta E_e[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})}$. As a result, defining the PES in terms of v_{ext} , as opposed to the molecular or crystal structure, permits the evaluation of the density, through the variation of E_e with v_{ext} . In other words, the HK theorem allows us to model IPs that, in principle, can be at the same footing as DFT and provide insights into the electronic structure of matter.

This prowess of the HK theorem has seldom been utilized while designing IPs.

Beyond the lack of attention to the HK theorem in atomistics, there lies a more fundamental challenge. The HK theorem applies only to the electronic energy (E_e), which is not a thermodynamically consistent quantity, i.e., the electronic energy per atom diverges in the thermodynamic limit (when the number of atoms tend to infinity). Thus, modeling the electronic energy directly is not a well-posed problem. The only two prior efforts [12, 13] to pioneer the idea of using the HK theorem for atomistics have attempted to directly use the HK map to machine learn the electronic energy (E_e), which is not thermodynamically consistent. Further, they do not satisfy the variational consistency of the density and forces being related to the variation of E_e with respect to $v_{\text{ext}}(\mathbf{r})$: $\rho_g(\mathbf{r}) = \frac{\delta E_e[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})}$ and $\mathbf{f}_I = \int \rho_g(\mathbf{r}) \nabla_{\mathbf{R}_I} v_{\text{ext}}(\mathbf{r}) d\mathbf{r}$. This is a subtle aspect linked to the fact that the previous efforts model $E_e[v_{\text{ext}}]$ as a two-step map, first from $v_{\text{ext}}(\mathbf{r})$ to $\rho_g(\mathbf{r})$ (or $\gamma(\mathbf{r}, \mathbf{r}')$, the one-electron reduced density matrix (1RDM)) and then from ρ (or γ) to E_e , which breaks the variational consistency. Thus, a theoretically well-posed approach to use the HK theorem in atomistics is lacking.

In this work, we alleviate the difficulties with using the HK theorem for atomistics by deriving an HK-like theorem for the PES (E , also called the total groundstate energy). The total groundstate energy, being the sum of electronic energy and the nuclear-nuclear repulsion, is thermodynamically consistent. We do so by introducing two auxiliary fields that are closely related to $v_{\text{ext}}(\mathbf{r})$. We term this reformulation as the *field theoretic atomistics* (FTA), to explicitly distinguish it from IPs. To elaborate, the FTA map inherently deals with fields as its inputs and outputs (e.g., $v_{\text{ext}}(\mathbf{r})$ and $\rho_g(\mathbf{r})$), whereas IPs deal with structure as input and scalars (energy, forces) as outputs. The FTA approach offers several key advantages over IPs. First, it handles both nuclear potential and any externally applied potential (e.g., from an electric field) on equal footing. Second, it does not require any chemical species embedding, and thereby, avoids any combinatorial complexities that arise in IPs while dealing with multiple chemical species. We machine learn the FTA map in terms of features of the auxiliary fields. We demonstrate that, for widely used benchmarks, our FTA models compete with state-of-the-art machine-learning IPs (MLIPs) in energy and force, while simultaneously predicting accurate densities and their dipole and quadrupole

80 moments. This highlights the promise of the FTA models to serve as an accurate and scalable surrogate to DFT.

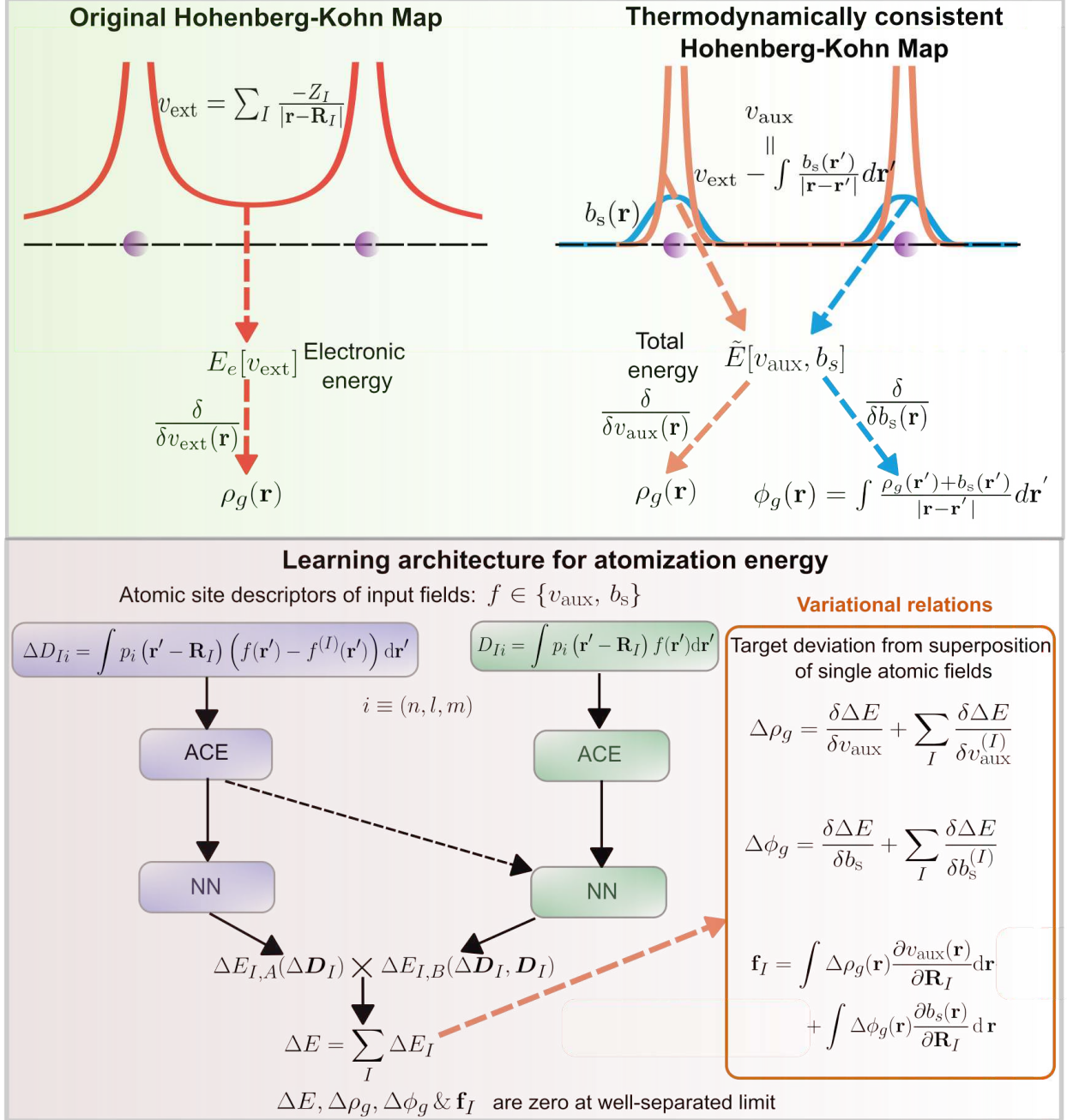


Figure 1: Schematic of field theoretic atomistics (FTA) approach. The original Hohenberg-Kohn (HK) map pertains to the electronic energy, which does not satisfy the thermodynamic limit. We reformulate the HK map for the total energy, in terms of auxiliary fields ($v_{\text{aux}}(\mathbf{r})$, $b_s(\mathbf{r})$), to ensure the thermodynamic limit. The variation of the energy with the auxiliary fields provide the ground-state density and electrostatic potential. We machine-learn the FTA energy map using a combination of atomic cluster expansion [14] and neural networks.

2 Results

Hohenberg-Kohn theorem to Field Theoretic Atomistics

We begin with the variational problem in DFT, where given an external potential ($v_{\text{ext}}(\mathbf{r})$) and number of electrons (N_e), the groundstate electronic energy E_e can be obtained as

$$E_e[v_{\text{ext}}, N_e] = \min_{\rho \in A_N} \left(F[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} \right), \quad \text{s.t.} \quad \int \rho(\mathbf{r}) = N_e, \quad (1)$$

where A_N denotes the space of N -representable densities (i.e., densities corresponding to an antisymmetric wavefunction). $F[\rho]$ is a universal density functional, comprising of three components, $F[\rho] = T_s[\rho] + E_{\text{xc}}[\rho] + E_{\text{H}}[\rho]$, where $T_s[\rho]$, $E_{\text{xc}}[\rho]$, and $E_{\text{H}}[\rho]$ are the non-interacting kinetic energy, exchange-correlation energy, and Hartree energy, respectively. While T_s and E_{xc} are known to be universal functionals of ρ , their forms are unknown, thereby requiring approximations. The Hartree energy, which represents the classical electrostatics interaction between electrons, is given as $E_{\text{H}}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$. Typically, $v_{\text{ext}}(\mathbf{r})$ is the nuclear potential: $v_{\text{ext}}(\mathbf{r}) = -\sum_I^{N_a} \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}$, where N_a is the number of atoms and Z_I and $\mathbf{R}_I$ are the atomic number and position of the I -th atom. The PES (or total groundstate energy) includes the nuclear-nuclear repulsion: $E = E_e[v_{\text{ext}}, N_e] + E_{\text{ZZ}}$, where $E_{\text{ZZ}} = \frac{1}{2} \sum_I \sum_{J \neq I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$. We note that while E satisfies the thermodynamic limit, E_e and E_{ZZ} individually do not. E_e contains $E_{\text{H}}[\rho]$ and $\int \rho v_{\text{ext}} d\mathbf{r}$, where both being electrostatic interactions grow quadratically with number of atoms, and hence, E_e does not satisfy the thermodynamic limit. Similar arguments apply to the violation of thermodynamic limit for E_{ZZ} . Thus, for thermodynamic consistency, we need to reformulate the variational problem in Eq. (1) in terms of E . To do so, we introduce a superposition of non-overlapping auxiliary charges on each nucleus: $b_{\text{s}}(\mathbf{r}) = \sum_I b_I(\mathbf{r})$, where $b_I(\mathbf{r}) = -Z_I b_{\text{u}}(|\mathbf{r} - \mathbf{R}_I|; r_c)$. Here $b_{\text{u}}(r, r_c)$ is a compactly supported positive unit charge distribution with a cutoff radius of r_c (refer

to Sec. S3 in the SI for the form of b_u). The r_c satisfies $2r_c < \min_{IJ} |\mathbf{R}_I - \mathbf{R}_J|$ to ensure b_I 's do not overlap. It is straightforward to show that $E_{zz} = \frac{1}{2} \sum_I \sum_{J \neq I} \int \int \frac{b_I(\mathbf{r}) b_J(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$. We also define an auxiliary potential $v_{\text{aux}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) - v_s(\mathbf{r})$, where $v_s(\mathbf{r}) = \int \frac{b_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$. We can define the PES as

$$E[v_{\text{aux}}, b_s, N_e] = \min_{\rho \in A_N} \left(\tilde{F}[\rho] + E_H[\rho] + \int \rho(\mathbf{r}) v_{\text{aux}}(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} \right) + E_{zz}, \quad \text{s.t.} \quad \int \rho(\mathbf{r}) d\mathbf{r} = N_e, \quad (2)$$

where $\tilde{F}[\rho] = T_s[\rho] + E_{\text{xc}}[\rho]$. We note that $E_H[\rho] + \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} + E_{zz}$ represents electrostatic energy of $\rho + b_s$, which can be reformulated as the following variational problem [15]:

$$E_H[\rho] + \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r} + E_{zz} = \max_{\phi} \underbrace{\left(-\frac{1}{8\pi} \int |\nabla \phi(\mathbf{r})|^2 d\mathbf{r} + \int (\rho(\mathbf{r}) + b_s(\mathbf{r})) \phi(\mathbf{r}) d\mathbf{r} \right)}_{P[\phi, \rho, b_s]} - E_{\text{self}}, \quad (3)$$

The maximizer of the functional $P[\phi, \rho, b_s]$, say $\phi^*(\mathbf{r})$, corresponds to the electrostatic potential of $\rho + b_s$, given by $\phi^*(\mathbf{r}) = \int \frac{\rho(\mathbf{r}') + b_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$. Further, the maxima of $P[\phi, \rho, b_s]$ corresponds to the electrostatic energy of $\rho + b_s$ along with the self-interaction of b_I 's. That is, $P[\phi^*, \rho, b_s] = \frac{1}{2} \int \int \frac{(\rho(\mathbf{r}) + b_s(\mathbf{r}))(\rho(\mathbf{r}') + b_s(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$. To recover the correct electrostatic energy, we subtract out from $P[\phi^*, \rho, b_s]$ the spurious self-interaction of b_I 's, given by $E_{\text{self}} = \sum_I \int \int \frac{b_I(\mathbf{r}) b_I(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$. Now, combining Eq. (2) and Eq. (3), we get the following saddle point (min-max) problem,

$$\tilde{E}[v_{\text{aux}}, b_s, N_e] = \min_{\rho \in A_N} \max_{\phi} \left(\tilde{F}[\rho] + \int \rho(\mathbf{r}) v_{\text{aux}}(\mathbf{r}) d\mathbf{r} + P[\phi, \rho, b_s] \right), \quad \text{s.t.} \quad \int \rho(\mathbf{r}) d\mathbf{r} = N_e, \quad (4)$$

where $\tilde{E}[v_{\text{aux}}, b_s, N_e] = E[v_{\text{aux}}, b_s, N_e] + E_{\text{self}}$. We note that E_{self} is independent of the minimization over ρ and ϕ , and is determined only by the form of the unit charge $b_u(r, r_c)$. Thus, given a model for $\tilde{E}[v_{\text{aux}}, b_s, N_e]$, the PES (E) can be trivially obtained by subtracting out the E_{self} . One can recast Eq. (4) as an unconstrained optimization by introducing a Lagrange multiplier (μ) for the constraint $\int \rho(\mathbf{r}) d\mathbf{r} = N_e$. Solving the saddle point problem gives the groundstate solution, which we denote as ρ_g , ϕ_g , and μ_g . So far, we have replaced

the canonical variational problem in DFT over E_e (which does not satisfy the thermodynamic limit) with a saddle point problem over E (which satisfies the thermodynamic limit). This saddle point reformulation of DFT, or variations of this, has been employed in various real-space DFT methods [16, 17, 18, 19, 20, 21, 22, 23] as a means to have a unified framework for both finite (molecules, clusters) and extended systems (solids).

Here, we show that the above saddle point reformulation results in various bijective maps and variational relations similar to the HK theorem. These bijective maps and variational relations are (refer to Sec. S1 in the SI for the proof):

$$(\rho_g(\mathbf{r}), \mu_g) \leftrightarrow (v_{\text{aux}}(\mathbf{r}), N_e); \text{ and } \phi_g(\mathbf{r}) \leftrightarrow b_s(\mathbf{r}) \quad (5)$$

$$\frac{\delta \tilde{E}[v_{\text{aux}}, b_s, N_e]}{\delta v_{\text{aux}}(\mathbf{r})} = \rho_g(\mathbf{r}); \quad \frac{\delta \tilde{E}[v_{\text{aux}}, b_s, N_e]}{\delta b_s(\mathbf{r})} = \phi_g(\mathbf{r}); \text{ and } \frac{\partial \tilde{E}[v_{\text{aux}}, b_s, N_e]}{\partial N_e} = \mu_g. \quad (6)$$

Using the above variational relations, atomic force $\mathbf{f}_I$ evaluates to

$$\mathbf{f}_I = \int \rho_g(\mathbf{r}) \frac{\partial v_{\text{aux}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} + \int \phi_g \frac{\partial b_s(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r}. \quad (7)$$

The above are the key results that lay the foundation of our FTA models. We remark that, the above FTA formulation does not assume any specific form for the universal density functional $F[\rho]$, and hence, is valid when used with any approximate XC functional in DFT. More importantly, the FTA formulation can be applied to any other electronic structure method (e.g., configuration interaction (CI), coupled-cluster (CC), quantum Monte Carlo (QMC), etc.), as different electronic structure method would merely alter the form of $F[\rho]$. Equations (4)-(6) allow us to machine learn $\tilde{E}$, thereby allowing for thermodynamically and variationally consistent density and forces. Beyond serving as exact theoretical conditions, the variational consistency leads to important symmetry relations. A key physically relevant relation is that ρ_g and ϕ_g transform covariantly under energy invariant transformations of the input fields (v_{aux} and b_s) in the $\tilde{E}$ functional. To elaborate, let T denote the representation of the Euclidean group (rotations, translations, inversions, reflections) [24] that transforms v_{aux} as $v'_{\text{aux}} = Tv_{\text{aux}}$ and b_s as $b'_s = Tb_s$. Using the energy invariance we can write

145 $\tilde{E}[v'_{\text{aux}}, b'_s, N_e] = \tilde{E}[v_{\text{aux}}, b_s, N_e]$, and subsequently analyzing the behavior of the differential
 146 on both sides with respect to v_{aux} we obtain the covariant transformation of ρ_g :

$$T^\dagger \rho_g[Tv_{\text{aux}}, Tb_s] = \rho_g[v_{\text{aux}}, b_s], \quad T^\dagger \phi_g[Tv_{\text{aux}}, Tb_s] = \phi_g[v_{\text{aux}}, b_s], \quad (8)$$

147 where $T^\dagger$ denotes the adjoint of T . We refer to Sec. 1.3 in the SI for the derivation of the
 148 above relation. We note that when T is an unitary operator ($T = (T^\dagger)^{-1}$), such as rotation,
 149 the transformation in Eq. 8 simplifies to an equivariance

$$\rho_g[Tv_{\text{aux}}, Tb_s] = T\rho_g[v_{\text{aux}}, b_s], \quad \phi_g[Tv_{\text{aux}}, Tb_s] = T\phi_g[v_{\text{aux}}, b_s]. \quad (9)$$

150 In other words, applying the group operation to the inputs (v_{aux}, b_s) transforms the output
 151 (ρ_g, ϕ_g) in a similar way. Another symmetry relation that manifests from ρ_g and ϕ_g being
 152 functional derivatives of an energy functional is the mixed derivative condition:

$$\frac{\delta \rho_g(\mathbf{r})}{\delta v_{\text{aux}}(\mathbf{r}')} = \frac{\delta \rho_g(\mathbf{r}')}{\delta v_{\text{aux}}(\mathbf{r})}, \quad \frac{\delta \phi_g(\mathbf{r})}{\delta b_s(\mathbf{r}')} = \frac{\delta \phi_g(\mathbf{r}')}{\delta b_s(\mathbf{r})}, \quad (10)$$

153 which can be easily verified by substitution of the variational relations for ρ_g and ϕ_g (cf.
 154 Eq. 6) in the above expressions. We remark that machine-learning frameworks have been
 155 developed for direct prediction of ρ_g from atomic-structure that satisfy the covariant trans-
 156 formation condition [25, 26], but they do not satisfy the mixed derivative condition. The
 157 advantage of ρ_g prediction in the FTA approach is that the mixed derivative condition is
 158 satisfied independent of the learning architecture, and further the covariant transformation
 159 condition requires only the energy to be invariant with respect to the Euclidean group trans-
 160 formation.

161 Modeling $\tilde{E}$ that can accurately predict ρ_g and ϕ_g (via Eq. 6) requires learning the sharp
 162 features in the density and the electrostatic potential, especially near the nuclei. In contrast,
 163 the difference of ρ_g (ϕ_g) from the superposition of atomic densities (atomic electrostatic
 164 potentials) is a much smoother field, and hence, more amenable to learning. Further, much
 165 of chemical bonding is mediated by these differences in densities and electrostatic potentials.

We, therefore, extend the above analysis to the atomization energy

$$\Delta E[v_{\text{aux}}, b_{\text{s}}, N_e, \{v_{\text{aux}}^{(I)}\}, \{b_{\text{s}}^{(I)}\}, \{N_e^{(I)}\}] = \tilde{E}[v_{\text{aux}}, b_{\text{s}}, N_e] - \sum_I \tilde{E}[v_{\text{aux}}^{(I)}, b_{\text{s}}^{(I)}, N_e^{(I)}], \quad (11)$$

where $v_{\text{aux}}^{(I)}$ and $b_{\text{s}}^{(I)}$ are the v_{aux} and b_{s} for the I -th isolated atom; and $N_e^{(I)} = Z_I$ (neutral atom). We emphasize that, in the above, although v_{aux} has an apparent dependence on $v_{\text{aux}}^{(I)}$, both are independent fields, as they are inputs to different energy functionals: v_{aux} to the molecular energy and $v_{\text{aux}}^{(I)}$ to the isolated atom energy for the I -th atom. Similarly, b_{s} and $b_{\text{s}}^{(I)}$ are independent fields. Using Eq. 6, it is straightforward to note that

$$\frac{\delta \Delta E}{\delta v_{\text{aux}}} + \sum_I \frac{\delta \Delta E}{\delta v_{\text{aux}}^{(I)}} = \Delta \rho_g; \quad \frac{\delta \Delta E}{\delta b_{\text{s}}} + \sum_I \frac{\delta \Delta E}{\delta b_{\text{s}}^{(I)}} = \Delta \phi_g; \quad \text{and} \quad \frac{\partial \Delta E}{\partial N_e} = \mu_g. \quad (12)$$

In the above, $\Delta \rho_g$ is the difference between ρ_g and the superposition of atomic densities: $\Delta \rho_g = \rho_g - \sum_I \rho_g^{(I)}$, with $\rho_g^{(I)}$ being the groundstate density of the I -th isolated atom. $\Delta \phi_g$ is defined similarly. As is customary in atomistic models, we invoke the atomic partitioning *ansatz* to write $\Delta E = \sum_I \Delta E_I$, where ΔE_I denotes the contribution from I -th atom. Theoretically, ΔE_I depends on all the inputs to ΔE , namely, the total quantities ($v_{\text{aux}}, b_{\text{s}}, N_e$) and the set of isolated atom quantities ($\{v_{\text{aux}}^{(I)}\}, \{b_{\text{s}}^{(I)}\}$, and $\{N_e^{(I)}\}$). However, as a simplification, we approximate ΔE_I to depend only the total quantities ($v_{\text{aux}}, b_{\text{s}}, N_e$) and the self-quantities ($v_{\text{aux}}^{(I)}, b_{\text{s}}^{(I)}, N_e^{(I)}$), i.e., we ignore the self-quantities from other atoms. This is not merely a matter of convenience, but motivated by the fact that the relevant chemistry around a nuclei can be modeled through the change in the local environment, which can be encapsulated through the total- and the self-quantities. So far, the FTA formulation along with the resulting atomization energy model of Eq. 11 has been presented in the context of local external potential, which typically pertains to all-electron DFT. However, the bulk of DFT calculations use the pseudopotential approximation, especially nonlocal pseudopotentials, for numerical efficiency. The above atomization energy model with its variational relations to $\Delta \rho_g$ and $\Delta \phi_g$ permits the use of reference data from pseudopotential DFT calculations. This is because both $\Delta \rho_g$ and $\Delta \phi_g$ from pseudopotential calculations are expected to be close to their counterparts from all-electron DFT. Thus, one can use the above atomiza-

tion energy formulation with all-electron v_{aux} and b_{s} but with reference $\Delta\rho_g$ and $\Delta\phi_g$ from pseudopotential calculations. In this work, we use all-electron DFT data as our reference.

Learning Field Theoretic Atomistics models

We model ΔE_I in terms of the atom-centered descriptors of $v_{\text{aux}}, b_{\text{s}}, v_{\text{aux}}^{(I)}, b_{\text{s}}^{(I)}$. As a first attempt at FTA, we restrict our models to only charge-neutral systems. For charge-neutral systems the information of N_e and $N_e^{(I)}$ is implicitly contained in b_{s} and $b_{\text{s}}^{(I)}$, as $\int b_{\text{s}}(\mathbf{r}) d\mathbf{r} = N_e$ and $\int b_{\text{s}}^{(I)}(\mathbf{r}) d\mathbf{r} = N_e^{(I)}$. Thus, in our FTA models, we drop the explicit dependence on N_e and $N_e^{(I)}$. We model $\Delta E_I[v_{\text{aux}}, b_{\text{s}}, v_{\text{aux}}^{(I)}, b_{\text{s}}^{(I)}, N_e^{(I)}] \approx \Delta E_I[\mathbf{x}_I, \mathbf{y}_I, \mathbf{x}_I^{\text{self}}, \mathbf{y}_I^{\text{self}}]$, where $\mathbf{x}_I, \mathbf{y}_I, \mathbf{x}_I^{\text{self}}, \mathbf{y}_I^{\text{self}}$ are the vectors containing the descriptors of $v_{\text{aux}}, b_{\text{s}}, v_{\text{aux}}^{(I)}, b_{\text{s}}^{(I)}$, given as

$$\begin{aligned} x_{i,I} &= \int u_i(\mathbf{r} - \mathbf{R}_I) v_{\text{aux}}(\mathbf{r}) d\mathbf{r}, & x_{i,I}^{\text{self}} &= \int u_i(\mathbf{r} - \mathbf{R}_I) v_{\text{aux}}^{(I)}(\mathbf{r}) d\mathbf{r}, \\ y_{i,I} &= \int w_i(\mathbf{r} - \mathbf{R}_I) b_{\text{s}}(\mathbf{r}) d\mathbf{r}, & y_{i,I}^{\text{self}} &= \int w_i(\mathbf{r} - \mathbf{R}_I) b_{\text{s}}^{(I)}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (13)$$

In the above, $u_i(\mathbf{r})$'s are probe functions for v_{aux} and $v_{\text{aux}}^{(I)}$; and $w_i(\mathbf{r})$'s are the probe functions for b_{s} and $b_{\text{s}}^{(I)}$. We consider u_i and w_i that take the form of atomic orbital:

$$u_i(\mathbf{r}) = f_n(r) \mathcal{Y}_{lm}(\theta, \phi), \quad w_i(\mathbf{r}) = g_n(r) \mathcal{Y}_{lm}(\theta, \phi), \quad (14)$$

where f_n and g_n are compactly supported radial functions; $\mathcal{Y}_{lm}$ is the real form spherical harmonic with angular momentum l and magnetic quantum number m ; r , θ , and ϕ denote the radial distance, polar angle and azimuthal angle of $\mathbf{r}$ from the origin, respectively; and the index $i \equiv (n, l, m)$. Writing ΔE_I in terms of the above descriptors, we have

$$\Delta E_I[v_{\text{aux}}, b_{\text{s}}, v_{\text{aux}}^{(I)}, b_{\text{s}}^{(I)}] \approx \Delta E_I[\mathbf{x}_I, \mathbf{y}_I, \mathbf{x}_I^{\text{self}}, \mathbf{y}_I^{\text{self}}], \quad (15)$$

where $\mathbf{x}_I$ is the vector containing $x_{i,I}$ (similar definitions hold for $\mathbf{x}_I^{\text{self}}$, $\mathbf{y}_I$, and $\mathbf{y}_I^{\text{self}}$). Using Eq. 12, the model $\Delta\rho_g$ and $\Delta\phi_g$ takes the form

$$\Delta\rho_g(\mathbf{r}) = \sum_I \left(\frac{\delta\Delta E_I}{\delta v_{\text{aux}}(\mathbf{r})} + \frac{\delta\Delta E_I}{\delta v_{\text{aux}}^{(I)}(\mathbf{r})} \right) = \sum_I \sum_i \left(\frac{\partial\Delta E_I}{\partial x_{i,I}} + \frac{\partial\Delta E_I}{\partial x_{i,I}^{\text{self}}} \right) u_i(\mathbf{r} - \mathbf{R}_I), \quad (16)$$

$$\Delta\phi_g(\mathbf{r}) = \sum_I \left(\frac{\delta\Delta E_I}{\delta b_s(\mathbf{r})} + \frac{\delta\Delta E_I}{\delta b_s^{(I)}(\mathbf{r})} \right) = \sum_I \sum_i \left(\frac{\partial\Delta E_I}{\partial y_{i,I}} + \frac{\partial\Delta E_I}{\partial y_{i,I}^{\text{self}}} \right) w_i(\mathbf{r} - \mathbf{R}_I). \quad (17)$$

In other words, $u_i(\mathbf{r} - \mathbf{R}_I)$ and $w_i(\mathbf{r} - \mathbf{R}_I)$ serve as the basis to represent $\Delta\rho_g$ and $\Delta\phi_g$, respectively. Our choice for the radial probe functions (f_n and g_n) is motivated by the above observation, i.e., they should serve as a basis for $\Delta\rho_g$ and $\Delta\phi_g$. In that light, we use a combination of short-ranged orthogonal Bessel functions and long-ranged damped-multipole functions for f_n and g_n (refer Sec. S2 in the SI for their forms). For well-separated atoms or an isolated atom, ΔE , $\Delta\rho_g$, and $\Delta\phi_g$ should all be zero. To satisfy this limit, we write ΔE_I as

$$\Delta E_I[\mathbf{x}_I, \mathbf{y}_I, \mathbf{x}_I^{\text{self}}, \mathbf{y}_I^{\text{self}}] = \Delta E_{I,A}[\Delta\mathbf{x}_I, \Delta\mathbf{y}_I] \Delta E_{I,B}[\Delta\mathbf{x}_I, \Delta\mathbf{y}_I, \mathbf{x}_I, \mathbf{y}_I], \quad (18)$$

where $\Delta\mathbf{x}_I = \mathbf{x}_I - \mathbf{x}_I^{\text{self}}$; and $\Delta\mathbf{y}_I = \mathbf{y}_I - \mathbf{y}_I^{\text{self}}$. The above form allows us to satisfy the well-separated or isolated atoms limits by ensuring that $\Delta E_{I,A}$ tends to zero when $\Delta\mathbf{x}_I$ or $\Delta\mathbf{y}_I$ tend to zero. We model both $\Delta E_{I,A}$ and $\Delta E_{I,B}$ using a combination of atomic cluster expansion (ACE) [14] and a feed-forward neural network (NN), the details of which are presented in the Methods section. We optimize the learnable parameters in our ACE and NN using the following loss function

$$\begin{aligned} \mathcal{L} = & \frac{t_E}{M} \sum_{\alpha=1}^M \left(\Delta E_{\text{ref}}^{(\alpha)} - \Delta E^{(\alpha)} \right)^2 + \frac{t_F}{M} \sum_{\alpha=1}^M \left[\sum_I \frac{1}{N_a} \left(\left\| \mathbf{f}_{I,\text{ref}}^{(\alpha)} - \mathbf{f}_I^{(\alpha)} \right\|^2 \right) \right] \\ & + \frac{t_\rho}{M} \sum_{\alpha=1}^M \left\| \Delta\rho_{g,\text{ref}}^{(\alpha)}(\mathbf{r}) - \Delta\rho_g^{(\alpha)}(\mathbf{r}) \right\|_{\text{J}}^2 + \frac{t_\phi}{M} \sum_{\alpha=1}^M \left\| \Delta\phi_{g,\text{ref}}^{(\alpha)}(\mathbf{r}) - \Delta\phi_g^{(\alpha)}(\mathbf{r}) \right\|_{\text{S}}^2, \end{aligned} \quad (19)$$

where α indexes the M training samples; t_E , t_F , t_ρ , and t_ϕ are the weights assigned to the energy, force, density, and potential loss terms; $\|\cdot\|$ is the Euclidian norm, $\|f(\mathbf{r})\|_{\text{S}} = \sqrt{\int (f(\mathbf{r}))^2 d\mathbf{r}}$ is the L_2 norm for a continuous function; and $\|f(\mathbf{r})\|_{\text{J}} = \sqrt{\int \int \frac{f(\mathbf{r})f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}$

is the Coulomb norm. The use of the Coulomb norm is motivated by the fact that the Coulomb norm assigns a higher weight on the low angular momentum (l) of the density. As a result, it nudges the model towards better dipole and quadrupole moments of the density—quantities that are important to measure the response of a system to external electric field. For efficient evaluation of the field loss terms (density and potential loss in Eq. 19), we represent the reference fields, $\Delta\rho_{g,\text{ref}}^{(\alpha)}(\mathbf{r})$ and $\Delta\phi_{g,\text{ref}}^{(\alpha)}(\mathbf{r})$ in the $u_i(\mathbf{r})$ and $w_i(\mathbf{r})$ probe function bases, respectively. Given that the predicted $\Delta\rho_g^{(\alpha)}(\mathbf{r})$ and $\Delta\phi_g^{(\alpha)}(\mathbf{r})$ can also be represented in the same probe function bases, one can greatly simplify the spatial integral in the field loss in terms of inexpensive matrix-vector products (see Sec. S4 and S5 in the SI for details).

rMD17-aspirin and 3BPA benchmarks

In this section, we assess the accuracy of the proposed FTA approach using widely used benchmark molecular datasets: the aspirin molecule from the rMD17 dataset [27], and the 3BPA dataset [28, 29] (a flexible molecule with rotatable bonds). Both the benchmark systems have multiple chemical species, and hence, a hard test for the FTA approach that bypasses explicit chemical species embedding. We demonstrate that FTA successfully learns a combined model that does well on energy, forces, electron-density and electrostatic potential predictions. We employ a learning architecture that combines ACE and NN on atom centered descriptors. Details of the datasets, learning architecture and training procedure are provided in the Methods section. We note that our focus here is a proof-of-concept demonstration of the key advantages and competence of the FTA approach. There is considerable scope for future research in applying FTA to more diverse benchmarks for molecular, surface and solid-state physics as well development of better ML architectures and training protocols that are theoretically well suited to FTA.

First, we discuss the results of FTA modeling on the rMD17-aspirin dataset. We train our FTA model on training set sizes ranging from 10 to 950 aspirin configurations, and test the predictions on a test set of 1000 aspirin configurations. Figure 2 shows the learning rate for force and the dipole moment of $\Delta\rho_g$, henceforth denoted as $\mathbf{d}^{\Delta\rho_g}$. We use two independent

training approaches, one with the field loss (density and potential loss) in the objective
 function (cf. Eq. 19) and the other without the field loss (i.e., with $t_\rho = 0$ and $t_\phi = 0$). For
 force prediction, both approaches have nearly identical behavior with a learning exponent
 of -0.41. However, for dipole moments, we observe dramatic differences between the two
 approaches. The model with the field loss has a learning exponent of -0.24 in $\mathbf{d}^{\Delta\rho_g}$, whereas
 the model without the field loss shows much larger dipole moment error and further a negative
 correlation in $\mathbf{d}^{\Delta\rho_g}$ errors with respect to training set size. We also compare the accuracy
 of $\Delta\rho_g$ and $\Delta\phi_g$ as well the first three moments of $\Delta\rho_g$, namely monopole ($m^{\Delta\rho_g}$), dipole
 ($\mathbf{d}^{\Delta\rho_g}$), and quadrupole moment ($\mathbf{q}^{\Delta\rho_g}$), in Table 1 (upper half). As expected, the model
 with field loss attains greater accuracy in $\Delta\rho_g$ and $\Delta\phi_g$ predictions than the one without
 field loss. Further, the model with field loss achieves 0.007%, 15% and 7% errors in the
 monopole, dipole and quadrupole moments respectively, whereas the corresponding metrics
 for the model without field loss are two orders of magnitude higher. This comparison of the
 two models—with and without the field loss—highlights the hidden degree of freedom in the
 PES of FTA models to predict the electron-density, that we exploit through the variational
 relations connecting the total energy to electron-density and electrostatic-potential. We
 remark that a 15% error in dipole moment is a respectable accuracy, as the errors in the
 dipole moment due to the exchange-correlation approximation inherent in DFT are known
 to be of similar magnitude (5–10% [30]). We also refer to Fig. 3, where we compare the
 iso-surfaces of $\Delta\rho_g$ prediction for a test set aspirin configuration against the reference iso-
 surfaces of $\Delta\rho_{g,\text{ref}}$ from DFT. The predicted iso-surfaces are qualitatively very close to the
 reference, and the model is able to reasonably capture the complex spatial structure of
 charge accumulation and depletion regions in the aspirin molecule [31]. We anticipate the
 seamless prediction of dipole and quadrupole moments of the electron-density in atomistics
 simulations to be hugely beneficial in computational chemistry and biological sciences, among
 other scientific domains, in providing insights into the underlying electronic-structure effects
 mediating relevant chemical and physical processes. For example, it is well understood
 that the dipole-dipole interactions between water molecules crucially governs the liquid-
 vapor phase transition and structural properties such as radial distribution functions [32].
 Further, the permanent dipoles of molecules play a key role in interactions with solvent and

membranes that govern transport and separation mechanisms relevant for drug design and nano-filtration applications [33, 34]. Molecular quadrupole moments also influence inter-molecular interactions, such as between aromatic molecules like benzene that are non-polar but with highly anisotropic electron clouds [35].

Next, in Tab. 1 (lower half), we examine the aspirin molecule error metrics in energy and forces for the FTA model trained with field loss and compare against those of state-of-the-art MLIPs. Remarkably, FTA outperforms all MLIPs considered in energy errors, achieving an MAE of 3.3 meV/atom at a small training set size of 50 configurations, that drops to 2.2 meV/atom at 950 training set size. On force MAE metrics, FTA achieves reasonable MAE errors of 42 meV/Å at 950 training set size, $\sim 2\times$ higher than ACE MLIP, the architecturally closest one. However, we will demonstrate in a subsequent out-of-distribution dihedral PES test on the 3BPA molecule that FTA is able to reproduce the reference PES quite closely inspite of the higher force error metrics compared to MLIPs. We remark that the force errors can be sensitive to the choice of the learning architecture. To clarify, our force learning exponent of -0.41 (Fig. 2), while reasonable when compared to slopes for state-of-the-art MLIPs for aspirin molecule that are between -0.4 to -0.7 (cf. Fig. 2 in Supplementary of Ref. [36]), lies on the lower end of the range. The steeper slopes are obtained with the NequIP equivariant architecture, which performs better than ACE (cf. Tab. 1). This indicates room for further improvement of the force prediction errors by developing improved architectures for FTA models. In this context, it is pertinent to mention that the completeness of the ACE expansion, a key result derived in Ref. [14], does not apply to the field theoretic map in this work, as the derivation of the completeness argument therein is based on treating the total energy of the system as a many-body functional of relative atomic positions, a discrete set of inputs unlike field inputs. Thus, an important future endeavor would be formulating a theoretically rigorous complete basis of polynomial features to approximate a field to energy map while preserving the necessary symmetries.

To demonstrate the out-of-distribution performance of the FTA models, we apply it to the 3-(benzyloxy)pyridin-2-amine (3BPA) dataset [28]. 3BPA has three consecutive rotatable bonds which leads to complex dihedral potential energy surface (PES) with several local

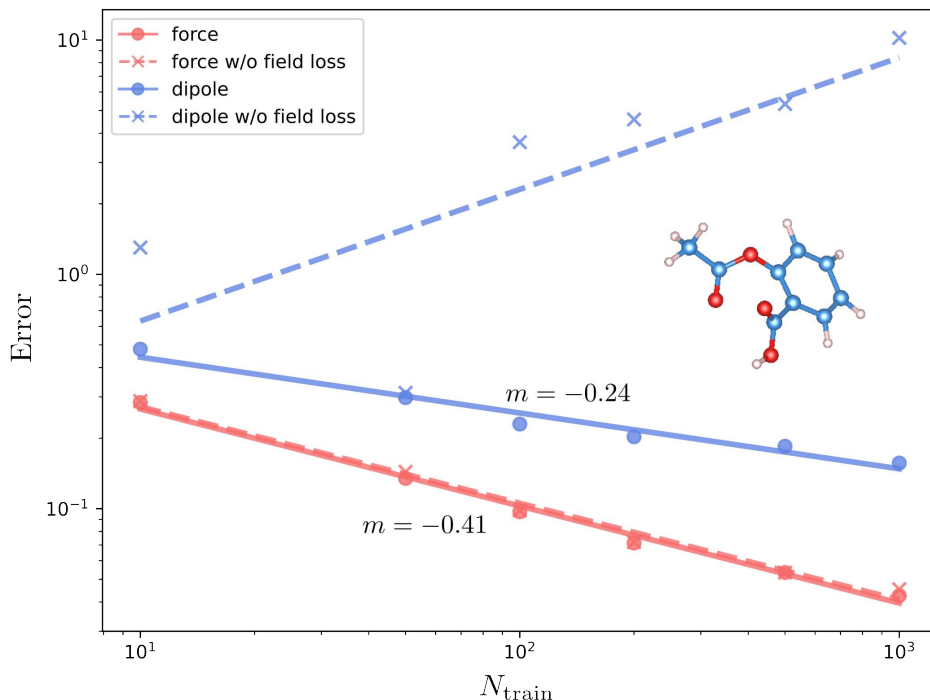


Figure 2: Learning curves of force and dipole moment for aspirin with training samples. For force, it shows the mean absolute error in $\text{meV}/\text{\AA}$. For dipole moment, it shows the mean absolute error divided by the mean of the absolute test set values (dimensionless quantity).

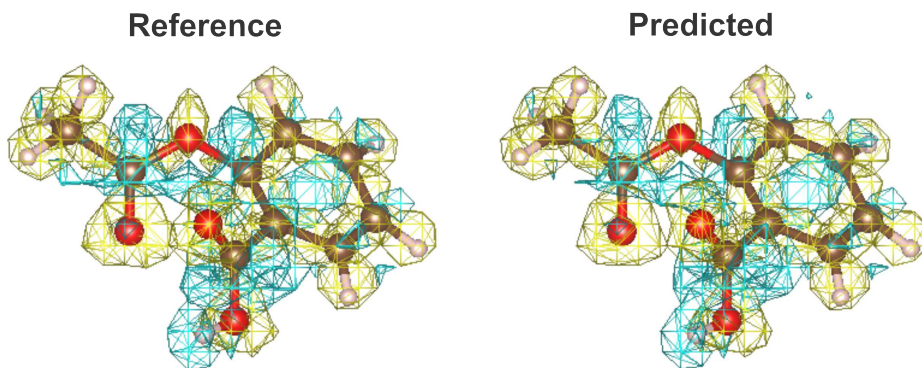


Figure 3: Comparison of the reference and predicted $\Delta\rho_g$ for a test aspirin configuration. The yellow and blue iso-surfaces represent $\Delta\rho_g$ values of 0.0095 and -0.0095 , respectively, which corresponds to 10% of the maximum value of the reference $\Delta\rho_g$. Brown, white and red colored atoms denote C, H, and O species respectively.

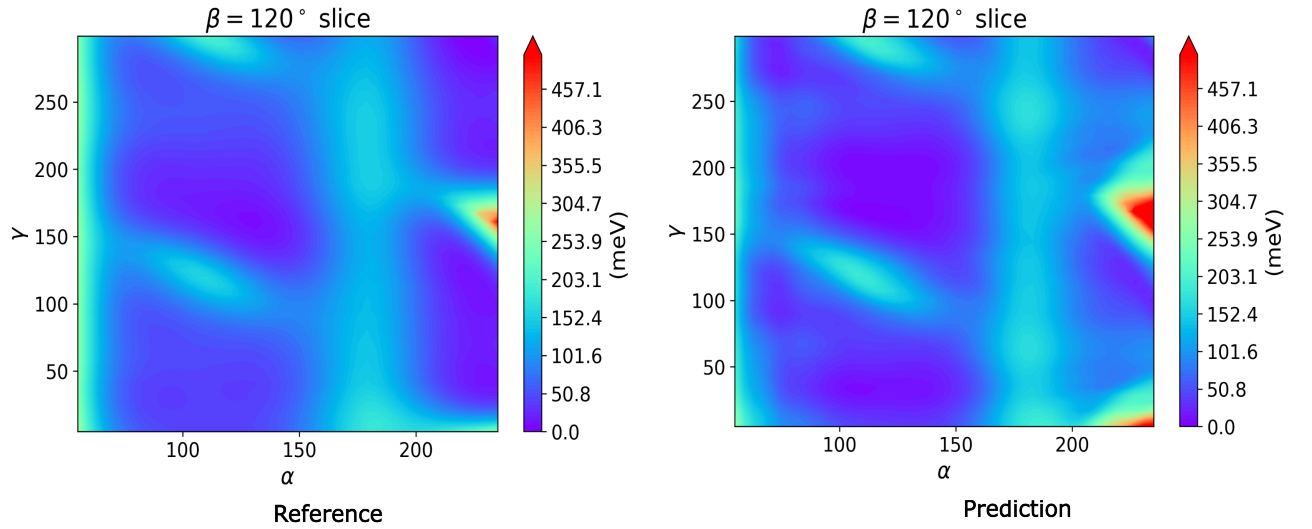


Figure 4: Comparison of the potential energy surface of 3BPA for the $\beta = 120^\circ$ dihedral slice.

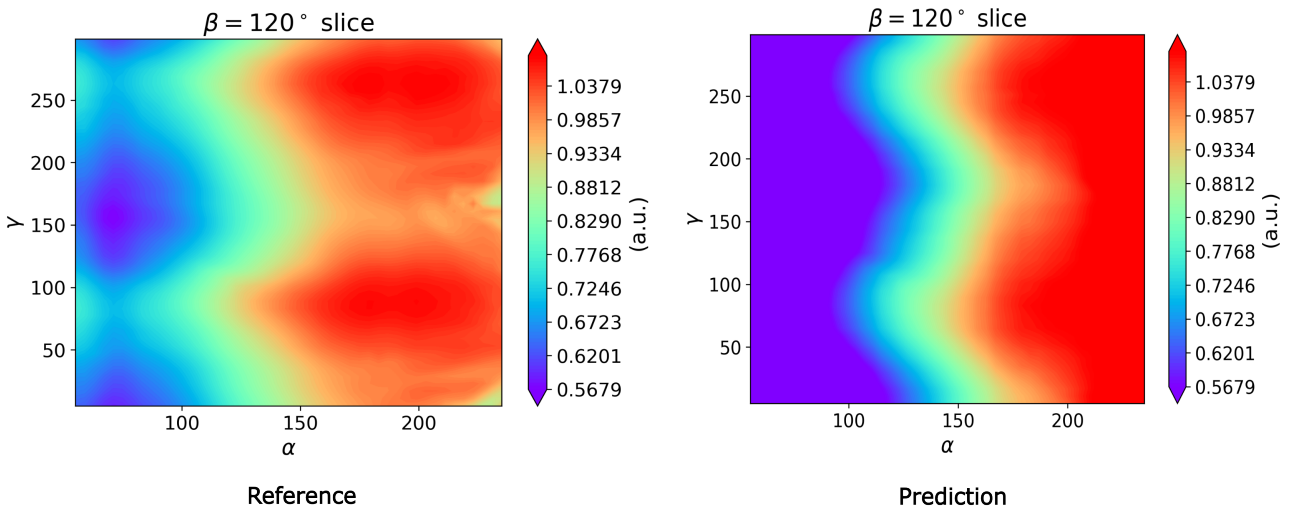


Figure 5: Comparison of the dipole moment magnitude ($|\mathbf{d}^{\Delta\rho_g}|$) of 3BPA for the $\beta = 120^\circ$ dihedral slice.

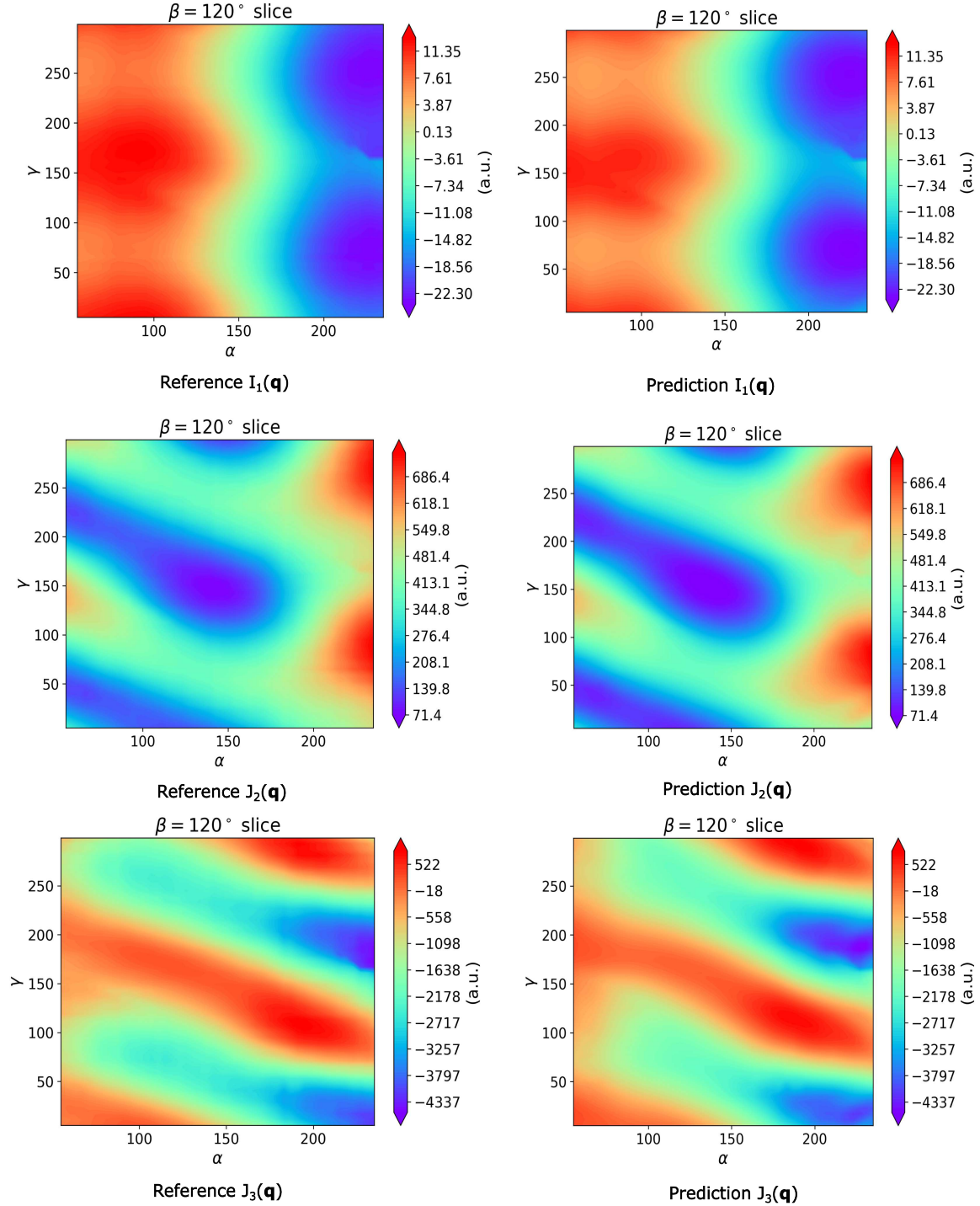


Figure 6: Comparison of the three invariants of the quadrupole moment tensor ($\mathbf{q}^{\Delta\rho_g}$) of 3BPA for the $\beta = 120^\circ$ dihedral slice. The expressions for the various invariants are given by $I_1(\mathbf{q}^{\Delta\rho_g}) = \text{Tr}(\mathbf{q}^{\Delta\rho_g})$, $J_2(\mathbf{q}^{\Delta\rho_g}) = \frac{1}{2} \|\mathbf{q}^{\Delta\rho_g} - \frac{1}{3} I_1(\mathbf{q}^{\Delta\rho_g}) \mathbf{I}\|_F^2$, and $J_3(\mathbf{q}^{\Delta\rho_g}) = \det(\mathbf{q}^{\Delta\rho_g} - \frac{1}{3} I_1(\mathbf{q}^{\Delta\rho_g}) \mathbf{I})$.

FTA ($N_{\text{train}} = 950$)												
Aspirin molecule	$e_1(\Delta\rho_g)$		$e_1(\Delta\phi_g)$		$\text{MAE}(m^{\Delta\rho_g}/N_e)$		$e_2(\mathbf{d}^{\Delta\rho_g})$		$e_2(\mathbf{q}^{\Delta\rho_g})$			
w/ field loss	1.5×10^{-3}		4.2×10^{-2}		6.8×10^{-5}		0.15		0.07			
w/o field loss	8.6×10^{-2}		9.2×10^{-2}		5.9×10^{-2}		10.2		5.2			

Aspirin molecule	$N_{\text{train}} = 950$								$N_{\text{train}} = 50$			
	MACE	NequIP	ACE	sGDML	GAP	ANI	GRACE	FTA	ACE	NequIP	GRACE	FTA
Energy	2.2	2.3	6.1	7.2	17.7	16.6	1.7	2.2	26.2	19.5	11.7	3.3
Forces	6.6	8.2	17.9	31.8	44.9	40.6	6.1	42.5	63.8	52.0	38.2	134.6

Table 1: Benchmark results for rMD17-aspirin. Top table: $\Delta\rho_g$ and $\Delta\phi_g$ errors for FTA with and without field loss in training. $m^{\Delta\rho_g}$, $\mathbf{d}^{\Delta\rho_g}$, $\mathbf{q}^{\Delta\rho_g}$ denote the monopole, dipole, and quadrupole moments respectively of $\Delta\rho_g$. The e_1 and e_2 error metrics are defined as follows: $e_1(f) = \sum_i \left(\frac{\|f_{\text{pred}}^i - f_{\text{ref}}^i\|}{\|f_{\text{ref}}^i\|} \right) / M$, and $e_2(f) = \frac{\sum_i \|f_{\text{pred}}^i - f_{\text{ref}}^i\|}{\sum_i \|f_{\text{ref}}^i\|}$, where M denotes the number of test systems. In e_1 and e_2 , we use Coulomb J norm for $\Delta\rho_g$, L_2 norm for $\Delta\phi_g$ and $\mathbf{d}^{\Delta\rho_g}$, and Frobenius norm for $\mathbf{q}^{\Delta\rho_g}$. Bottom table: Comparison of energy and force MAEs of FTA (with field loss) against MLIPs. The energy units are in meV/atom and force units are in meV/Å. The benchmark results for MLIPs are taken from the following Refs. [28, 37, 38].

FTA ($N_{\text{train}} = 500$ on 300 K data)												
3BPA molecule	$e_1(\Delta\rho_g)$		$e_1(\Delta\phi_g)$		$\text{MAE}(m^{\Delta\rho_g}/N_e)$		$e_2(\mathbf{d}^{\Delta\rho_g})$		$e_2(\mathbf{q}^{\Delta\rho_g})$			
1200 K	1.9×10^{-3}		4.1×10^{-2}		5.4×10^{-5}		0.25		0.24			
$\beta = 120^\circ$ dihedral slice	7.5×10^{-4}		3.4×10^{-2}		2×10^{-5}		0.17		0.08			

3BPA molecule	$N_{\text{train}} = 500$ on 300 K data							
	MACE	NequIP	ACE	sGDML	GAP	ANI	BOTNet	FTA
1200 K Energy	29.8	40.8	85.3	774.5	166.8	76.8	39.1	4.4
1200 K Forces	62.0	86.4	187.0	711.1	305.5	129.6	81.9	307.2
All dihedral slices Energy	7.8	23.2	-	-	-	-	16.3	1.3
All dihedral slices Forces	16.5	23.1	-	-	-	-	20.0	60.1

Table 2: 3BPA benchmark results on out-of-distribution tests: 1200 K MD trajectory samples and dihedral slices. Top table: $\Delta\rho_g$ and $\Delta\phi_g$ errors for FTA. We refer to Table 1’s caption for other notations and definition of the e_1 and e_2 error metrics. Bottom table: comparison of energy and force RMSE of FTA against MLIPs. The energy units are in meV/atom and force units are in meV/Å. The FTA model is trained with field loss terms. The benchmark results for MLIPs are taken from the following Refs. [28, 37, 38]. The dashed entries in the lower table denote unavailable data.

minima, and hence, constitutes a stringent out-of-distribution test. The training set consists of 500 configurations of the 3BPA from molecular dynamics (MD) trajectories at 300K. The testing, in terms of energy, force, and field predictions is done using two out-of-distribution sets: one with configurations from 1200K MD trajectories configurations and the other with

314 dihedral rotations. The test set structures are farther away from the training set compared to
 315 the rMD17-aspirin benchmark. Particularly, doing well on the dihedral PES test demands
 316 a smooth extrapolation of the fitted model as they involve out-of-equilibrium geometries.
 317 Table 2 shows the relevant results, comparing the energy and force RMSE errors of FTA
 318 against widely used MLIPs. First, we observe that the FTA model outperforms all the
 319 MLIPs considered in energy predictions, achieving an accuracy of a few 1–5 meV/atom on
 320 both 1200K configurations and dihedral slices. In comparison, the best performing MLIP,
 321 MACE achieves 8–30 meV/atom energy errors. We remark that MACE has a more ex-
 322 pressive learning architecture compared to the ACE architecture used in the FTA model.
 323 Next, we observe that the force errors of FTA for both the 1200K and dihedral test sets is
 324 about $1.6\times$ higher than the ACE model, which is architecturally closest to the FTA model.
 325 Notwithstanding the higher force RMSE errors, in Fig. 4, we demonstrate that FTA closely
 326 reproduces the reference DFT dihedral PES for the $\beta = 120^\circ$ slice (slice that is farthest away
 327 from training points [28]), with good qualitative and quantitative agreement of the peaks
 328 and the valleys against the reference. The above results on energy and forces on both the
 329 rMD17-aspirin and 3BPA benchmarks suggest that the FTA approach is competitive against
 330 state-of-the-art MLIPs. Finally, we discuss the field predictions for 3BPA dataset. In the
 331 upper half of Tab. 2, we demonstrate that FTA attains good error metrics on $\Delta\rho_g$ and $\Delta\phi_g$,
 332 with the e_1 metrics comparable to the rMD17-aspirin case. Notably, our $\mathbf{d}^{\Delta\rho_g}$ and $\mathbf{q}^{\Delta\rho_g}$
 333 relative error metrics are 17–25% and 8–24% respectively, even in the out-of-distribution
 334 tests. To further probe the quality of the $\mathbf{d}^{\Delta\rho_g}$ and $\mathbf{q}^{\Delta\rho_g}$ predictions, in Fig. 5 and Fig. 6,
 335 we plot the magnitude of $\mathbf{d}^{\Delta\rho_g}$ and invariants of $\mathbf{q}^{\Delta\rho_g}$ tensor (I_1 , J_2 , and J_3) as a function
 336 of the α and γ dihedral angles on the $\beta = 120^\circ$ slice and compare with the reference DFT
 337 values. Physically, the I_1 invariant of $\mathbf{q}^{\Delta\rho_g}$, which is its trace, measures the spatial spread
 338 of $\Delta\rho_g$ in an isotropic sense. We also considered the anisotropic effects in the dihedral slice
 339 through the J_2 and J_3 invariants that are functions of the traceless quadrupole moment
 340 tensor ($\mathbf{q}^{\Delta\rho_g} - \frac{1}{3}I_1(\mathbf{q}^{\Delta\rho_g})\mathbf{I}$). We remark that J_2 and J_3 invariants are relevant for electro-
 341 static interactions as in the multi-pole expansion for the electrostatic potential of a charge
 342 distribution, the $\frac{1}{R^3}$ term is dependent on the traceless quadrupole moment of the charge
 343 distribution. As evident from Fig. 5 and Fig. 6, we observe a good qualitative agreement

with the reference DFT data in the $\mathbf{d}^{\Delta\rho_g}$ magnitude, and excellent agreement in the $\mathbf{q}^{\Delta\rho_g}$ invariants. It is interesting to note the complex structure of the $\mathbf{d}^{\Delta\rho_g}$ and $\mathbf{q}^{\Delta\rho_g}$ slice plots, which quite likely contain important qualitative information about charge re-distribution due to the steric hindrance caused by rotating bonds in 3BPA. Our results demonstrate that FTA theory is able to reliably predict the electronic-structure underlying the molecular PES, both in interpolative and extrapolative regimes. We believe that the variational origin of our $\Delta\rho_g$ prediction (cf. Eq. 16), as opposed to learning a direct map from (v_{aux}, b_s) to $\Delta\rho_g$ (untethered to the PES) plays a key role in this regard.

3 Discussion

In this work, we introduce field theoretic atomistics (FTA) as a theoretically rigorous and practically useful large-scale surrogate to DFT or any electronic structure method, in general. In FTA, we reformulate the Hohenberg-Kohn (HK) energy map in terms of auxiliary fields $(v_{\text{aux}}(\mathbf{r})$ and $b_s(\mathbf{r}))$ to lend it thermodynamic and variational consistency. FTA uses the HK theorem to define the groundstate density and atomic forces as variation of the energy with the input auxiliary fields. This field theoretic and variational aspect makes FTA an electronic structure method, unlike interatomic potentials, where the structure to energy map omits all electronic information. Our machine-learned FTA models exhibit good accuracy for energies, forces, and electron densities, including for out-of-distribution benchmarks. Particularly noteworthy is their ability to reproduce accurate dipole and quadrupole moments from the predicted densities.

The explicit treatment of electron density in FTA enables access to phenomena such as electron-phonon coupling in molecular and condensed-matter systems [39, 40]. Further, FTA, by virtue of its field theoretic formulation, can naturally incorporate any externally applied electric field. This allows it to seamlessly couple with the solvation models used in electrochemical and biochemistry applications [41, 42]. While FTA introduces a new paradigm for atomistic modeling, achieving chemical accuracy across diverse chemical environments de-

mands further development. One key direction is to enhance FTA’s generalization to systems with significant long-range interactions through improved machine-learning architectures and nonlocal descriptors. Another promising avenue is to extend the FTA formulation to variable number of electrons (grand-canonical ensemble), thereby enabling large-scale atomistics in open systems with a fixed chemical potential. Overall, we expect the combination of electronic-structure foundation and scalability in FTA to open new avenues and provide deeper insights across computational chemistry and materials science.

4 Methods

DFT calculations

The DFT computations of the ground-state energy, forces and electron-density in this work were performed using the PySCF package [43, 44]. For the rMD17-aspirin calculations we employed PBE exchange-correlation functional and the def2-SVP basis set. In case of the 3BPA, we employed ω B97X exchange-correlation functional and the 6-31G(d) basis set. We use a refined PySCF quadrature grid (level 8) to evaluate the ground-state density, required for training our FTA models.

Description of the datasets

For all the datasets used in this work, we have recomputed the reference DFT data on ground-state energy, forces, and electron-density using the PySCF software.

Aspirin molecule from rMD17 dataset: The revised MD17 (rMD17) dataset consists of MD trajectory samples of small organic molecules [27]. In particular, the dataset has five train-test splits for each molecule, with each split containing 1000 train and 1000 test configurations sampled randomly from the AIMD trajectory at 500 K. In this work, we

consider only the aspirin molecule (2-(acetyloxy)benzoic acid), the largest system in the dataset. The aspirin molecule consists of 21 atoms and (C,H,O) chemical species.

3BPA dataset: The 3BPA dataset contains train-test splits of a flexible drug-like organic molecule (3-(benzyloxy)pyridin-2-amine) [28, 29]. The 3BPA molecule consists of 27 atoms and (C,H,N,O) chemical species. There are 500 training snapshots sampled randomly from the AIMD trajectory at 300 K. The test sets consist of AIMD trajectory snapshots at 600 K and 1200 K, and a torsional PES test set sampled along dihedral rotations of the three rotatable bonds. In the torsional PES test set, three 2D dihedral slices are considered for $\beta = 120^\circ$, $\beta = 150^\circ$, and $\beta = 180^\circ$. In particular, $\beta = 120^\circ$ slice has very few nearby training set points from the 300 K trajectory [28]. In this work, we study the 1200 K MD trajectory samples and torsional PES test sets.

Equivariant machine learning architecture

We recall that our model is expressed as a separable form (cf. Eq. 18), where one branch of the model is $\Delta E_{I,A}[\Delta \mathbf{x}_I, \Delta \mathbf{y}_I]$ and the other branch is $\Delta E_{I,B}[\Delta \mathbf{x}_I, \Delta \mathbf{y}_I, \mathbf{x}_I, \mathbf{y}_I]$. Below we discuss our learning architecture to model both the branches while ensuring the well-separated limit is satisfied for the product of the branches ΔE_I , an exact condition (cf. Sec. 2). Broadly, for our learning architecture, we choose a combination of atomic cluster expansion (ACE) [14] and deep neural networks (NN) as depicted in Fig. 1. In the first step, we employ the ACE expansion to learn rotationally invariant features from our descriptors $(\Delta \mathbf{x}_I, \Delta \mathbf{y}_I, \mathbf{x}_I, \mathbf{y}_I)$. The descriptors are obtained by sampling the input fields $(v_{\text{aux}}, b_{\text{s}})$ using atom centered probe functions that are represented as separable products of radial functions and real spherical harmonics (cf. Eq. 13). As a result, our descriptors at each atomic site I , generically denoted by $\mathbf{D}_I$, transform equivariantly with respect to the input fields. The ACE expansion for a rotational invariant scalar P at an atomic site I as a function of $\mathbf{D}_I$ is

defined as the following polynomial expansion [14]

$$P(\mathbf{D}_I; K) = \sum_{v=1}^{v=K} \sum_{nl} c_{nl}^{(v)} B_{Inl}^{(v)}, \quad (20)$$

where the expansion is truncated at the K^{th} correlation order, $c_{nl}^{(v)}$ are learnable parameters, and $B_{Inl}^{(v)}$ is the hierarchical many-body ACE basis. The $B_{Inl}^{(v)}$ tensors in the ACE expansion are constructed from v^{th} order rotationally invariant products of the D_{Inlm} tensor, using properties of product of spherical harmonic tensors. Thus, the ACE expansion is able to learn higher-order features from D_{Inlm} .

Since ACE is a linear expansion in a many-body basis, next we leverage NN for learning more expressive nonlinear functional forms on the rotationally invariant ACE outputs. Specifically, we use two NN layers: a $f_A^{(\text{NN})}$ for the $\Delta E_{I,A}$ branch and a $f_B^{(\text{NN})}$ for the $\Delta E_{I,B}$ branch. Further, we use multiple ACE channels N_c for the Δ -field descriptors $(\Delta \mathbf{x}_I, \Delta \mathbf{y}_I)$ and use one ACE channel for the total-field descriptors $(\mathbf{x}_I, \mathbf{y}_I)$, and concatenate the scalar outputs P in the following manner to form input feature vectors into the NN layer

$$\begin{aligned} \mathbf{Q}_{\mathbf{D}_I}^{(N_c)} &= [P^{(1)}(\mathbf{D}_I), \dots, P^{(N_c)}(\mathbf{D}_I)], \\ \Delta E_{I,A} &= f_A^{(\text{NN})} \left([\mathbf{Q}_{\Delta \mathbf{x}_I}^{(N_c)}, \mathbf{Q}_{\Delta \mathbf{y}_I}^{(N_c)}] \right), \\ \Delta E_{I,B} &= f_B^{(\text{NN})} \left([\mathbf{Q}_{\Delta \mathbf{x}_I}^{(N_c)}, \mathbf{Q}_{\Delta \mathbf{y}_I}^{(N_c)}, \mathbf{Q}_{\mathbf{x}_I}^{(1)}, \mathbf{Q}_{\mathbf{y}_I}^{(1)}] \right), \end{aligned} \quad (21)$$

where $\mathbf{Q}_{\Delta \mathbf{x}_I}^{(N_c)}$ denotes $[P^{(1)}(\Delta \mathbf{x}_I), \dots, P^{(N_c)}(\Delta \mathbf{x}_I)]$, and accordingly for the other field descriptor types. We note that $f_A^{(\text{NN})}$ only takes Δ -field descriptors while $f_B^{(\text{NN})}$ takes both Δ - and total-field descriptors. Further, we set the bias parameters in $f_A^{(\text{NN})}$ to be zero and choose activation functions that are zero valued at zero input. The above construction choices in conjunction with $\mathbf{Q}_{\Delta \mathbf{x}_I}^{(N_c)}$ and $\mathbf{Q}_{\Delta \mathbf{y}_I}^{(N_c)}$ being zero when $\Delta \mathbf{x}_I$ and $\Delta \mathbf{y}_I$ are zero (property of the ACE expansion) ensures that $\Delta E_{I,A}$ tends to zero at the well-separated/isolated atoms limit. Thus, we have now a learning architecture that is exact in atomization energy, forces, $\Delta \rho_g$ and $\Delta \phi_g$ in the well-separated/isolated atoms limit. In the above, we remark that the disparity in number of channels between Δ -field and total-field ACE channels is based on our

empirical observations that higher number of Δ -field ACE channels attain lower training loss on $\Delta\rho_g$ and $\Delta\phi_g$.

Model and training parameters

We begin with discussing the choices of the weights in the objective function, then the probe function parameters, and finally the parameters in the learning architecture. In both the rMD17-aspirin and 3BPA dataset training, we assign the following weights in the loss function (cf. Eq. 19): $t_E = 1 \times 10^7$, $t_F = 3 \times 10^{10}$, $t_\rho = 1.8 \times 10^7$, and $t_\phi = 3 \times 10^3$ corresponding to the energy, force, density, and potential loss terms. Next, the parameters for the atomic site centered probe functions to compute the rotationally equivariant descriptors ($\mathbf{x}_I$, $\mathbf{y}_I$, $\Delta\mathbf{x}_I$, $\Delta\mathbf{y}_I$) of the input fields (v_{aux} and b_s) are set as follows. We use a combination of short-ranged orthogonal Bessel (SR-OB) functions and long-ranged damped-multipole (LR-DM) functions for the radial portion of our probe functions, and $l^{\text{max}} = 3$ for the angular portion. We use a total of 22 ($20 + 2$) and 17 ($15 + 2$) radial probe functions for v_{aux} and b_s respectively, with radial cut-offs of 4–6.5 Bohr for SR-OB functions and around 10 Bohr for LR-DM functions. We refer to Sec. S2 of the SI for details of their construction. The same probe function choices are used for both rMD17-aspirin and 3BPA training. Subsequently, for the ACE expansion, that uses the descriptors as inputs, we set the correlation order to be $K = 4$ and $K = 2$ for the $\Delta E_{I,A}$ and $\Delta E_{I,B}$ respectively. We motivate this choice from the observation that $\Delta\mathbf{x}_I$ and $\Delta\mathbf{y}_I$ have a relatively smaller variance in their component values across the angular momentum channels compared to $\mathbf{x}_I$ and $\mathbf{y}_I$ which have large values for the $l = 0$ components due to the dominant spherically symmetric self-atom portion of the input fields. Thus $\Delta\mathbf{x}_I$ and $\Delta\mathbf{y}_I$ should be more amenable to learning higher order correlations in the ACE expansion that are expected to be smaller in magnitude compared to the lower order terms. We also sparsify the ACE expansion through limiting the maximum angular momentum and radial basis index for the higher correlation orders ($K \geq 3$) to avoid over-parametrization. In particular, we use ($n^{\text{max}} = 10$, $l^{\text{max}} = 3$) for $K = 3$ and ($n^{\text{max}} = 4$, $l^{\text{max}} = 2$) for $K = 4$. Further, we use 40 ACE channels for Δ -field descriptors ($N_c = 40$ in Eq. 21) and 1 ACE

channel for total-field descriptors. The output of the ACE channels is transferred into the NN layer. For the NN layer, in both $\Delta E_{I,A}$ and $\Delta E_{I,B}$, we use feed-forward neural network consisting of two hidden layers and SiLU activation functions. The number of neurons in each layer is coarsened by a factor 0.75 starting from the input layer. The input layer size depends on the number of ACE channels. The feed-forward networks are implemented via the Pytorch software package [45].

The ACE parameters in all the channels, and weights and biases in the NN layer are optimized together using the AdamW optimizer [46], with a weight decay of 5×10^{-5} , a mini-batch size of 16, and an initial learning rate of 6×10^{-3} that is adaptively damped by a factor 0.8 if the valid loss does not decrease for 600 epochs or more. We continue the optimization to a maximum of 150,000 epochs or if the validation loss over 1000 consecutive epochs does not reduce, whichever condition is satisfied first.

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Data availability: The authors declare that all the data supporting the results of this study are available upon reasonable request to the corresponding author.

Code availability: The code used to machine learn FTA models is available upon reasonable request to the corresponding author.

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