

Physics Area - PhD course in
Theory and Numerical Simulation of Condensed Matter

Representations of Atomic Environments and Effects on Body-Ordering and Electrostatics in Machine-Learning Potentials

Candidate

Apolinario Miguel Tan

Advisor

Stefano de Gironcoli

October 2026

Acknowledgment

I would like to thank the following people in my community who helped make this thesis possible:

To my supervisor, Stefano, for his persistence in guiding me academically during my whole stay at SISSA. This thesis would not have been possible without your help.

To Franco and Gabriele, who shared their effort and insight in making sure I have a grounded understanding of the nitty-gritty in my projects.

To Abdul, Atefe, Francesca, Luca, Mina, and Vansh, for the enjoyable experiences shared with the rest of the MLMS group.

To the 321 group: Abbas, Anna, Anto, Diego, Edo, Greg, Ivan, Laura, Marti, Ricc, Ruiyi, for the shared experiences, laughs, and tears during our PhD journey.

Para sa mga Pinoy sa at dumaan sa Trieste, sa pagbibigay sa akin ng pagkakataong manahanan pa rin, kahit nalalayo sa sariling tahanan.

Para kay Tatay, Nanay, at Kuya, sa lubos na tulong, suporta, at pagmamahal na ipinamahagi niyo sa akin.

At para kay Ninay, sa pagsasama sa akin sa bawat hakbang ng paglalakbay ko. Pauwi na ako, mahal.

Abstract

Machine learning interatomic potentials (MLIPs) achieve DFT-level accuracy by replacing rigid functional forms with neural network architectures that allow for much more effective regression at the cost of less intuitive representations. This thesis explores how representations of atomic environments used by MLIPs behave in two regimes: at short range in how body-ordered expansions converge with respect to their basis functions, and at long range, in improving the modeling of the electronic response of systems sensitive to electrostatic interactions.

We determined that Atomic Cluster Expansion (ACE) models are only able to recover the DFT dimer curve if the self-interactions inherent in their efficient tensor product construction are filtered with a purification operator. Moreover, we highlight that the canonical many-body expansion has a non-monotonic and non-convergent scaling with higher body orders in trimers and systems with symmetric interactions.

We also studied the ad hoc modeling of long-range electrostatics through physically motivated charge flow models, namely charge equilibration (QEq). We showed how QEq-based treatments that parametrize through local atomic descriptors fail to capture the correct dielectric response, as diagnosed by the bare susceptibility χ_0 , and extended the capabilities of our in-house code PANNA to include the split charge equilibration (SQE) model. Phonon dispersions from trained SQE models show signatures of finite longitudinal optical-transverse optical splitting in MgO where short-range and charge equilibration counterparts fail to manifest, suggesting that the SQE model has the necessary ingredients to capture finite screening in ionic crystals.

Both results show that physically grounded constraints on MLIP representations recover behavior that unconstrained flexibility misses: recovering the canonical expansion through purification methods as well as imposing constraints on charge flow through the bond topology in SQE.

Contents

List of Publications	5
1 Introduction	6
1.1 Classical force fields and <i>ab initio</i> molecular dynamics	6
1.2 Machine learning interatomic potentials	7
1.3 Local atomic representations and body-ordering	8
1.4 Long-range electrostatics and charge flow models	10
1.5 Thesis outline	12
2 Convergence of body orders in MLIPs	13
2.1 Body-ordering in force fields	13
2.2 Datasets and methods	16
2.2.1 Datasets	16
2.2.2 Descriptors	17
2.2.3 Fitting protocol	19
2.3 Results and Discussion	20
2.3.1 Carbon datasets	20
2.3.2 Silicon datasets and the purified bases	23
2.4 Convergence of the MBE in tight-binding models	26
2.4.1 Nonconvergence of hydrogen clusters	28
2.4.2 Tight-binding approximation on <i>m</i> -mers	30
2.4.3 Parametrizing hopping terms	31
2.4.4 Trimer cases	32
2.4.5 Fully symmetric H-clusters	35
2.5 Summary	37
3 Ad-hoc electrostatics in force fields	38
3.1 DFT linear response	38
3.1.1 Susceptibility, χ	39
3.1.2 Dielectric matrix, ϵ	40
3.1.3 χ_0 is crucial	41

3.2	Charge Equilibration (QEq)	43
3.3	QEq has an incorrect χ_0	44
3.4	Split-charge equilibration (SQE)	47
3.4.1	Elements and properties of bond-space variables	47
3.4.2	SQE model	50
3.5	ACKS2	54
3.5.1	QEq from cDFT	55
3.5.2	ACKS2: explicitly adding kinetic energy	56
3.5.3	ACKS2 and response functions	60
3.5.4	Linking SQE to ACKS2	61
4	Long-range improvements to PANNA	64
4.1	Short-range MLIP and descriptor: PANNA and LATTE	65
4.2	PANNA-QEq	67
4.3	PANNAJAX-QEq	70
4.4	Long-range forces and phonon dispersions	70
4.4.1	Phonon dispersions	70
4.4.2	Phonons from long-range electrostatics	71
4.4.3	Phonons for short-range and QEq models	73
4.5	PANNAJAX-SQE	75
4.5.1	Creating the $\mathbf{L}_{tb}$ matrix	75
4.5.2	Bond variables are ill-conditioned	76
4.5.3	Periodic p_b are renormalized	76
4.6	Phonon dispersions in SQE	78
4.6.1	SQE parameters	78
4.6.2	Results	78
5	Summary and outlook	82
A	Supplementary information for the body-order convergence project	85
A.1	Simulation parameters	85
A.2	Additional plots	86
A.2.1	Force plots between DFT and dimer-trained potential	86
A.2.2	Loss analysis of diverse dataset dimer curves	87
A.2.3	Biasing the diverse dataset with dimer data	88
A.2.4	Learning curves of diverse dataset runs	89
A.2.5	Learning curves and dimer curves for 5k and 10k runs	91
A.3	Derivation of the symmetric tight-binding result	92
B	Generic case for the atom-space mapping of SQE	97

C	Additional information for PANNA code implementation	99
C.1	Carbon chain test	99
C.2	Creating the topology matrix	100
C.3	Parameterizing bond hardness	102

List of Publications

1. **A. M. Tan**, F. Pellegrini, and S. de Gironcoli, "Convergence of Body Orders in Linear Atomic Cluster Expansions," *The Journal of Physical Chemistry A*, vol. 129, pp. 7229-7237, Aug. 2025.

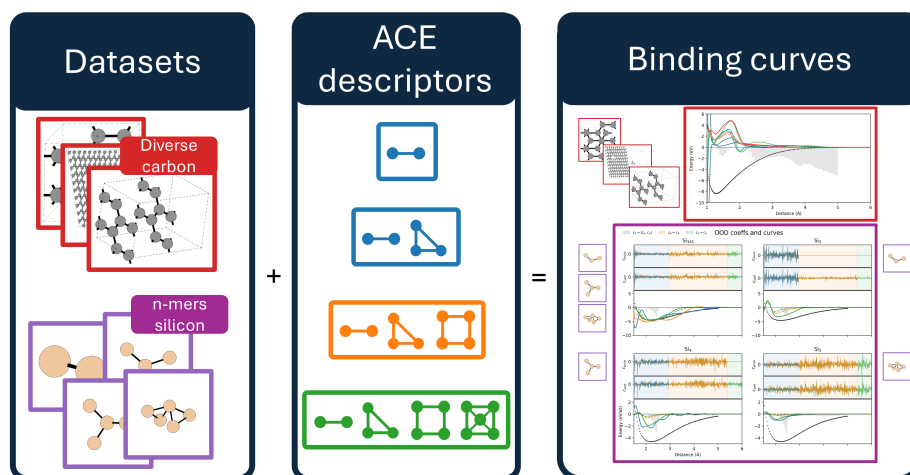


Figure 1: Main graphic for the publication [1].

Chapter 1

Introduction

1.1 Classical force fields and *ab initio* molecular dynamics

Prior to the use of machine learning techniques to model the potential energy surfaces of materials, there have been two paradigms in building force fields. On one hand, we have classical force fields which use an inflexible functional form that is fixed *a priori* from physical reasoning. It traces its roots to Lennard-Jones potentials, where intermolecular forces are modeled with a pair interaction,

$$E_{LJ}(R) = 4\epsilon \left(\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right), \quad (1.1)$$

which has become the prototypical model in describing repulsion and attraction between particles. Parameters such as well-depth ϵ and distance at zero potential σ are interpretable which allows a very intuitive understanding of the functional forms used. Other pair potentials such as the Morse or Buckingham potentials increase the number of physical parameters to improve fitting. The benefit of pair potentials goes beyond pedagogy and simplicity as they are able to capture physical phenomena well despite their pairwise-additive nature (i.e. ignoring 3-body and higher-order interactions).

These pairwise potentials unfortunately are not able to distinguish higher-order correlations. They miss the effects from higher body-order physics from even simple cases: a pair potential would provide the same energy for a water molecule that changes its bond angle while keeping its bond lengths constant. Pair potentials also suffer from missing many-body effects, and incorrectly predict elastic constants [2]. Pair potentials have then been augmented with environment-dependent descriptions of the local environment to implicitly capture the many-body character of interatomic interactions, one of the first being the Embedded Atom Method (EAM) [3, 4], which

has been successfully employed to describe metallic deformations and surfaces. The Stillinger-Weber potential [5] introduced explicit 3-body terms through angular descriptors, providing a much better description of tetrahedral phases. 4-body terms were later introduced for condensed matter systems [6] which were parametrized with the help of *ab initio* molecular dynamics (AIMD). These models gave rise to the bond-order potentials [7–10] where the orders were systematically parametrized leading to a much better description of the local atomic environment. The catch of bond-order potentials is that the number of functions needed to describe the system grows combinatorically large as the body-order goes higher, and the many-body expansion on which these bond-order potentials rely fails to adequately model systems lacking symmetries such as surfaces [11, 12]. Despite these improvements, physically motivated force fields also suffer from a lack of transferability. As a simple example, the set of parameters to describe an elemental carbon system may perform rather poorly when applied to an amorphous structure or even a molecule.

A different method that tackles the problem of interatomic modeling is through the already mentioned AIMD, either Born-Oppenheimer or Car-Parrinello [13] where Kohn-Sham orbitals are given a fictitious mass and propagated as dynamical variables alongside the nuclei through a Lagrangian formalism. In AIMD, forces are generated directly from density functional theory (DFT) at each MD time step, which removes the need for an intuited functional form. This method allows for a description of the quantum mechanical effects that is grounded in the DFT level of theory, using fewer priors than classical force fields. It also has the benefit of accessing electronic properties such as dipoles, band structures, and response functions alongside energies and forces. Unfortunately, its dependence on DFT is double-edged as it inherits the $\mathcal{O}(N^3)$ scaling with N degrees of freedom as opposed to the sub-cubic scaling present in classical force fields.

The top-down and bottom-up paradigms of classical interatomic potentials and AIMD have their particular strengths and weaknesses, and one typically must discern which method works well for the system, properties, and scale that they want to study. The breakthrough in bridging the time and length scales accessible to these methods came with the use of artificial neural networks to parametrize the potential energy surface.

1.2 Machine learning interatomic potentials

The limited number of parameters that hinder the transferability of classical force fields was addressed by Behler and Parrinello [14] by using a fully connected feed-forward neural network (NN) to address the difficulty of modeling silicon across its different phases. Similar to classical force fields, machine learning interatomic po-

tentials (MLIPs) rely on the assumption that the total energy of any system can be decomposed into atomic contributions,

$$E_{\text{tot}}(\{\mathbf{R}\}) = \sum_i E_i(\{\mathbf{R}\}). \quad (1.2)$$

Their descriptors, called atom-centered symmetry functions (ACSFs), ensured that translation, rotation, inversion, and permutation symmetries were followed. They used supervised learning to train on a small set of structures that were labeled from DFT calculations, and regressed the model on energies and forces. With the inter-atomic distances as inputs, they were able to describe 2- and 3-body terms, and they were able to capture the radial distribution function of silicon melts much closer to the DFT result compared to other classical force fields. The strength of MLIPs lies in having orders of magnitude more parameters than any classical force field, a number that can be tuned through the size of the network architecture. This allowed them to have an unprecedented level of transferability. From the perspective of AIMD, the overhead of regressing the model to its target energies and forces is much lower than the costs needed by standard DFT calculations.

The silent cost of using MLIPs comes from interpretability. The parameters that NNs have are not grounded in physical intuition, which makes it difficult to extract insight beyond the results. Classical force fields, while rigid in their form, are built from physical intuition and analyses of their successes and failures are easier to manage and harder to dismiss as a black-box model. Because of this, research on representations of atomic environments for the use of MLIPs was, and continues to be, an active area of research. In the next few sections we see how descriptors for MLIPs represent local environments, as well as how established methods are adapted to capture effects that are not captured by radial cutoffs of typical lengths.

1.3 Local atomic representations and body-ordering

To make atomic descriptors tractable, each atom i should have a finite number of atoms it interacts with in its neighborhood. A reasonable way to limit the list of neighbors per atom is through imposing a finite radial cutoff where atoms farther than some distance R_c from the central atom do not contribute to the atomic energy, E_i . To ensure that the force fields calculated do not suffer from discontinuities at the boundaries, the energy must vanish smoothly. This is typically done through cutoff

functions, and the ACSFs and their modifications employ the following [15, 16],

$$f_c(R_{ij}) = \begin{cases} \frac{1}{2} \left(\cos \left(\frac{\pi R_{ij}}{R_c} \right) + 1 \right), & R_{ij} \leq R_c \\ 0, & R_{ij} > R_c \end{cases}. \quad (1.3)$$

The use of these cutoff functions to describe electronic effects is supported by the nearsightedness of electronic structure as discussed by Prodan and Kohn [17], where systems with finite gaps have density matrix elements that vanish quickly with distance. Local electronic structure is then insensitive to distant perturbations, permitting the validity of instituting these cutoffs.

In the subsequent discussion, we see how these local descriptors have evolved since their first iteration in ACSFs. ACSFs were the first descriptors that were created for MLIPs. Modifications have been made [16] to make them more efficient, and the modified functions are given as,

$$\begin{aligned} G_i^{\text{Rad}}[s, R_{ij}] &= \sum_{j \neq i} e^{-\eta(R_{ij}-R_s)^2} f_c(R_{ij}), \\ G_i^{\text{Ang}}[s, R_{ij}, R_{ik}] &= 2^{1-\zeta} \sum_{j,k \neq i} (1 + \cos(\theta_{ijk} - \theta_s))^\zeta \\ &\quad \times e^{-\eta(R_{ij}/2 + R_{ik}/2 - R_s)^2} \times f_c(R_{ij}) f_c(R_{ik}), \end{aligned} \quad (1.4)$$

$$(1.5)$$

where the geometric hyperparameters needed to sample the relevant space are sampling centers R_s , and angular parameters θ_s , η , and ζ .

A different perspective in modeling the local environments came from the works of Bartók et al. in using Gaussian-smearred neighbor densities, called the Soft Overlap of Atomic Positions (SOAP) [18]. SOAP describes the atomic environment by smoothing the densities, allowing for a descriptor that captures up to 3-body interactions as the power spectrum is expanded in radial basis functions and spherical harmonics (angles). These descriptors are implemented with similarity kernels through the Gaussian Approximation Potential (GAP) [19].

Despite the initial success of these MLIPs, studies such as [20] have shown that descriptors going even up to 4-body terms encounter degeneracies in describing simple atomic environments, and thus may need higher-order correlations to provide faithful descriptions. Breakthroughs that achieved arbitrary N -body scaling came from moment tensor potentials (MTP) by Shapeev [21] and the Atomic Cluster Expansion (ACE) by Drautz [22] and coworkers wherein a so-called “density trick” is used to collapse the neighborhood into a set of one-body projections, or the atomic base. Higher body orders K are then achieved by taking recursive products of these projections, thus avoiding the combinatoric $\mathcal{O}(N^K)$ scaling as typically done to construct the higher K terms. The cost of these tensor products is $\mathcal{O}(N)$ as the construction

of the projections needs to pass through the neighbor list once. ACE uses a spherical basis of radial functions with spherical harmonics, and symmetrizes the products using generalized Clebsch-Gordan coefficients to provide a basis that has fine control over the correlation order ν ¹.

A subtle caveat, and possible disadvantage over the standard way of constructing the body-ordered terms, is that the tensor product is unrestricted, so the K -th body order feature will inevitably contain renormalized lower-order or “self-interaction” terms. These tensor product-based descriptors have proven to be effective, and have been utilized in message-passing graph neural networks such as MACE [23] and its foundational model variant [24].

The ability of MLIP descriptors to capture the local environments has consistently been proven, and a review of these physically-inspired features has been undertaken in [25]. The next section discusses a particular instance when implementing finite R_c may not provide an accurate description of the system and why an ad hoc treatment is needed.

1.4 Long-range electrostatics and charge flow models

In electrostatics, the fraction of the energy that has failed to be captured by these interaction spheres, E_{tail} , scales as [26],

$$E_{\text{tail}} \sim \int_{R_c}^{\infty} 4\pi r^2 u(r) dr, \quad (1.6)$$

where the distance scaling of $u(r) \propto r^\alpha$ depends on the nature of the interaction. E_{tail} will be finite only if $\alpha < -3$. Electrostatic interactions have $\alpha = -1$, which makes the cutoff approximation invalid.

The treatment of electrostatic interactions of atomic charges Q_{Rs} in potentials goes as far back as the Ewald method, where the Coulomb energies of periodic systems,

$$E_{\text{Coul}} = \frac{1}{2} \sum_{Rs, R's'} \frac{Q_{Rs} Q_{R's'}}{|\tau_{Rs} - \tau_{R's'}|}, \quad (1.7)$$

are summed in both real and reciprocal spaces. τ_{Rs} is the position of an atom s in the cell at lattice site R .

A second failure concerns charge transfer even if the atomic neighborhoods can be covered by reasonable R_c . Test systems studied by Ko et al. [27] show that similar initial states relax to different configurations depending on the charge states. An

¹In the notation of Drautz [22], the correlation order $\nu = K - 1$.

MLIP without the atomic charge information will not be able to distinguish between these states, which asserts the need to codify charge information when the system requires it.

To this day, finding suitable ad hoc solutions to long-range forces remains an active area of research for MLIPs [28]. One can categorize the solutions into two strategies. The first learns nonlocal features: LODE [29, 30] constructs descriptors from a long-range potential field rather than a density, and related schemes embed a reciprocal-space channel similar to the Ewald summation [31–33]. These retain the flexibility of neural network-based models and are agnostic to physical descriptions of charge, but they inherit the expressivity of the network. The second strategy fixes a physically motivated parametrization of atomic charges and learns only its parameters. Some methods incorporate additional information such as the location of Wannier centroids in the training protocol [34, 35], or leverage charge equilibration-based models in the workflow [27, 36–39]. The methods inspired by physical models typically do not perform consistently well for both metals and insulators, and one has to choose depending on their system of interest. It remains a challenge to model systems that have metal-insulator interfaces, or to model an electrostatically sensitive system without declaring too many priors on whether it is metallic or insulating. This thesis focuses on the latter, particularly in capturing charge flow in the environment as discussed by Jensen in his review connecting the dominant models [40]. He discusses the failures of the charge equilibration/fluctuating charge model as the first successful one, details its pathological shortcomings, and gives an overview of the other methods that try to address their shortcomings:

- Charge Response Kernel (CRK) uses a charge response kernel matrix $\mathbf{K}$ over all atom pairs. Uses fixed charges so it does not allow charge transfer between fragments.
- Split Charge Equilibration (SQE) uses a bond-space parameterization of charge flow and is a natural extension of charge equilibration, but the penalty of charge flow between atoms diverge as the bond dissociates.
- Atom-Condensed Kohn-Sham DFT Approximated to Second-Order (ACKS2) uses a Legendre transform to use both charge and potential degrees of freedom to provide a mixed-variable representation of charge flow. Its derivations follow closely linear response and conceptual DFT [41].
- Bond Capacity (BC) uses potential degrees of freedom (but atomic charges are recoverable) and utilizes the atomic softness, which has a more numerically reasonable behavior at bond dissociation (goes to 0 instead of infinity for hardness).

1.5 Thesis outline

In this thesis, we aim to answer two problems arising from the representations of atomic environments in MLIPs. Chapter 2 investigates if it is possible to systematically converge body-ordered descriptors order by order to eventually construct more efficient feature representations. We also perform simple investigations into the original many-body expansion to see if the commonly assumed convergence at low orders (i.e., $K = 4$) is valid in general. For the long-range interactions, Chapter 3 discusses the missing ingredients from charge equilibration-based models through linear response functions and Chapter 4 explains the implementation of the split-charge equilibration model to address the pathological shortcomings of charge equilibration. We summarize the findings and discuss future outlooks in Chapter 5.

Original contributions from this work are highlighted in Fig. 1.1.

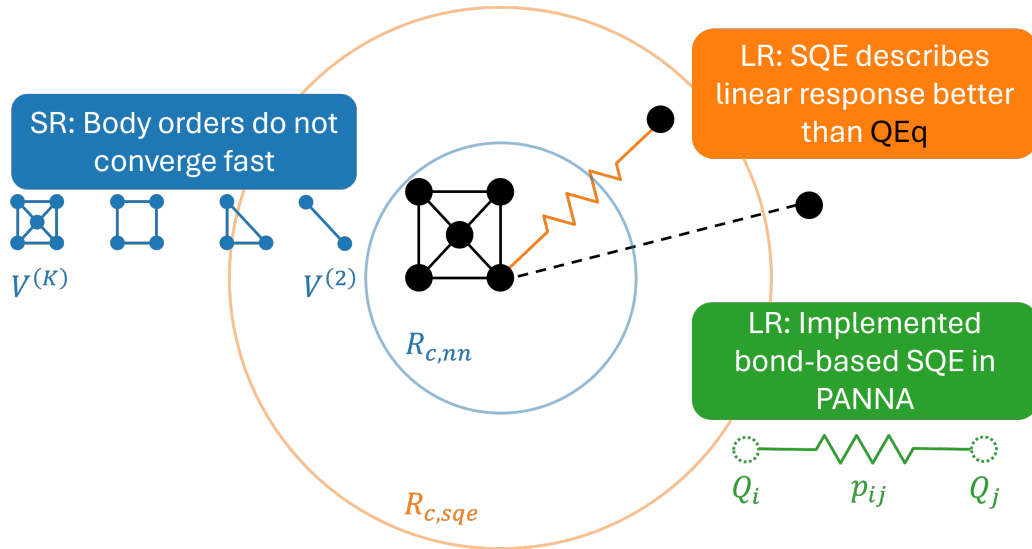


Figure 1.1: Graphical summary of projects, highlighting original contributions. Chapter 2 (in blue) discusses how body orders, whether calculated using the original or tensor product expansion, do not converge fast even at simple data and constrained models, at DFT and tight-binding levels of theory. Chapter 3 (orange) forwards that the split-charge equilibration (SQE) model improves upon the linear response description of the more commonly used charge equilibration (QEq) ad-hoc fix for capturing long-range interactions. Finally, Chapter 4 showcases the how a bond-based SQE model is built on top of the existing PANNA code, and provides results that corroborate the assertion from the previous chapter.

Chapter 2

Convergence of body orders in MLIPs

This chapter covers the discussions found in our work on "Convergence of Body-Orders in Linear Atomic Cluster Expansions", in JPC A [1]. We investigated the convergence of body-ordered descriptors in short-ranged MLIPs as well as a brief exploration of the many-body expansion itself. The first section discusses the underlying structures of the descriptors built from tensor products, their advantages and caveats. Then we discuss the computational setup and the results from the tests highlighting that the ACE basis, whether self-interacting or purified, fails to recover the two-body energetics. The final section discusses whether the purified or canonical expansion itself is worth the trouble as a study of body-orderedness by Chong et al. [42] suggests that convergence of clusters at lower orders may not be as intuitive as thought. Simple tests on trimers and symmetric cases are done at the tight-binding level of theory.

2.1 Body-ordering in force fields

The total energy of a system can be decomposed into N -body contributions through the (canonical) cluster expansions,

$$E(\{\mathbf{R}_i\}) = V^{(0)} + \sum_i V^{(1)}(\mathbf{R}_i) + \sum_{\substack{i,j \\ i \neq j}} V^{(2)}(\mathbf{R}_i, \mathbf{R}_j) + \sum_{\substack{i,j,k \\ i \neq j \neq k \neq i}} V^{(3)}(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \dots, \quad (2.1)$$

and have been used as the local environmental descriptors to study thermodynamics in substitutional alloys [43] as well as empirical potentials of condensed matter and molecular systems [5, 8, 44].

It has been shown that the expansion in Eq. 2.1 is complete [45] when the number of atoms matches the highest order of the expansion. The caveat comes from its

intractability, i.e. going to higher orders is combinatorially prohibitive. Its usefulness comes from the fact that the total energy seemingly converges after a few body orders K [5, 12, 44].

The cluster expansion has also been used to describe local environments in MLIPs. The assumption behind these descriptors stems from the atomic energy decomposition of the total energy as described by Eq. 1.2. The atomic energies E_i are expanded in the number of neighbors. Methods to construct E_i have undergone rapid developments in the last few years, with symmetry-respecting descriptors that truncate the expansion after a few terms [14, 18, 46, 47] or even take advantage of tensor products to obtain an arbitrarily high body order [21–23]. A detailed review on symmetry-respecting local descriptors has been done in [25], but recent developments can even start from unconstrained models [48].

A widely adopted version of the tensor products is the Atomic Cluster Expansion (ACE) proposed by Drautz [22]. Each E_i is expanded with a non-orthogonal basis with unrestricted sums. We first start by describing a one-particle basis function ϕ_k ,

$$\phi_k(\mathbf{R}_{ij}) = \mathcal{R}_n(R_{ij})Y_{lm}(\hat{\mathbf{R}}_{ij}), \quad \mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j \quad (2.2)$$

where $k = (n, l, m)$ is the compound index that describes the quantum numbers need for the radial basis function (e.g. Chebyshev or Bessel radial) and spherical harmonics $Y_{lm}(\hat{\mathbf{R}}_{ij})$ that take as inputs the unit vectors of $\mathbf{R}_{ij}$. To collect all neighbors of the atom i , we pool all its neighbors to its atomic basis,

$$A_{k,i} = \sum_{j \in \mathcal{N}(i)} \phi_k(\mathbf{R}_{ij}). \quad (2.3)$$

These atomic basis functions sum all $\phi_k(\mathbf{R}_{ij})$ neighbors of atom i . We note that $A_{k,i}$ is two-body by nature as it just sums all the pairs in the neighborhood $\mathcal{N}$ of i . From here, the basis functions of higher body-orders centered around i are created through repeated products of the atomic basis which we denote with $\mathbf{A}_{\mathbf{k},i}$,

$$\mathbf{A}_{\mathbf{k},i} = A_{k_1}A_{k_2}...A_{k_\nu} = \prod_{t=1}^{\nu_{\max}} A_{k_t,i}. \quad (2.4)$$

$\mathbf{k} = (k_1, k_2, \dots, k_\nu)$ is short for all the different k multiplied together ν times, which we call the correlation index. Using a trimer for an example, the highest order basis function is created with,

$$\mathbf{A}_{\mathbf{k},i} = A_{k_1}A_{k_2} = \prod_{t=1}^{\nu=3} A_{k_t,i}.$$

A 3-body term is built with a $\nu = 2$ correlation index, so we have $\nu = K - 1$. Finally,

the atomic energy described by a K -body basis using ACE is,

$$E_i(\{\mathbf{R}_i\}) = \sum_{\nu=0}^{\nu_{\max}} \sum_{\mathbf{k}=k(k_1, \dots, k_\nu)} c_{\mathbf{k}} \mathbf{A}_{\mathbf{k},i} = \sum_k c_k^{(1)} A_{k,i} + \sum_{k_1 \geq k_2} c_{k_1 k_2}^{(2)} A_{k_1,i} A_{k_2,i} + \dots, \quad (2.5)$$

This version of the expansion is also complete [49] and respects the necessary symmetries¹, and its implementations have been effective in MLIPs [50–54]. MACE [23, 24], one of the state-of-the-art families of MLIPs, extends the formalism of ACE as a graph neural network, but the interpretability of the expansion is traded for a much more expressive model than linear potentials.

Implementations of these interatomic potentials using the ACE framework need to consider the basis complexity, in particular the number of basis functions and the maximum K . Typically, the selection is a heuristic process and no systematic construction has been proposed yet. While linear ACE potentials achieve competitive fitting and validation errors, the stability of these solutions and the interpretability of the basis functions have not been studied as much beyond efforts to eliminate the self-interactions inherent in the tensor products [55] and uncertainty quantification studies [56].

Nowadays, MLIPs are increasingly used through foundation models [24] as baselines: MLIPs that do not need to be trained from scratch. These stand in stark contrast to training bespoke models where the full generation process is considered. The scope of this study is to answer: **do body-ordered bases converge systematically at lower-order energetics?** We investigate the convergence of linear ACE models at different maximum body order $K_{\max}$ in terms of their projection onto the lowest terms of the original cluster expansion in Eq. 2.1. In particular, we look at the convergence of the MLIPs in energies and forces on different datasets as a function of the number and type of basis functions, and compare it to the stability of a real body-ordered expansion. Our study focuses on the first nontrivial term: the pair interaction or the two-body term. This can be easily obtained from a given potential by studying the energy profile of two isolated atoms, a dimer, as a function of distance,

$$E_{2b,i}(\mathbf{r}_i, \mathbf{r}_j) = V^{(2)}(\mathbf{r}_i - \mathbf{r}_j). \quad (2.6)$$

We try to determine whether the pair energetics might converge to the real dimer dissociation curve, or to another arbitrary function for a dataset that may not contain dimers.

It is worth noting that while nonlinearities inherent in neural network architectures can improve the performance of MLIPs by representing higher-order terms when the

¹Rotational symmetry is preserved through by coupling them with generalized Clebsch-Gordan coefficients, as discussed in the original ACE paper by Drautz [22].

expansion is truncated, caution must be exercised in how they are applied in the sense of keeping the body-ordering faithful [57]. We aim not to build the most accurate potentials but simply to have a slightly more grounded understanding of the ACE framework. As such, we limit our tests to training simpler linear models as well as not employing very high body orders, where returns are diminished.

2.2 Datasets and methods

2.2.1 Datasets

To make the study as controlled as possible, we use elemental structures of carbon and silicon in this work. For carbon, three datasets were used: the first set has 247 dimer structures at distances between 0.5 and 8 Å, with half selected for the validation set. The other two are sets of 1000 structures (out of the 50000 full training set) coming from a collection of carbon allotropes at low pressures, between 0 and 0.1 GPa [58]. One subset is a homogeneous collection of diamond-like structures clustered using a Euclidean distance of configurations X and Y [59, 60],

$$d_{XY} = \frac{1}{2} \left(\frac{1}{N_Y^{\text{at}}} \sum_{i=1}^{N_Y^{\text{at}}} |\mathbf{g}_X - \mathbf{g}_Y|^2 \right)^{1/2}, \quad (2.7)$$

where $\mathbf{g}$ is a vector of some fingerprint vector $\mathbf{G}$ that describes the atomic environment of all atoms in the unit cell for a given configuration. This set is characterized through a histogram of distances to a reference diamond structure in Fig. 2.1. The final set consists of structures obtained using farthest-point sampling [61] to ensure that the subset best represents the diversity from the full set done by SHaidu et al. [60]. We will refer to these two latter subsets as the diamond and diverse subsets. A validation set was constructed from 1000 diverse structures that have not been seen in any of the training sets. The carbon data were calculated using **Quantum Espresso** [62] with the rVV10 functional [63] with basis set kinetic energy cutoff for wavefunctions and charge density at 80 and 480 Ry, respectively as discussed in the original work by Shaidu.

Another dataset of molecular silicon structures taken from [56] was also considered as a simpler case where the maximum K in the basis sets used is comparable to the number of neighbors of the structures. A 90:10 split was done for the training and validation sets.

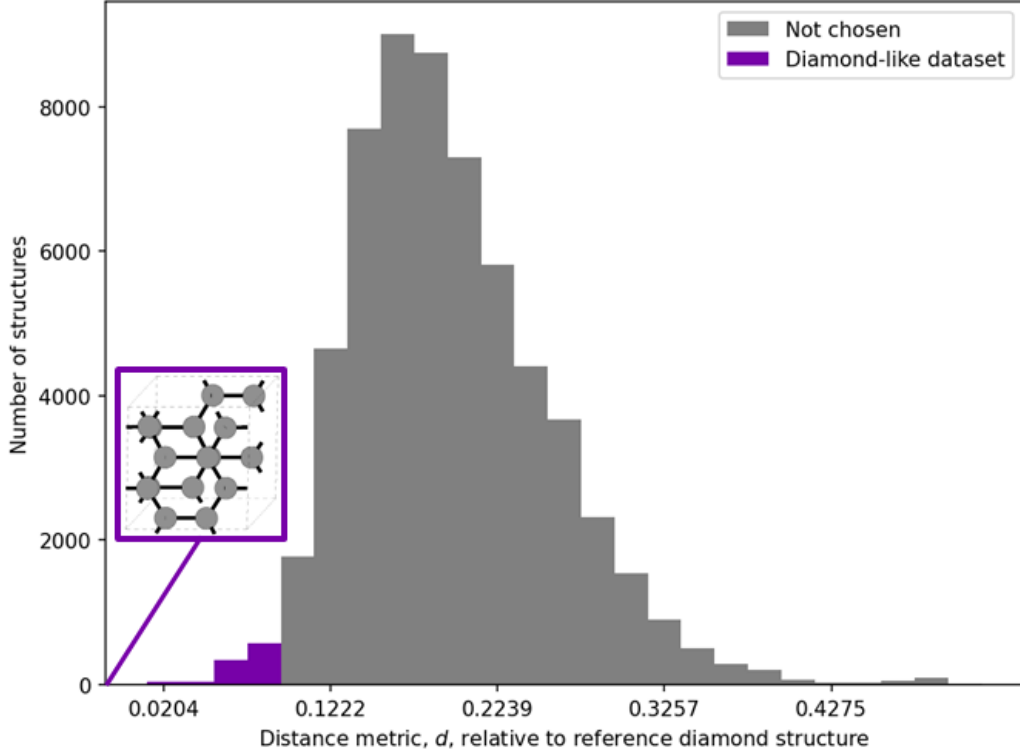


Figure 2.1: Histogram of fingerprint distances of the configurations in the carbon dataset in [60] relative to a reference diamond-like structure (inset).

2.2.2 Descriptors

We use ACE descriptors as implemented in the `pacemaker` [52] and `ACEpotentials.jl` [54] packages. We briefly show the two equivalent forms of the expansion, indicating the usual ACE expansion containing the self-interacting terms and the purified expansion discussed throughout the results.

Expansions begin from the atomic energy E_i found as the summands in Eq. 1.2. They are built from the one-particle basis $\phi_{\mathbf{k}}$ (Eq. 2.2) which are then pooled into the atomic basis $A_{\mathbf{k},i}$ in Eq. 2.3 that describes the neighborhood of atom i . Low n, l were chosen to keep a minimal basis and to maintain rotational symmetry.

From here we specify two different ways to pool the $\phi_{\mathbf{k}}$:

1. First, the self-interacting expansion as described earlier from Eqs. 2.2-2.5,

$$E_i = \sum_{\mathbf{k}} c_{\text{self},\mathbf{k}} A_{\mathbf{k},i}, \quad A_{\mathbf{k},i} = \prod_{t=1}^{\nu} A_{k_t,i} = \prod_{t=1}^{\nu} \sum_j \phi_{k_t}(\mathbf{R}_{ij}). \quad (2.8)$$

The product in Eq. 2.8 is what makes ACE efficient. $A_{\mathbf{k},i}$ scales linearly in the number of neighbors J , whereas the distinct-neighbor sum in Eq. 2.10 scales as $\binom{J}{K}$. The price is the pair interaction with itself², as seen by expanding the

²Note that this is different from the self-interaction of DFT, where a spurious interaction of an

two-body case,

$$\mathbf{A}_{k_1 k_2, i} = \underbrace{\sum_{j_1 \neq j_2} \phi_{k_1}(\mathbf{R}_{ij_1}) \phi_{k_2}(\mathbf{R}_{ij_2})}_{\mathcal{A}_{k_1 k_2, i}^e} + \underbrace{\sum_j \phi_{k_1}(\mathbf{R}_{ij}) \phi_{k_2}(\mathbf{R}_{ij})}_{\text{self-interaction}}, \quad (2.9)$$

2. We avoid the renormalization of terms coming from the self-interactions with a purification algorithm by Ho et al. [55]. Each K -body term is generated from distinct neighbors, and its atomic basis is indicated by $\mathcal{A}_{\mathbf{k}, i}$,

$$E_i = \sum_{\mathbf{k}} c_{\text{pure}, \mathbf{k}} \mathcal{A}_{\mathbf{k}, i}, \quad \mathcal{A}_{\mathbf{k}, i} = \sum_{j_1 \neq \dots \neq j_K} \prod_{t=1}^K \phi_{k_t}(\mathbf{R}_{ij_t}), \quad (2.10)$$

where $\mathcal{A}_{\mathbf{k}, i}$ refers to the pooled basis for the canonical expansion. To avoid the combinatorial construction of the body-ordered terms with the purification operator $\mathcal{P}_g^{k_1 k_2}$ with linearizes the product of one-particle functions $\phi_k(R_{ij})$,

$$\phi_{k_1}(R_{ij}) \phi_{k_2}(R_{ij}) = \sum_g \mathcal{P}_g^{k_1 k_2} \phi_g(R_{ij}), \quad (2.11)$$

where the operator $\mathcal{P}_g^{k_1 k_2}$ are linearization coefficients and the index g runs over all one-particle basis functions that are part of the linearization. Eqs. 2.10 and 2.8 span the same space but distribute energy across body-orders differently.

We provide an example for the differences between bases in Fig. 2.2.

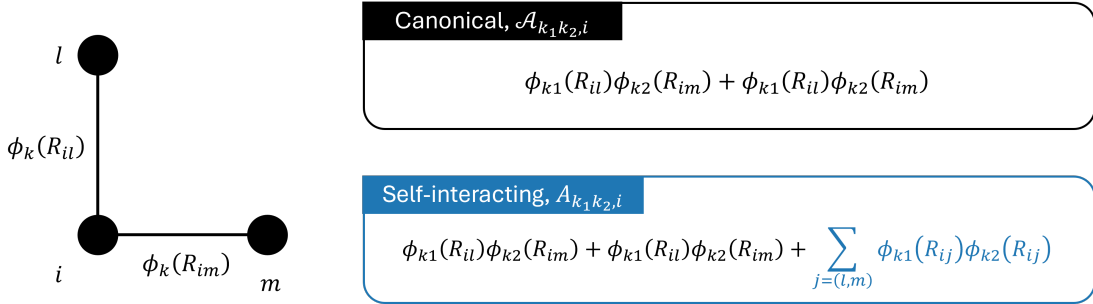


Figure 2.2: Trimer example showing the differences in bases used for the self-interacting and canonical expansion. The terms on the right describe a three-body interaction, surrounding atom i . $\mathcal{A}_{k_1 k_2, i}$ has each term built from unique pairs R_{il}, R_{im} whether built combinatorially or through the purification operator $\mathcal{P}$. The self-interacting counterpart $\mathbf{A}_{k_1 k_2, i}$ will have products of ϕ_k coming from the same pair, which effectively describes a pair, hence the renormalized interaction.

We distinguish the coefficients of the two bases as c_{pure} and c_{self} : the former isolate the contribution of each order, while the latter carry the self-interaction absorbed from *atom* with itself is corrected.

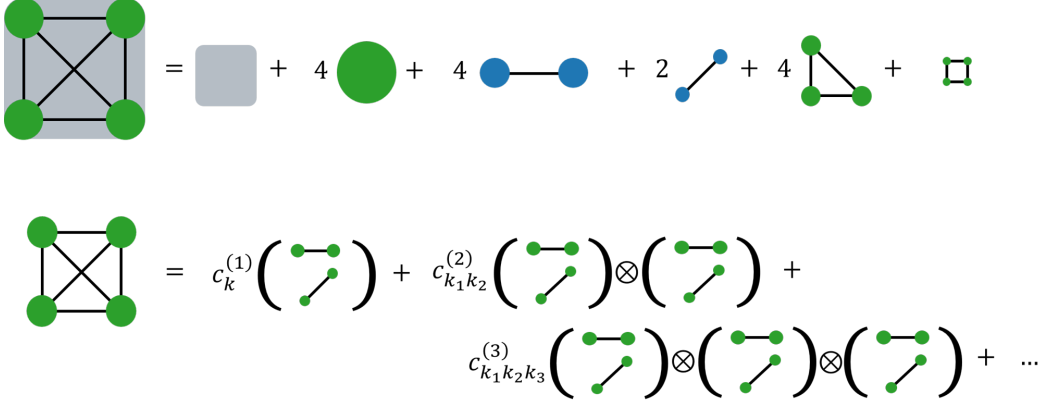


Figure 2.3: Decomposition of the body-ordered energies of a 4-atom system using the (top) canonical and (bottom) self-interacting expansions.

lower orders. A generalized visualization of the difference between the self-interacting and purified bases with the coefficients may be seen in Fig. 2.3.

2.2.3 Fitting protocol

Training was performed with a least-squares error method for both the `pacemaker` and `ACEpotentials.jl` packages. For `pacemaker`, the loss function is,

$$\mathcal{L}_P = (1 - \lambda) \Delta_E^2 + \lambda \Delta_F^2 + \Delta_{\text{coeff}} + \Delta_{\text{rad}}. \quad (2.12)$$

Δ_E^2 and Δ_F^2 are the corresponding energy and force root-mean-square errors (RMSE), and λ is the coefficient that balances energy and force contributions to $\mathcal{L}_P$. Δ_{coeff} penalizes the basis function coefficients, which include both L1 and L2 regularizations. Δ_{rad} regularizes the coefficients of the radial components of the basis function.

On the other hand, `ACEpotentials.jl` minimizes the loss function $\mathcal{L}_A$ through a kernel ridge regression method,

$$\mathcal{L}_A = ||\mathbf{W}(\mathbf{y} - \mathbf{A}\mathbf{c})||^2 + \lambda ||\mathbf{\Gamma}\mathbf{c}||^2, \quad (2.13)$$

where $\mathbf{W}$ encodes the relative loss weightings for energies and forces, $\mathbf{y}$ is the labeled data, and $\mathbf{A}$ is the basis matrix. The model regresses the parameters $\mathbf{c}$ by minimizing $\mathcal{L}_A$. $\mathbf{\Gamma}$ is a more generic L2 regularization matrix, and λ is the hyperparameter coefficient with details discussed in the original paper by Witt et al. [54]. For the regression methods, we used Bayesian Linear Regression to let the model dictate appropriate values for λ and $\mathbf{\Gamma}$. Evaluation of the dimer curves was done using the Atomic Simulation Environment (ASE) [64]. Besides the parameters involving descriptor complexities, other parameters were set to default for both tests to keep the comparison controlled.

For the bases, we start from the $K = 2$ body-ordered functions and introduce more terms of the same order. We validate the models at each addition of basis functions, and check when the current version of the model begins to overfit. Before the validation error deviates from the training error, we introduce higher-order terms from $K = 3$ while keeping the number of lower-order terms fixed, and then repeat the procedure for higher orders up to $K = 5$.

2.3 Results and Discussion

2.3.1 Carbon datasets

The initial test is fitting the dimer dataset with an increasing number of basis functions, N_f , up to 250 elements and $K = 4$ body order. The loss and dimer curves are shown in Fig. 2.4. The colors of the curves indicate the complexity of the basis set used, from exclusively $K = 2$ body order functions, up to $K = 3$ and up to $K = 4$ body orders. The top plot shows the loss $\mathcal{L}_P$ as a function of the number of functions in the system. The validation loss converges even with just two-body functions and overfits with the addition of higher-order functions, jumping 2 orders of magnitude as even more complex functions are added. This is to be expected as the dataset consists solely of 2-body structures. The bottom panel shows the dimer curves of the potentials with the largest N_f for each $K_{\max}$. We see that all potentials are able to reproduce the DFT dimer curve.

The energy loss for the representative potentials is around 5 meV/at, while the force RMSE exceeds 2500 meV/Å for the overfitting potential ($N_f = 250$). This is due to the short-range region of the curve having diverging energies, making the deviation from DFT results more sensitive to errors. A comparison of the forces at the short-range region may be found in Fig. A.1 in the Appendix.

The results for the homogeneous diamond-like dataset are shown in Fig. 2.5. One can see that the training loss from the diamond-trained potentials is considerably lower upon the introduction of $K = 3$ functions. We see that the validation on the diverse set shows overfitting when $K = 4$ functions are added. The dimer curves from these potentials do not show a convergent behavior despite the losses converging already, and they remain far from the expected dimer behavior dictated by DFT. This may be attributed to the dataset not having a diverse collection of structures, resulting in small variations in the radial distribution function and hence a flat curve.

We also look at the dimer curves produced by the diverse sets, but we extend the basis complexity to $K_{\max} = 5$ in Fig. 2.6. For this part, we have also included the full set of 50000 structures. These curves have higher variability compared to the ones produced by the diamond-like dataset. Within a particular $K_{\max}$, there is

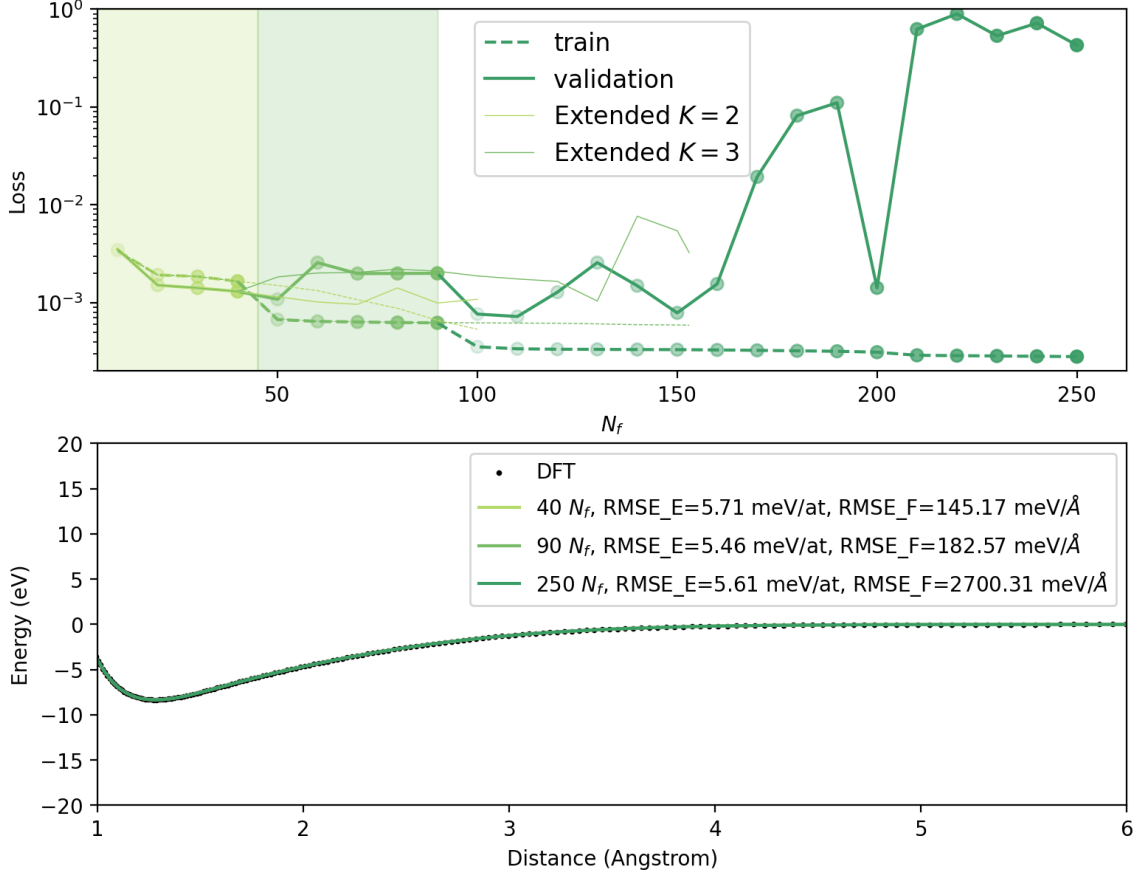


Figure 2.4: (Top) Loss vs. number of basis functions N_f for the dimer dataset. Training and validation errors are presented as dashed and solid curves. Colors indicate potentials built from different basis sets: exclusively two-body or $K_{\max} = 2$ (light green), $K_{\max} = 3$ (green), and $K_{\max} = 4$ functions (dark green). Light solid lines indicate the loss if more functions were introduced without introducing higher K . (Bottom) dimer curves for each of the potentials trained at certain N_f , with reference DFT data as points. Heavy lines represent the potential with the largest N_f before functions of higher K are introduced.

little variability in the curves when more functions are added, but the curves with increasing $K_{\max}$ do not seem to converge even with 5-body ordered terms.

We note that the lack of pairs around the 2.0 Å region is due to the low-pressure nature of the data, which limits the degree of distortion. Both the subset and the full set had a similar distribution of pair distances, owing to the subset being able to represent the full set closely from the farthest point sampling.

Next, we try the same setup using `ACEpotentials.jl` with the diverse subset in Fig. 2.7. The dimer curves show improvements in the equilibrium bond length r_0 and the energy minimum. We can attribute this to `ACEpotentials.jl` requiring additional geometric priors and more rigorous regularization schemes. The routines involving Bayesian Linear Regression used in the code [54] to calculate the coefficients c also allow for the automatic selection of regularization parameters λ in Eq. 2.13 thus

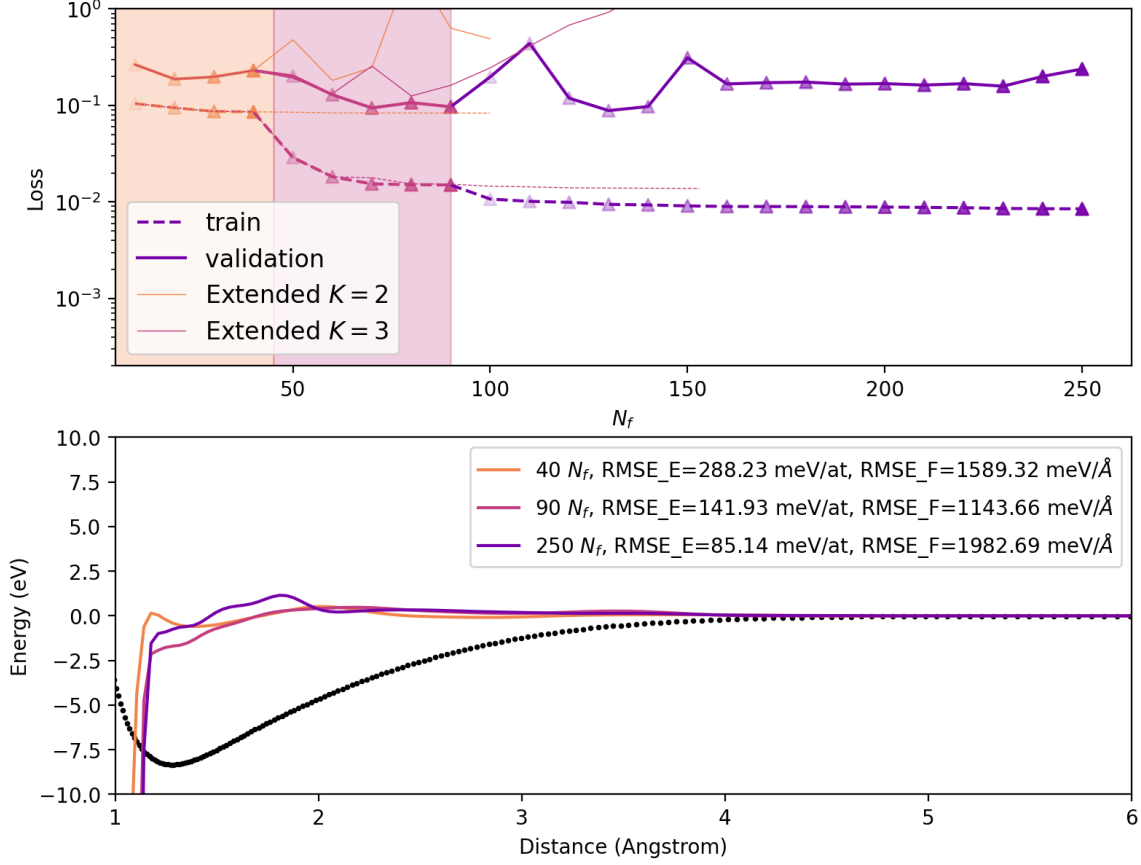


Figure 2.5: $\mathcal{L}_P$ vs. N_f (top) and dimer curves (bottom) for the homogeneous, diamond-like dataset. Orange, pink, and purple plots correspond to $K_{\max} = 2, 3$, and 4 potentials, respectively. Black dots indicate reference DFT values. The x-values of the dimer curve start at the minimum distance found in the homogeneous dataset.

reducing the number of hyperparameter sweeps done. In contrast, **pacemaker** lacks a more detailed radial basis construction³, so the qualitative features of its curves rely more heavily on a richer dataset.

Still, it seems that the potentials made from purified bases do not produce a marked improvement over the self-interacting basis, as seen from the overlapping curves. Despite this, the study of the Gram conditioning matrix from [55] indicates that the potentials lose stability when the total number of neighbors J exceeds $K_{\max}$ of the basis used to describe the potential.

We also compare the performance of the linear models through their losses to the performance of different bespoke MLIPs trained on the same dataset in [65] in Table 2.1⁴. We found that the linear ACE models with the most complex descriptor

³The radial basis construction in **pacemaker** focuses on inner cutoffs that penalize oscillatory behavior at the short-range regions where data is absent, but optimizing this region is outside of the scope of this work.

⁴ACEpotentials.jl has no results from $n_{\text{set}} = 50000$ due to memory issues.

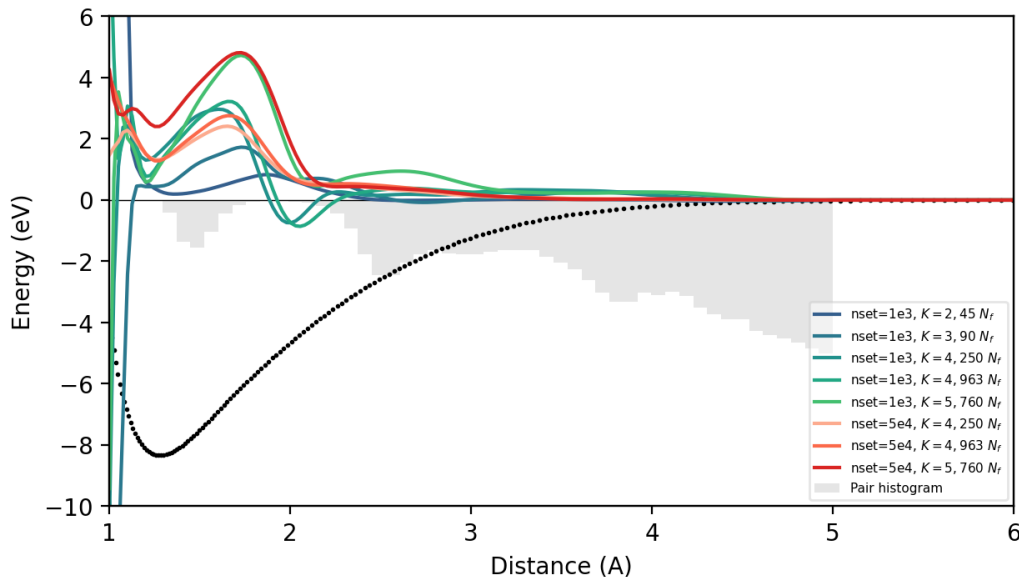


Figure 2.6: Dimer curves for the diverse 1000-structure (blue-green) and 50000-structure (orange-red) datasets for various descriptor sizes. Histogram of pair distances across the full dataset are included in gray. No convergence is observed for either set as higher K functions are introduced.

sets were able to outperform all PANNA potentials and even the $l = 1$ version of the NequIP potential [66]. We may attribute the poor performance of the neural network potentials to the fact that 1000 structures may not be enough, and the resulting potentials may overfit given the limited data. However, the linear models still perform relatively worse than their NN counterparts when the full carbon set is used, suggesting that nonlinearities provide the improvement in training larger datasets. Despite this, the inability of the linear models to capture the two-body interaction is not due to poor losses, but to the nature and truncation of the expansion used.

2.3.2 Silicon datasets and the purified bases

A similar investigation was done on a dataset of silicon structures. These contain dimers, trimers, tetramers, and pentamers, so the maximum number of neighbors matches $K_{\max} = 5$. We train potentials from subsets of 100 trimers, 100 tetramers, and 500 pentamers, and a mixture of the structures leaving out the dimers to mimic the diverse carbon set setup. Fig. 2.8 shows that the out-of-distribution (OOD) silicon potentials, those trained without dimers, also have curves that do not converge to the DFT result. Additionally, the mixed (Si_{345}) set bears the closest resemblance to the diverse carbon dataset. The potentials trained from this set also exhibit the overlapping of purified and self-interacting potentials. The non-overlapping expansion coefficients may suggest the instability of the solutions for the potentials at different K .

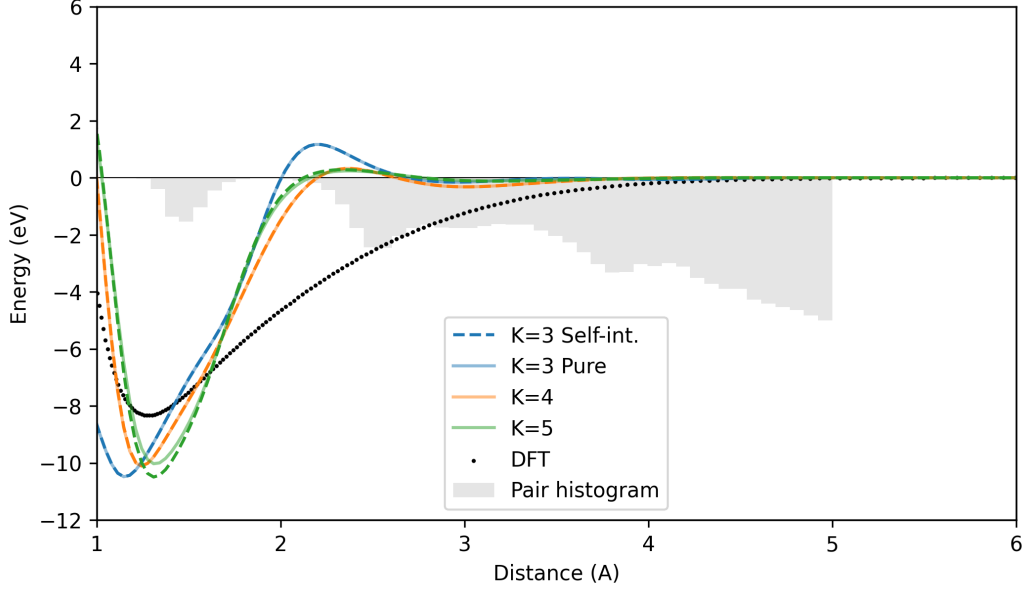


Figure 2.7: Dimer curves for the 1000-structure carbon dataset obtained from the ACEpotentials.jl model. Dashed lines indicate the ACE basis ($K_{\max} = 3, 4, 5$) with self-interactions similar to the one in pacemaker, while the solid lines are trained with a basis purified of self-interactions. Using a purified basis for the carbon dataset yields practically identical dimer curves to those from the self-interacting basis for $K_{\max} = 4$, with a qualitative difference in the energy well for the $K_{\max} = 5$ potential.

For the potentials trained from pure trimers (Si_3), we see signatures of convergence in the purified basis. The dimer curves at all $K_{\max}$ overlap, and the basis coefficients c_{pure} for the 2- and 3-body functions (in the blue region) are consistent with each other. The pure coefficients corresponding to $K \geq 4$ functions are zero, suggesting that the self-interactions are absent. In the tetramer-trained potentials, curves for the $K_{\max} = 3$ basis set already deviate from the others due to the lower-order c_{pure} misrepresenting the higher-order tetramer interactions. A similar trend is seen for the pentamer-trained potentials with the $K = 4$ basis sets, which misrepresent the higher-order interactions. Overall, the features from the dimer curves do not converge as basis functions become more complex with higher K . This makes it difficult to apply the potentials to structures not present in the training sets.

While generalization to the DFT curve did not occur, we can still see how the purified coefficients of the models perform when doing interpolative tasks and dimers are included in the training set, which we call in-domain testing. It can be seen in Fig. 2.9 that all curves converge to the DFT results regardless of the $K_{\max}$ of the potentials. By also looking at the coefficients of the potentials we see that the purification method is successful in disentangling lower-order terms from the contributions of functions at higher K . We also note a similar set for c_{self} and c_{pure} for the dimer-trained potentials. This may be because the self-interaction terms are not needed to

Table 2.1: Comparison of linear ACE models to neural network potentials in MAE for energies and forces for the carbon dataset in [60] for datasets containing $n_{\text{set}} = 1000$ and 50000 structures. Energy errors (E) with respect to the DFT results are in meV/atom and force components (F) are in meV/Å.

	$n_{\text{set}} = 1000$		$n_{\text{set}} = 50000$	
Linear Potentials	E	F	E	F
pacemaker				
$K = 4, N_f = 250$	48.50	241.27	44.06	222.42
$K = 4, N_f = 493$	18.30	199.23	17.55	176.48
$K = 4, N_f = 930$	15.40	167.73	15.27	166.70
$K = 5, N_f = 793$	14.88	160.78	14.74	159.80
ACEpotentials.jl				
$K = 3, N_f = 297$	38.10	336.84	-	-
$K = 4, N_f = 802$	18.00	210.14	-	-
$K = 5, N_f = 929$	16.72	202.78	-	-
Neural Networks				
PANNA small	22.40	248.85	17.76	162.37
PANNA mid	20.93	241.36	12.41	137.45
PANNA big	17.88	242.02	8.21	166.95
NequIP $l = 1$	20.40	213.00	7.96	110.00
NequIP $l = 2$	6.83	105.00	5.21	51.40
MACE	6.81	103.14	1.82	51.31

describe the energetics for just the dimers.

Finally, we check the mismatch of the overlap of c_{pure} in the $K = 2, 3$ functions for the Si_{234} sets and the $K = 2, 3, 4$ functions for the Si_{2345} sets. These mismatches may be signatures of aliasing that happens because the basis is not complex enough to capture the higher orders of the many-body expansion. To get a deeper look at the stability of the pair potential, we look at the c_{pure} of the $K = 2$ functions for datasets where K_{max} matches the maximum number of particles J in Fig. 2.10. We include the Si_2 potential with the $K = 3$ basis as the reference coefficient set. Interestingly, no other potential captured the reference coefficients completely, with greater deviations coming from the Si_{234} and Si_{2345} potentials. The high validation error for the Si_{234} suggests that more $K = 5$ basis functions are needed as well as more pentamer structures.

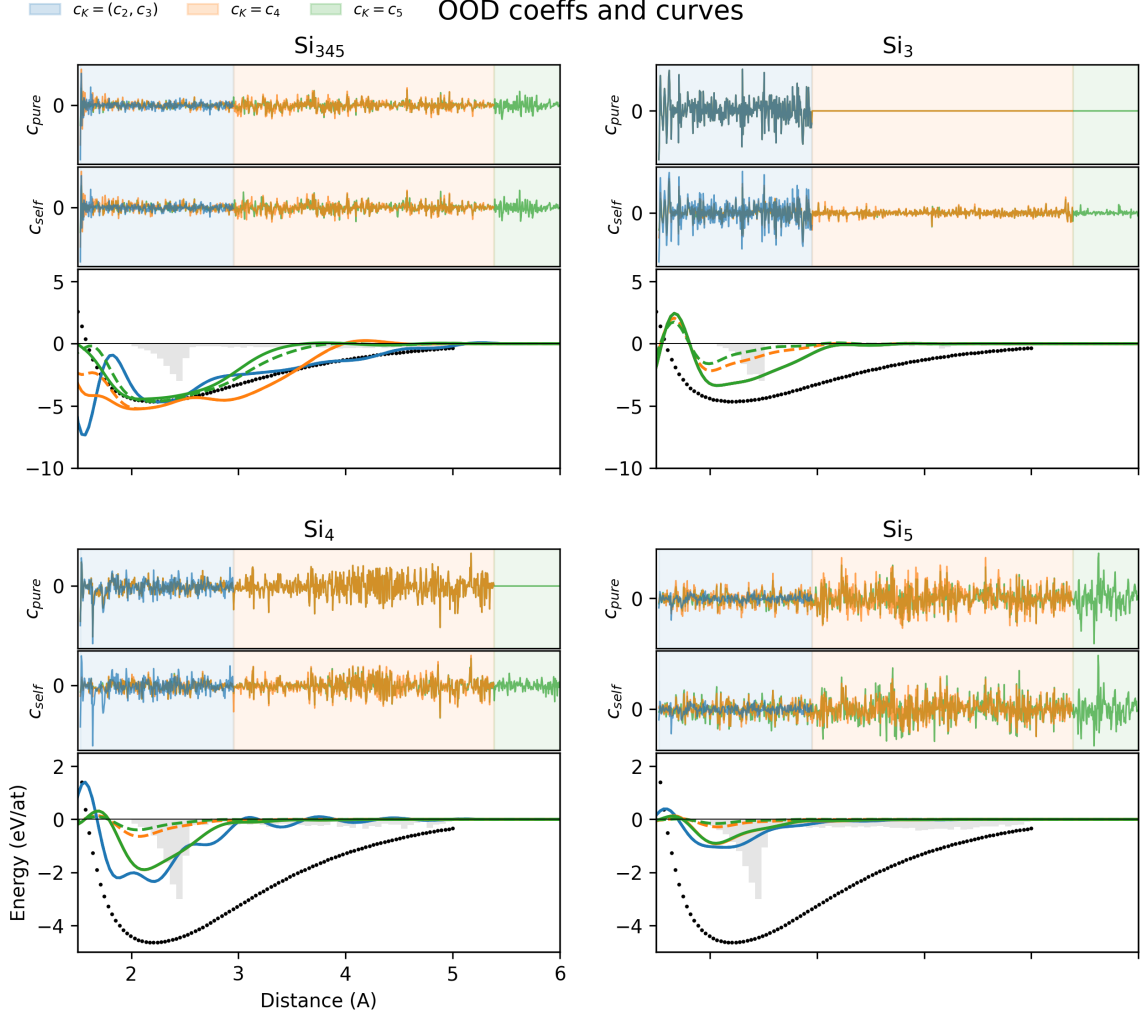


Figure 2.8: (Bottom of each quadrant) Dimer curves of potentials from the silicon structures in [56] trained on different subsets. Si_{mn} indicates that potentials were trained from datasets that include m -mers and n -mers, black points show the DFT dimer energies, and gray bars indicate the distributions of pairs in the dataset. (Upper plots of each quadrant) Coefficients of the purified (c_{pure}) and self-interacting (c_{self}) potentials. Blue, orange, and green lines correspond to coefficients of potentials capped at $K = 3$, $K = 4$, and $K = 5$ body-ordered functions while blue, orange, and green shaded regions indicate coefficients corresponding to $K = 3$, $K = 4$, and $K = 5$ body-ordered functions.

2.4 Convergence of the MBE in tight-binding models

Although MLIPs are excellent interpolants, their ability to extrapolate remains questionable. Without the purification of self-interactions in ACE-based models that effectively decouple terms of different orders, convergence of clusters by body-order remains difficult. While formulating a training protocol to train order-by-order seems to be the next step (i.e., obtaining low and stable errors in the two-body terms first,

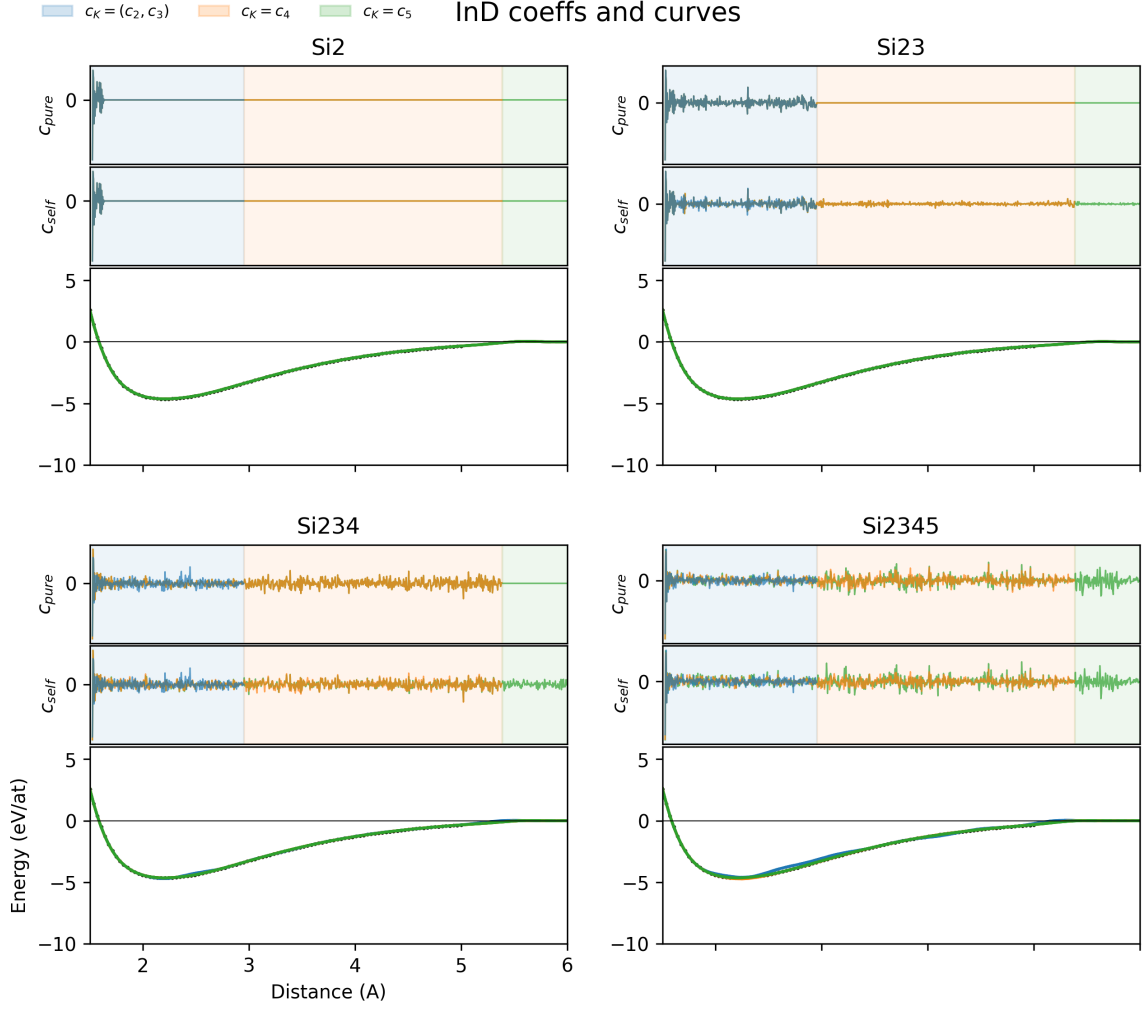


Figure 2.9: (Top of each quadrant) ACE coefficients and (bottom of each quadrant) dimer curves of silicon potentials trained on different subsets, including dimers in all of them. All dimer curves recover the correct DFT values, and purified potentials behave as expected with no higher-order renormalizations. All c_{self} , except for the Si_2 training, had higher-order renormalizations as seen in the nonzero $K = 3, 4$ coefficients for Si_{23} and $K = 4$ for Si_{234} . c_{pure} coefficients are similar for the $K = 2, 3$ terms in Si_{23} -trained potentials, and similar for $K = 4$ terms in the Si_{234} potentials.

then three-body, etc.), we want to verify if a typically assumed empirical convergence of cluster expansions is true. Thus we try to answer the question: how does the canonical cluster expansion converge in body-orders when using simple data such as purely dimers or trimers, without help from the model?

This section responds to the recent results from Chong et al. [42], which challenges the claim that body-ordering helps ACE-based potentials [52, 54] learn lower-dimensional representations. We try to investigate conditions at which the expansion is convergent. In [42], hydrogen clusters of m -mers ($m = 2, \dots, 8$) were sampled from earlier ab-initio work on Hydrogen clusters by Cheng et al. [67], and their energetics were calculated for each m -mer. Fig. 2.11 shows the m -mer convergence from

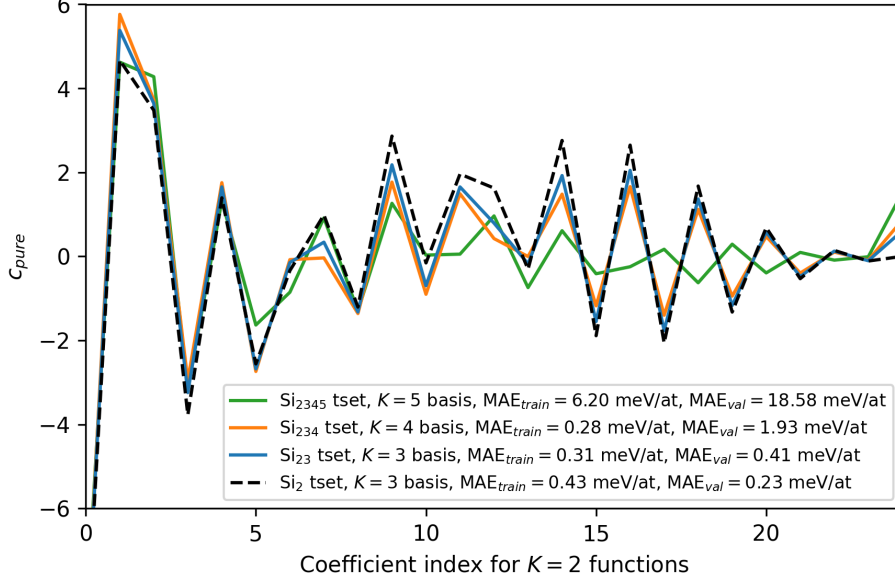


Figure 2.10: c_{pure} of the $K = 2$ basis functions for potentials with basis complexities matching the max number of particles, $K = J$.

two subsets: clusters with low density ρ and high-pressure bulk at high ρ ⁵. Results were surprising because the body-orders were not converging for either subset as m increases. The energetic contributions of the higher m -mers were not decaying fast enough for different levels of theory: from MLIPs, to DFT, and even methods using density matrix renormalization group (DMRG). Upon further investigation, it seems that not only does this poor convergence of MBEs apply to structures with poor symmetries such as surfaces in [11], but it is more of a rule than an exception.

2.4.1 Nonconvergence of hydrogen clusters

Further work on body-ordering in MLIPs [42] showed body-ordered decomposition experiments of hydrogen octamers, with specific energetics tied to a particular sub-cluster. We review the pertinent equations following their notation. The many-body expansion (MBE) of a system/structure A of N atoms is given by,

$$E_A(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) = \sum_{i=1}^N V^{(1)}(\mathbf{R}_i) + \sum_{i < j} V^{(2)}(\mathbf{R}_i, \mathbf{R}_j) + \sum_{i < j < k} V^{(3)}(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) + \dots + V^{(N)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N), \quad (2.14)$$

⁵High density clusters were created by taking a random hydrogen bulk configuration, and selecting the $m - 1$ nearest neighbors to create a dataset of m -clusters. Low density clusters were sampled by selecting each atom and its nearest neighbor, then adding the other necessary pairs of atoms to create the m -mer. Additional details of the sampling may be read from the work by CHong et al. in [42].

where i, j, k are atom indices and $\mathbf{R}$ are the corresponding positions. They define the clusters $V^{(m)}$ as the energetics of the m -th body order with lower-order contributions removed,

$$V^{(m)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_m) = E^{(m)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_m) - \sum_{1 \leq K < m} \sum_{i' < j' < \dots < K'} V^{(K)}(\mathbf{R}_{i'}, \mathbf{R}_{j'}, \dots, \mathbf{R}_{K'}). \quad (2.15)$$

The inner sum is identical to the one in Eq. 2.14 and the outer sum contains all the lower-order contributions.

The body-orderedness of the systems was tested by extracting hydrogen m -mers H_m from structures generated in [67]. Along with keeping consistency with the study of body-orderedness done by Chong, Hydrogen is the simplest choice in showing the convergence, especially when calculating on the tight-binding level of theory as will be done in Sec. 2.4.2. Different levels of theory (DMRG, DFT (PBE, B3LYP), MLIPs) were tested to show how each order m was contributing to the total system energy. For a fair comparison, the m -th order contribution was normalized by both the combinatorial weight and the number of atoms in the cluster,

$$\tilde{V}_A^{(m)} = \frac{\sum_{i < j < \dots < m} V^{(m)}(\mathbf{R}_i, \mathbf{R}_j, \dots, \mathbf{R}_m)}{\frac{N!}{m!(N-m)!} \cdot m}, \quad (2.16)$$

which showed non-convergent behavior for all levels of theory, regardless of whether the m -mers were sampled from low- or high-density structures. For the last part, we

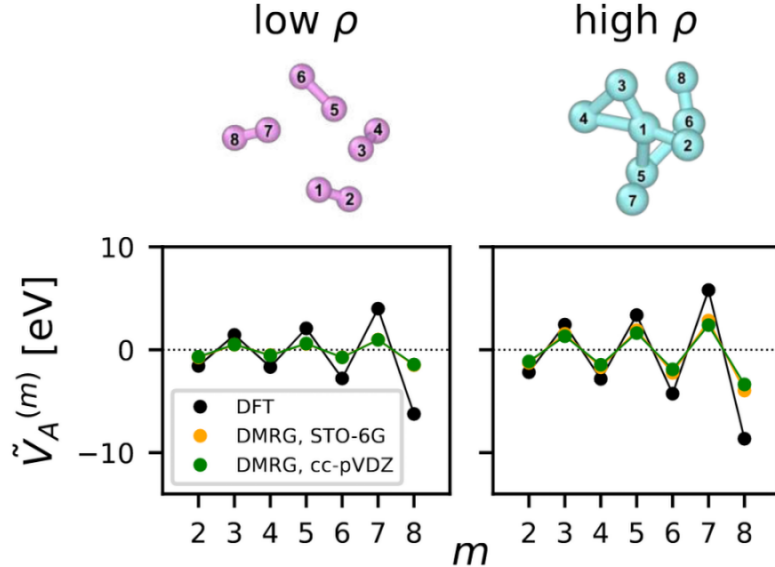


Figure 2.11: Alternating energetics of $\tilde{V}_A^{(m)}$ for structure A and subcluster m . Taken from [42].

investigated if this non-convergent trend is present in the opposite direction: a lower

level of theory, namely tight-binding models.

2.4.2 Tight-binding approximation on m -mers

Consider a two-atom system, situated at positions $\mathbf{R}_A, \mathbf{R}_B$. A generic wavefunction describing the system is a linear combination of atomic states,

$$|\psi\rangle = c_A|A\rangle + c_B|B\rangle.$$

We obtain the dimer energy from the following secular equation,

$$\begin{vmatrix} E_{\text{at}} - \varepsilon & t_{AB} \\ t_{AB} & E_{\text{at}} - \varepsilon \end{vmatrix} = 0. \quad (2.17)$$

Without loss of generality, we shift energies such that $E_{\text{at}} = 0$ leading to eigenvalues $\varepsilon = \pm t_{AB}$. Assuming ground state conditions, we expect the eigenstate with the lower energy to be filled since the hopping term is attractive, $t_{AB} \leq 0$. Finally, the system has both electrons occupying the lowest state⁶, $\varepsilon = +t_{AB} < 0$. The total energy $E^{(2)}$ is then just the sum of the eigenenergies. Since $m = 2$ is the smallest subcluster,

$$E^{(2)} = 2t_{AB} = V^{(2)}(\mathbf{R}_{AB}), \quad (2.18)$$

where $\mathbf{R}_{AB}$ is the distance between atoms A and B .

In the case of a trimer ($m = 3$), the wavefunction is now a linear combination of three states,

$$|\psi\rangle = c_A|A\rangle + c_B|B\rangle + c_C|C\rangle.$$

There will also be three electrons to fill the energy levels. Two will occupy the lowest level due to spin degeneracy, and another one will occupy the next lowest energy. The secular determinant is,

$$\begin{vmatrix} -\varepsilon & t_{AB} & t_{AC} \\ t_{BA} & -\varepsilon & t_{BC} \\ t_{CA} & t_{CB} & -\varepsilon \end{vmatrix} = 0. \quad (2.19)$$

From symmetry, $t_{ij} = t_{ji}$. The corresponding characteristic equation is,

$$-\varepsilon^3 + 2t_{AB}t_{BC}t_{CA} + \varepsilon(t_{AB}^2 + t_{BC}^2 + t_{CA}^2) = 0. \quad (2.20)$$

When all three particles interact, Eq. 2.20 has a closed form and so does the total

⁶Assume that the two spin states are degenerate.

trimer energy ground state,

$$E^{(3)} = 2\varepsilon_0 + \varepsilon_1. \quad (2.21)$$

$\varepsilon_0, \varepsilon_1$ are the ground and first excited energy levels, respectively. Trimer subcluster energetics following Eq. 2.15 for $m = 3$ for a configuration A are determined from,

$$\begin{aligned} V_A^{(3)} &= E^{(3)} - \sum_{1 \leq K < 3} \sum_{i' < j' < \dots < K'} V^{(K)}(\mathbf{R}_{i'}, \mathbf{R}_{j'}, \dots, \mathbf{R}_{K'}), \\ &= E^{(3)} - \sum_{i' < j'} V^{(2)}(\mathbf{R}_{i'}, \mathbf{R}_{j'}), \\ V_A^{(3)}(\{t_{ij}\}) &= 2\varepsilon_0(\{t_{ij}\}) + \varepsilon_1(\{t_{ij}\}) - 2(t_{AB} + t_{BC} + t_{CA}). \end{aligned} \quad (2.22)$$

We also use Eqs. 2.18 and 2.21 for $V^{(2)}$ and $E^{(3)}$, respectively. The parameters $\{t_{ij}\}$ can be obtained by parametrizing an H_2 dimer curve, and give us the trimer eigenenergies.

2.4.3 Parametrizing hopping terms

We parametrize t_{ij} from SCF calculations using Quantum Espresso at the same level of theory and parameters from PBE calculations of bulk Hydrogen in [67], using `ecutwfc=80.0` with a smearing of `2e-3`. $H_2(\mathbf{R})$ was fit using a generic Morse interatomic potential [2],

$$V_{\text{fit}}^{(2)}(r) = U_0 \left(e^{n(1-r/r_0)} - 2e^{n(1-r/r_0)/2} \right), \quad (2.23)$$

where U_0 is the well depth, r_0 is the equilibrium bond distance, and n controls the well width. Before fitting the DFT data, we shift the energies by setting the energy of the configuration with the largest r to be $E^{(2)}(r_{\text{max}}) = 0$. From this procedure we get⁷ $E_{\text{at}} = -0.918960405$ Ry. Optimized parameters were then obtained using a nonlinear least squares fit in `scipy`, and are: $U_0 = 6.71959298$, $r_0 = 0.79502698$, $n = 2.3883543$. We then use the parametrized form of Eq. 2.23 to calculate the hopping term via Eq. 2.18,

$$t_{ij} = \frac{1}{2} V^{(2)}(\mathbf{R}_{ij}),$$

on a set of configurations $\{A\}$. We try this on a set of simple hydrogen trimers that are rescaled from silicon structures in an earlier study of uncertainty measures for ACE potentials in [56]. Both the cell dimensions and the positions are rescaled according to the nearest neighbor distance.

⁷Divide $E^{(2)}(r_{\text{max}})$ by 2. The departure of the result from the expected 1 Ry may come from the computational choices (e.g., PBE pseudopotential, `ecutwfc=80`, etc.) aiming to be consistent with [67].

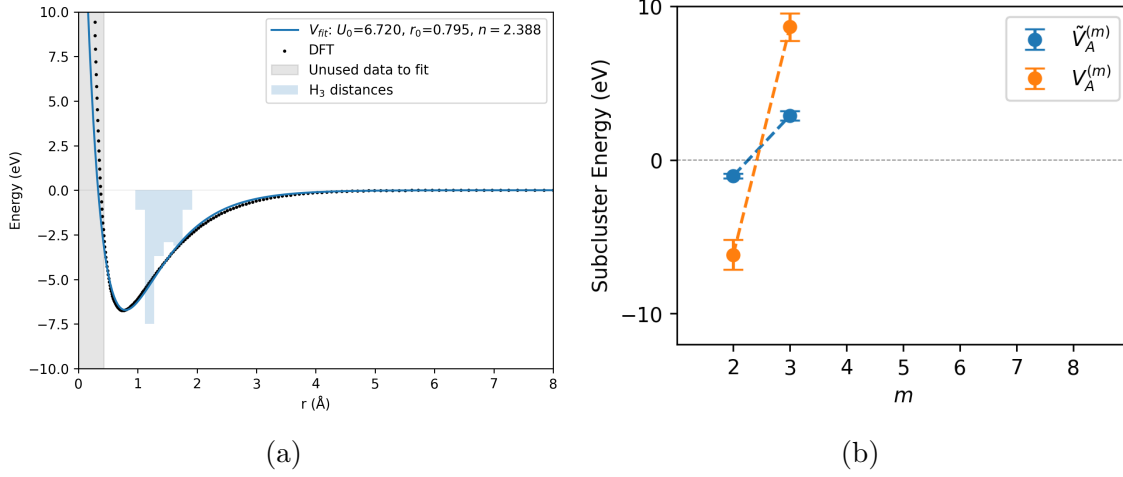


Figure 2.12: (a) Fitted Morse potential, V_{fit} , for hydrogen dimer data calculated using similar parameters and pseudopotentials in [67]. Repulsive region ($r < 0.43$ Å) not included in fit. Distances in the rescaled H_3 dataset are indicated in light blue. (b) Recreated subcluster contribution plots from [42] using the H_3 dataset rescaled from Si_3 data from [56]. Blue and orange markers show normalized subcluster values, $\tilde{V}_A^{(m)}$, in Eq. 2.16 and base values, $V_A^{(m)}$, in Eq. 2.15, respectively.

2.4.4 Trimer cases

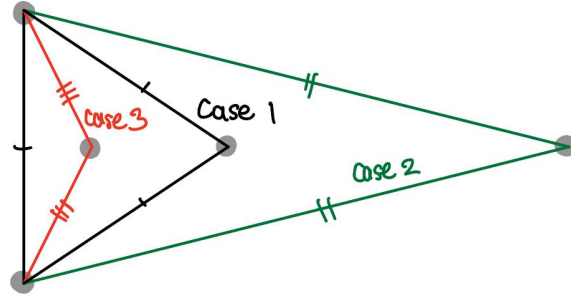


Figure 2.13: Geometric cases for the trimer: case 1 equilateral, case 2 isolated atom, and case 3 quasi-linear molecule.

In case 1 of Fig. 2.13, the interaction t is constant. The relevant determinant in the atom basis is,

$$\begin{vmatrix} |A\rangle & |B\rangle & |C\rangle \\ -\varepsilon & t & t \\ t & -\varepsilon & t \\ t & t & -\varepsilon \end{vmatrix} = 0, \quad (2.24)$$

leading to the characteristic equation, $\varepsilon^3 - 3t^2\varepsilon - 2t^3 = 0$. The eigenvalues are $\varepsilon_0 = 2t$,

and two degenerate $\varepsilon_{1/2} = -t$ ⁸. $E^{(3)}$ and the subcluster $V^{(3)}$ are then,

$$E^{(3)} = 2\varepsilon_0 + \varepsilon_1 = 2(2t) - t = 3t, \quad (2.25)$$

$$V^{(3)} = E^{(3)} - \sum_{i' < j'} V^{(2)}(\mathbf{R}_{i'}, \mathbf{R}_{j'}) = 3t - 3(2t) = -3t > 0. \quad (2.26)$$

Recalling from Eq. 2.18 that $V^{(2)} = 2t$, we see that the $K = 2$ and $K = 3$ energies have opposite signs.

In case 2 of Fig. 2.13 we consider the isosceles trimer with a base corresponding to the interaction $t_{AB} = t$ and the legs corresponding to $t_{AC} = t_{BC} = w$. The secular determinant is,

$$\begin{vmatrix} |A\rangle & |B\rangle & |C\rangle \\ -\varepsilon & t & w \\ t & -\varepsilon & w \\ w & w & -\varepsilon \end{vmatrix} = 0.$$

We first consider the limiting case of $w = 0$ corresponding to atom C being fully isolated from the dimer. The system reduces to two degrees of freedom leading to the eigenvalues $\varepsilon_0 = t, \varepsilon_1 = 0, \varepsilon_2 = -t$. The eigenvectors corresponding to $\varepsilon_0/\varepsilon_2$ will be the bonding/antibonding pair. The total energy will only come from the dimer without any 3-body interaction so, $E^{(3)} = 2t$ and $V^{(3)} = 2t - 2t = 0$.

When all atoms interact we have,

$$\begin{pmatrix} 0 & t & w \\ t & 0 & w \\ w & w & 0 \end{pmatrix}. \quad (2.27)$$

The dominant $V^{(2)}$ interaction is t , so we intuit a transformed basis where the isolated atom C interacts with the bonding/antibonding states of A and B ,

$$\{|\psi\rangle\} = \left\{ \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}, \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right\}. \quad (2.28)$$

We then represent the Hamiltonian in Eq. 2.27 in this basis and swap the second and

⁸In the atomic basis, the corresponding eigenvectors are,

$$|\psi_0\rangle = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \quad |\psi_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}, \quad |\psi_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \\ 0 \end{pmatrix},$$

but in principle other suitable orthonormal vector pairs in the degenerate subspace of $\varepsilon = -t$ can be chosen.

third basis states (rows and columns) to get a block diagonal form,

$$\begin{aligned}
H' &= \begin{pmatrix} t & 0 & \sqrt{2}w \\ 0 & -t & 0 \\ \sqrt{2}w & 0 & 0 \end{pmatrix} \\
H' &= \begin{array}{c|ccc} & |\psi_1\rangle & |C\rangle & |\psi_2\rangle \\ \hline \langle\psi_1| & t & \sqrt{2}w & 0 \\ \langle C| & \sqrt{2}w & 0 & 0 \\ \langle\psi_2| & 0 & 0 & -t \end{array}. \tag{2.29}
\end{aligned}$$

Solving for the upper left block gives,

$$\varepsilon_{\pm} = \frac{t}{2} \left(1 \pm \sqrt{1 + 8 \left(\frac{w}{t} \right)^2} \right). \tag{2.30}$$

Since the full trace vanishes and $\varepsilon_2 = -t$, we have $\varepsilon_+ + \varepsilon_- = t$. As $t < 0$, ε_+ is the lowest out of the three eigenvalues. Checking which is the next highest eigenvalue,

$$\begin{aligned}
\varepsilon_- &\geq \varepsilon_2 \\
\sqrt{1 + 8 \left(\frac{w}{t} \right)^2} - 1 &\geq 2 \\
\varepsilon_- &< \varepsilon_2. \tag{2.31}
\end{aligned}$$

Note that this inequality is conditional on the ordering of eigenvalues. Once done, we can then get the total energy of the system,

$$E^{(3)} = 2\varepsilon_+ + \varepsilon_- = t \left(\frac{3}{2} + \frac{1}{2} \sqrt{1 + 8 \left(\frac{w}{t} \right)^2} \right), \tag{2.32}$$

as well as the $m = 3$ subcluster contribution,

$$V^{(3)} = E^{(3)} - \sum_{\{r_{ij}\}} V^{(2)}(r_{ij}) \tag{2.33}$$

$$\begin{aligned}
&= t \left(-\frac{1}{2} - 4 \left(\frac{w}{t} \right) + \frac{1}{2} \sqrt{1 + 8 \left(\frac{w}{t} \right)^2} \right) \\
V^{(3)} &\approx t \left(2 \left(\frac{w}{t} \right)^2 - 4 \left(\frac{w}{t} \right) \right), \tag{2.34}
\end{aligned}$$

where we use the approximation $w \ll t$. We want to see if $V^{(3)}$ decays faster than $V^{(2)}$. Looking explicitly,

$$\sum V^{(2)} = t \left(4 \left(\frac{w}{t} \right) + 2 \right). \tag{2.35}$$

Eqs. 2.34–2.35 show that $V^{(3)}$ and $V^{(2)}$ both scale linearly with w/t , which is curious as the typical notion that higher body orders decay faster seems not to hold even for a simple case.

For the last case corresponding to the red lines of Fig. 2.13, the Hamiltonian is similar to Eq. 2.27, but with the symmetric interaction stronger, $w \gg t$. Doing similar calculations as done in the isolated atom case, we have the energies and 3-body subcluster contributions as,

$$E^{(3)} = t \sqrt{1 + 8 \left(\frac{w}{t}\right)^2}, \quad (2.36)$$

$$V^{(3)} = t \left(\sqrt{1 + 8 \left(\frac{w}{t}\right)^2} - \left(2 + 4 \left(\frac{w}{t}\right)\right) \right). \quad (2.37)$$

We compare with the two-body subcluster, $\sum V^{(2)} = t(4w/t + 2)$, and note that the limiting behaviors are when the particles are collinear (corresponding to $w/t = 2$), and when the triangle becomes equilateral, with $w/t = 1$. The three cases are summarized in Fig. 2.14. We see the non-smooth behavior at the equilateral case due to how $E^{(3)}$ is calculated: the ordering of the eigenenergies is changed upon moving from the isolated atom to the quasilinear case.

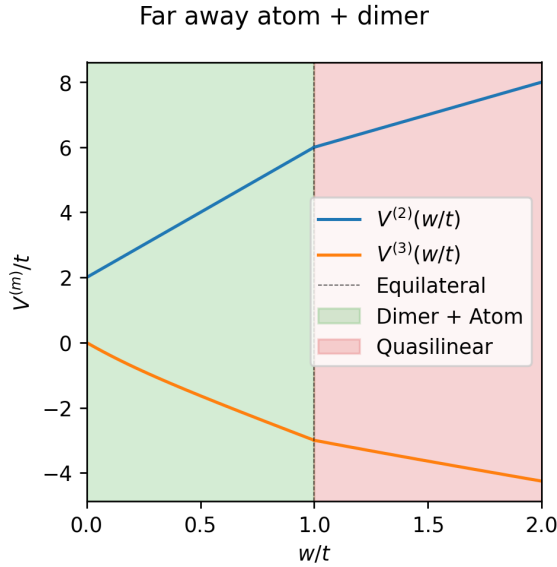


Figure 2.14: Subcluster $V^{(m)}/t$ for the three cases as a function of w/t . Non-smooth behavior in the equilateral case, $w/t = 1$, due to switching of second lowest ε for the $E^{(3)}$ calculation according to Eq. 2.21.

2.4.5 Fully symmetric H-clusters

The trimer cases above suggest that the higher body orders do not intuitively converge. This is made explicit by a case that can be solved for arbitrary size: the fully

symmetric cluster of N hydrogen atoms, where each pair interacts with the same hopping $t < 0$, so that $H_{ij} = t(1 - \delta_{ij})$. With all atomic offsets set to zero, the many-body expansion collapses to a purely combinatorial sum, $E^{(N)} = \sum_K \binom{N}{K} V^{(K)}$, since all subclusters of a given order K are equivalent,

$$HU = \begin{pmatrix} 0 & t & \dots & t \\ t & 0 & \ddots & t \\ \vdots & \ddots & \ddots & t \\ t & \dots & t & 0 \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \\ \vdots \\ U_N \end{pmatrix} = \varepsilon U. \quad (2.38)$$

The eigenvectors $U_{a,j} = N^{-1/2} e^{i2\pi aj/N}$ diagonalize H exactly, with the phases summing to zero for every $a \neq 0$, and gives the spectrum

$$\varepsilon_a = \begin{cases} (N-1)t, & a = 0 \\ -t, & a = 1, \dots, N-1, \end{cases} \quad (2.39)$$

i.e., a single bonding level and an $(N-1)$ -fold degenerate manifold. Filling the N electrons with spin degeneracy, $E^{(N)} = 2\varepsilon_0 + (N-2)\varepsilon_{(a \neq 0)} = Nt$ for $N \geq 2$ (with $E^{(0)} = E^{(1)} = 0$): the total energy is strictly linear in cluster size, as each added atom contributes one bond's worth of energy regardless of how many pairs it forms.

Inverting the expansion order by order, $V^{(N)} = E^{(N)} - \sum_{K < N} \binom{N}{K} V^{(K)}$, then yields

$$V^{(N)} = (-1)^N Nt, \quad N \geq 2, \quad (2.40)$$

which is confirmed in closed form by recognizing the alternating sum as a derivative of the binomial expansion of $(1-x)^N$ evaluated at $x = 1$.

Eq. 2.40 highlights a curious result that supports the trimer investigations and corroborates results from [42] as seen in Fig. 2.11: body-order contributions grow linearly in magnitude while alternating in sign. The linear total energy Nt is recovered only through the near-total cancellation of terms that individually diverge with N , so truncating the expansion at an arbitrary order has no guarantee of convergence. This is the symmetric N -body extension of the trimer result of Sec. 2.4.4, where $V^{(3)}$ was already found to decay no faster than $V^{(2)}$. In fact, a study by Hermann et al. in 2007 [68] shows that the MBE does not generally converge, and only convincingly does so for closed-shell systems such as noble gases. A more detailed discussion may be found in Appendix A.3.

2.5 Summary

Overall, we endeavored to determine if there is a systematic way to converge cluster expansions order by order, and our results were published in [1]. Looking at simple elemental systems of carbon and silicon, in-domain and out-of-domain tests were done in determining convergence to the pair interactions. Our tests show that all extrapolative tests failed to capture the correct dimer curves predicted by DFT, while the in-domain tests show that signatures of body-ordered convergence appear only when the non-orthogonal ACE basis is purified to recover the canonical MBE in Eq. 2.1. Additionally, our tests on simple trimers and symmetric systems show that the canonical MBE itself does not converge in body order in general, even at the tight-binding level of theory. While body-ordered descriptors have proven to be effective in MLIPs, this study suggests that caution must be exercised in claiming that they learn the lower-order energetics systematically.

Chapter 3

Ad-hoc electrostatics in force fields

We begin with a short overview of the response functions and properties from Density Functional Perturbation Theory (DFPT) from [69], then elucidate the charge equilibration (QEq) methods from [36, 37, 70]. We then discuss the shortcomings of the QEq method, which is mainly obtained from unpublished work by Coiana and de Gironcoli [71]. Two methods seeking to address these pathologies are highlighted subsequently:

1. Split-charge equilibration (SQE) as an empirical extension of QEq [72, 73], and
2. Atom-condensed Kohn-Sham approximated to second order (ACKS2) [74, 75] as an reframing of charge flow using conceptual DFT.

The connections of the two models are inspired from [40].

The physical examples, and derivations of the response functions from these two models, in particular to the independent particle susceptibility χ_0 , are *original work coming from this thesis*. A summary of the chapter may also be seen in Fig.

3.1 DFT linear response

The total energy functional in DFT is given by the Hohenberg-Kohn formulation,

$$E[n] = F[n] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \quad (3.1)$$

where V_{ext} is the external potential felt by the system and $F[n]$ is the universal functional,

$$F[n] = T_s[n] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]. \quad (3.2)$$

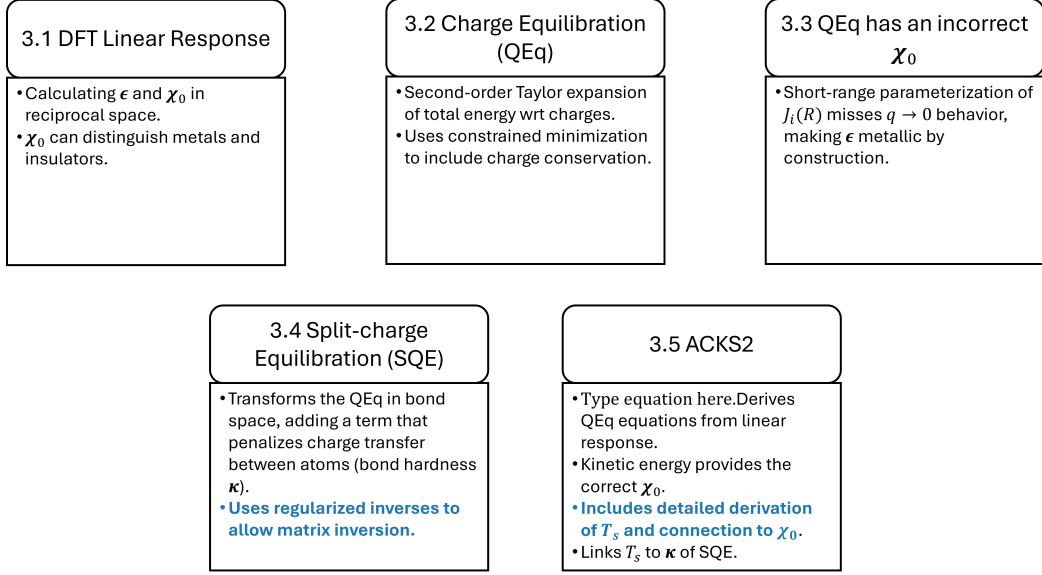


Figure 3.1: Summary of Chapter 3. Original contributions are highlighted in blue.

T_s and E_{xc} are the non-interacting kinetic energy and exchange-correlation functionals of the density, respectively. The minimization of $E[n]$ provides its ground state energy,

$$0 = \frac{\delta F}{\delta n} + V_{\text{ext}}(\mathbf{r}). \quad (3.3)$$

When V_{ext} is perturbed by some δV_{ext} , we get the linear response,

$$\int d\mathbf{r}' \frac{\delta^2 F}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \delta n(\mathbf{r}') + \delta V_{\text{ext}}(\mathbf{r}) = 0. \quad (3.4)$$

3.1.1 Susceptibility, χ

Differentiating with respect to the density once more leads to the inverse susceptibility¹, χ^{-1} ,

$$\chi^{-1}(\mathbf{r}, \mathbf{r}') := \frac{\delta V_{\text{ext}}(\mathbf{r})}{\delta n(\mathbf{r}')} = -\frac{\delta^2 T_s}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} - \frac{1}{|\mathbf{r} - \mathbf{r}'|} - f_{xc}(\mathbf{r}, \mathbf{r}'), \quad (3.5)$$

where f_{xc} is the exchange-correlation kernel,

$$f_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}.$$

We also consider the Kohn-Sham energy functional,

$$E_s[n] = T_s[n] + \int V_s(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \quad (3.7)$$

¹We refer to the susceptibility in bold, χ , to distinguish it from the electronegativity in later sections, χ .

whose second-order response defines the inverse of the bare susceptibility. We can thus re-express the inverse susceptibility in terms of its bare counterpart,

$$\chi_0^{-1}(\mathbf{r}, \mathbf{r}') := \frac{\delta V_s(\mathbf{r})}{\delta n(\mathbf{r}')} = -\frac{\delta^2 T_s}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}, \quad (3.8)$$

$$\chi^{-1}(\mathbf{r}, \mathbf{r}') = \chi_0^{-1}(\mathbf{r}, \mathbf{r}') - \frac{1}{|\mathbf{r} - \mathbf{r}'|} - f_{xc}(\mathbf{r}, \mathbf{r}'). \quad (3.9)$$

3.1.2 Dielectric matrix, ϵ

From χ , we can determine the dielectric matrix (DM) in terms of the scalar potentials V (see Appendix E4 of [76]). How a system responds to linear perturbations caused by an external potential is modulated by the inverse dielectric matrix (IDM) [77],

$$\Delta V_{\text{int}}(\mathbf{r}) = \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r}, \mathbf{r}') \Delta V_{\text{ext}}(\mathbf{r}'), \quad (3.10)$$

where ΔV_{int} is the internal response of the system, and ΔV_{ext} is the perturbation of the external potential. The IDM characterizes the electronic response of the materials,

$$\epsilon^{-1}(\mathbf{r}, \mathbf{r}') = \frac{\delta V_{\text{int}}(\mathbf{r})}{\delta V_{\text{ext}}(\mathbf{r}')} = \frac{\delta V_{\text{ext}}(\mathbf{r}) + \delta V_H(\mathbf{r})}{\delta V_{\text{ext}}(\mathbf{r}')}, \quad (3.11)$$

$$\epsilon^{-1}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') + \frac{\delta V_H(\mathbf{r})}{\delta V_{\text{ext}}(\mathbf{r}')}. \quad (3.12)$$

Here, V_H is the Hartree potential, and we have also exploited translational invariance. The relation to the density can be made explicit by applying a functional chain rule to Eq. 3.12,

$$\begin{aligned} \epsilon^{-1}(\mathbf{r}, \mathbf{r}') &= \delta(\mathbf{r} - \mathbf{r}') + \int d\mathbf{s} \frac{\delta V_H(\mathbf{r})}{\delta n(\mathbf{s})} \frac{\delta n(\mathbf{s})}{\delta V_{\text{ext}}(\mathbf{r}')} \\ \epsilon^{-1}(\mathbf{r}, \mathbf{r}') &= \delta(\mathbf{r} - \mathbf{r}') + \int d\mathbf{s} \frac{1}{|\mathbf{r} - \mathbf{s}|} \chi(\mathbf{r}, \mathbf{s}). \end{aligned} \quad (3.13)$$

The derivative of V_H is $\frac{1}{|\mathbf{r} - \mathbf{s}|}$, and the other term is just the susceptibility (inverse of Eq. 3.5).

We can deal with the convolution in the integral in Eq. 3.13 much more easily in reciprocal space. Taking the Fourier transform (FT) for a monochromatic perturbation with wave vector $\mathbf{q}$,

$$\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}) = \delta_{\mathbf{G}\mathbf{G}'} + \frac{4\pi}{|\mathbf{q} + \mathbf{G}|^2} \chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'), \quad (3.14)$$

where $\mathbf{G}$ are the reciprocal lattice vectors, and $4\pi/|\mathbf{q} + \mathbf{G}|^2$ and $\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$ are

the FTs of $1/R$ and the susceptibility, respectively. As we are mainly concerned with the macroscopic effects, and thus the macroscopic dielectric constant, we restrict our focus to the $\mathbf{G} = \mathbf{G}' = 0$ component of the IDM and neglect “local-field” (LF) effects²,

$$\epsilon_{00}^{-1}(\mathbf{q}) = 1 + \frac{4\pi}{q^2} \chi(\mathbf{q}). \quad (3.15)$$

Throughout the discussion, the IDM refers to the ϵ_{00}^{-1} component. Taking the FT of χ from Eq. 3.9,

$$\epsilon^{-1}(\mathbf{q}) = 1 + \frac{4\pi}{q^2} \left(\text{FT}[\chi_0^{-1}(\mathbf{r}, \mathbf{r}')] - \text{FT}\left[\frac{1}{|\mathbf{r} - \mathbf{r}'|}\right] - \text{FT}[f_{xc}(\mathbf{r}, \mathbf{r}')] \right)^{-1}. \quad (3.16)$$

We use the random phase approximation (RPA) by neglecting contributions from f_{xc} in Eq. 3.16 as it does not provide a qualitative difference in the results³. With these two approximations, we can express the macroscopic ϵ with a simpler form,

$$\epsilon^{-1}(\mathbf{q}) \approx 1 + \frac{4\pi}{q^2} \left(\chi_0^{-1}(\mathbf{q}) - \frac{4\pi}{q^2} \right)^{-1}, \quad (3.17)$$

$$\epsilon(\mathbf{q}) \approx 1 - \frac{4\pi}{q^2} \chi_0(q). \quad (3.18)$$

We see that Eq. 3.18 takes on the well-known form of ϵ^{RPA} . The behavior of the dielectric constant ϵ relies on the bare susceptibility, χ_0 .

3.1.3 χ_0 is crucial

χ_0 is also known as the Kohn-Sham polarizability [80] or linear response kernel [74, 81–83]. This is related to the form listed in Eq. 14 of the review of charge flow models by Jensen [40],

$$\chi_0(\mathbf{r}, \mathbf{r}') = \left(\frac{\delta \rho(\mathbf{r})}{\delta u(\mathbf{r}')} \right)_N = \left(\frac{\delta^2 E}{\delta u(\mathbf{r}) \delta u(\mathbf{r}')} \right)_N.$$

For nonmagnetic systems it has the form,

$$\chi_0(\mathbf{r}, \mathbf{r}') = 2 \sum_{vc} \frac{f(\varepsilon_c) - f(\varepsilon_v)}{\varepsilon_c - \varepsilon_v} \langle c | \mathbf{r}' \rangle \langle \mathbf{r}' | v \rangle \langle v | \mathbf{r} \rangle \langle \mathbf{r} | c \rangle, \quad (3.19)$$

where the sum runs over valence v and conduction c KS orbitals $\{\langle \mathbf{r} | i \rangle\} = \{\psi_i(\mathbf{r})\}$. f and ε are the electron occupations and eigenenergies of the KS orbitals. To give a better understanding of its behavior at different perturbations of wave vector $\mathbf{q}$, we

²While the effects coming from the $\mathbf{G} \neq 0$ /off-diagonal components of ϵ^{-1} introduce quantitative differences, they do not change the overall behavior of the IDM at the macroscopic limit. Further discussions may be found in [78, 79].

³The choice of f_{xc} does matter when doing DFT calculations, but this approximation is made to simplify the form of the $\mathbf{q} \rightarrow 0$ limit of the IDM.

look into its corresponding Fourier Transform (FT) [79, 84, 85],

$$\chi_0(\mathbf{q}, \mathbf{G}, \mathbf{G}') \propto \sum_{v, \mathbf{k}} \frac{f(\varepsilon_c) - f(\varepsilon_v)}{\varepsilon_c(\mathbf{k} + \mathbf{q}) - \varepsilon_v(\mathbf{k})} \langle \mathbf{k} + \mathbf{q}, c | e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} | \mathbf{k}, v \rangle \langle \mathbf{k}, v | e^{-i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}'} | \mathbf{k} + \mathbf{q}, c \rangle,$$

where the sum (or integral) over wave vectors $\mathbf{k}$ is performed over the Brillouin zone (BZ). We are interested in the macroscopic contribution, so we focus on the $\mathbf{G} = \mathbf{G}' = 0$ part of χ_0 ,

$$\chi_0(\mathbf{q}) \propto \sum_{v, \mathbf{k}} \frac{f(\varepsilon_c) - f(\varepsilon_v)}{\varepsilon_c(\mathbf{k} + \mathbf{q}) - \varepsilon_v(\mathbf{k})} \langle \mathbf{k} + \mathbf{q}, c | e^{i\mathbf{q} \cdot \mathbf{r}} | \mathbf{k}, v \rangle \langle \mathbf{k}, v | e^{-i\mathbf{q} \cdot \mathbf{r}'} | \mathbf{k} + \mathbf{q}, c \rangle. \quad (3.20)$$

In the succeeding discussion, we split the sum into the inter-band ($v \neq c$) and intra-band ($v = c$) contributions. The inter-band contribution will always have a finite ratio $\Delta f / \Delta \varepsilon$, but the leading term of the orbital factor scales quadratically with $\mathbf{q}$ because there is no overlap, so $\langle \mathbf{k} + \mathbf{q}, c | \mathbf{k}, v \rangle = 0$ and,

$$\lim_{\mathbf{q} \rightarrow 0} \chi_0(\mathbf{q}) \propto i\mathbf{q} \langle \mathbf{k} + \mathbf{q}, c | \mathbf{r} | \mathbf{k}, v \rangle \sim \mathcal{O}(q^2). \quad (3.21)$$

In metals, some bands cross the Fermi energy ε_F , and Δf and $\Delta \varepsilon$ can vanish. In this limit, the ratio becomes the derivative and this may give an $\mathcal{O}(1)$ contribution, and that the ratio turns to a derivative, $\partial f / \partial \varepsilon$, which is the density of states at the Fermi energy level,

$$\chi_0(\mathbf{q}) \propto \frac{\partial f}{\partial \varepsilon} = n(\varepsilon_F). \quad (3.22)$$

The electron occupation follows the Fermi-Dirac distribution and its derivative is proportional to the energy gap $\Delta \varepsilon = \varepsilon - \varepsilon_F$,

$$f(\varepsilon) = \frac{1}{1 + \exp(\beta \Delta \varepsilon)}, \quad (3.23)$$

$$\frac{df}{d\varepsilon} = \frac{\beta \exp(\beta \Delta \varepsilon)}{(1 + \exp(\beta \Delta \varepsilon))^2}, \quad (3.24)$$

with $\Delta \varepsilon < 0$, and the density of states at the Fermi energy level is proportional to the exponential of this gap. $|\Delta \varepsilon|$ is much larger for insulators than for metals, so the density of states at the Fermi level is almost always zero for insulators. For the intra-band contribution,

$$\chi_0(\mathbf{q}) = \begin{cases} \mathcal{O}(q^2) & \text{for insulators,} \\ n(\varepsilon_F) & \text{for metals.} \end{cases} \quad (3.25)$$

We recognize that reproducing the distinct behavior for $\chi_0(\mathbf{q})$ for metals and insulators is an essential component in modeling the correct response. In the following section, we discuss a commonly used ad hoc treatment of electrostatics that describes nonlocal charge transfer, charge equilibration, and see how well it describes polarization.

3.2 Charge Equilibration (QEq)

Charge Equilibration (QEq) [70] is a second-order expansion about charges. It is also known as the electronegativity equalization method (EEM), chemical potential equalization (μ Eq), or the fluctuating charge (FQ) model. For finite systems, it is given by,

$$E_{QEq}(\{Q_j\}, \{R_{ij}\}) = \sum_i^N E_i^{(0)} + \sum_i^N \chi_i Q_i + \frac{1}{2} \sum_i^N J_i Q_i^2 + \frac{1}{2} \sum_{i \neq j} Q_i V_{ij}(R_{ij}) Q_j, \quad (3.26)$$

$$E_{QEq} = \mathbf{E}^0 + \mathbf{Q}^T \chi + \frac{1}{2} \mathbf{Q}^T \tilde{\mathbf{J}} \mathbf{Q} \text{ (matrix form)}, \quad (3.27)$$

where E_i , χ_i , and J_i are the single-atom energy, atomic electronegativity⁴, and atomic hardness of each atom i , respectively. V_{ij} is the Coulomb kernel between two different charges. We combine the atomic hardness and Coulomb terms with $\tilde{J}$,

$$\tilde{J}_{ij} = J_{ij} \delta_{ij} + V_{ij} (1 - \delta_{ij}), \quad (3.28)$$

with the diagonals being the atomic hardness terms and the off-diagonal terms covering the Coulomb interactions. Point charges have a bare $1/R$ interaction that can diverge at short distance, so the kernel can be modified to describe smeared Gaussian charges [37],

$$V_{ij} = \frac{\text{erf}(\gamma_{ij} R_{ij})}{R_{ij}}, \quad \gamma_{ij} = (\alpha_i^2 + \alpha_j^2)^{-1/2}, \quad (3.29)$$

where α_i is the smearing width of charge i and $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ is the interatomic distance between atoms i, j . The sums run over all N atoms.

Calculating the charges requires minimizing the Lagrangian⁵ of Eq. 3.26 with

⁴This can also include the coupling of the charges to some electric field, $\mathcal{E}$.

⁵The Lagrangian counterpart of Eq. 3.26 is given by,

$$\mathcal{L}_{QEq} = \sum_i E_i^{(0)} + \sum_i \chi_i Q_i + \frac{1}{2} \sum_i J_i Q_i^2 + \frac{1}{2} \sum_{i \neq j} Q_i V_{ij} Q_j + \lambda \left(\sum_i Q_i - Q_{\text{tot}} \right). \quad (3.30)$$

respect to the charges, subject to charge neutrality,

$$\frac{\partial \mathcal{L}_{QE q}}{\partial Q_{\bar{i}}} = 0, \quad (3.31)$$

$$= \chi_{\bar{i}} + \lambda + J_{\bar{i}} Q_{\bar{i}} + \sum_{j \neq \bar{i}} V_{ij} Q_j,$$

$$\mathbf{Q} = -\tilde{\mathbf{J}}^{-1} (\chi + \mathbf{1}\lambda). \quad (3.32)$$

The equilibration of χ for all atoms and the charge conservation condition account for a rank- N linear system,

$$\frac{\partial E_{QE q}}{\partial Q_1} = \frac{\partial E_{QE q}}{\partial Q_2} = \dots = \frac{\partial E_{QE q}}{\partial Q_N}, \quad \sum_i^N Q_i = Q_{\text{total}}. \quad (3.33)$$

The linear system can be cast in matrix form as

$$\begin{pmatrix} Q_1 \\ Q_2 \\ \vdots \\ Q_N \\ \lambda \end{pmatrix} = \begin{pmatrix} J_1 & V_{12} & \dots & V_{1N} & 1 \\ V_{12} & J_2 & \dots & V_{2N} & 1 \\ \vdots & \vdots & \ddots & \vdots & 1 \\ V_{1N} & V_{2N} & \dots & J_N & 1 \\ 1 & 1 & 1 & 1 & 0 \end{pmatrix}^{-1} \begin{pmatrix} -\chi_1 \\ -\chi_2 \\ \vdots \\ -\chi_N \\ Q_{\text{tot}} \end{pmatrix}, \quad (3.34)$$

where λ is the Lagrange multiplier that ensures total charge conservation.

The charges $\mathbf{Q}$ obtained from QEq suffer from (1) overshooting of polarization with system size, and (2) unphysical charge transfer at large interatomic distances. Evidence of this has been well documented [38–40, 86], and various methodologies have been proposed to mitigate this by working in bond space [72, 87, 88], capturing missing elements from DFT specifically [74, 75], or exploring capacitance-based models [89]. A more comprehensive review of the different charge-flow models can be found in [40]. The next section details, from density response functions, what is missed by the QEq model.

3.3 QEq has an incorrect χ_0

To connect QEq to the density response functions in Sec. 3.1, we start with the definition of a charge Q_i of atom i as a sum of contributions coming from the nucleus Q^0 that is kept constant and a variational contribution, Δ ,

$$Q_i = Q_i^0 + \Delta_i. \quad (3.35)$$

E_{QE} in Eq. 3.26 is re-expressed as an expansion of Δ about Q^0 and the electrostatic potentials due to the nuclei, ϕ^{ext} ,

$$E(\{Q_i\}, \{\phi^{\text{ext}}\}) = \sum_i E_s^{(0)} + \sum_i \left. \frac{\partial E}{\partial Q_i} \right|_{\mathbf{Q}^0} Q_i + \frac{1}{2} \sum_i \left. \frac{\partial^2 E}{\partial Q_i^2} \right|_{\mathbf{Q}^0} Q_i^2 + \frac{1}{2} (\phi_i^{\text{ext}} + \phi_i^H) Q_i. \quad (3.36)$$

The first- and second-order derivatives are defined to be the atomic electronegativities and hardnesses,

$$\left. \frac{\partial E}{\partial Q_i} \right|_{\mathbf{Q}^0} = \chi_i, \quad \left. \frac{\partial^2 E}{\partial Q_i^2} \right|_{\mathbf{Q}^0} = J_i. \quad (3.37)$$

The nuclear ϕ^{ext} and Hartree ϕ^H potentials are,

$$\phi_i^{\text{ext}} = \sum_j \frac{Q_j^0}{R_{ij}}, \quad \phi_i^H = \sum_j \frac{\Delta_j}{R_{ij}}. \quad (3.38)$$

Equilibrating Eq. 3.36 with respect to Q gives,

$$\begin{aligned} 0 &= \frac{dE}{dQ_i} = \sum_j \frac{\partial^2 E}{\partial Q_i \partial Q_j} dQ_j + \frac{\partial^2 E}{\partial Q_i \partial \phi_j^{\text{ext}}} d\phi_j^{\text{ext}} \\ 0 &= \sum_j \frac{\partial^2 E}{\partial Q_i \partial Q_j} dQ_j + d\phi_i^{\text{ext}}, \end{aligned} \quad (3.39)$$

where we note that the total energy couples to ϕ^{ext} linearly with Q ,

$$\sum_j \frac{\partial^2 E}{\partial Q_i \partial \phi_j^{\text{ext}}} d\phi_j^{\text{ext}} = \frac{\partial}{\partial Q_i} \left(\sum_j \frac{\partial E}{\partial \phi_j^{\text{ext}}} \right) d\phi_j^{\text{ext}} = \delta_{ij} d\phi_j^{\text{ext}}.$$

Taking another charge derivative in Eq. 3.39 gives the linear response condition noting that $d\phi_i^{\text{ext}}/dQ_j \propto \frac{1}{R_{ij}}$,

$$\begin{aligned} \frac{d^2 E}{dQ_i dQ_j} &= \frac{\partial^2 E}{\partial Q_i \partial Q_j} \delta_{ij} + \frac{1}{R_{ij}}, \\ -\chi_{ij}^{-1} &:= J_i + \frac{1}{R_{ij}}, \end{aligned} \quad (3.40)$$

where we have used Eq. 3.37 to substitute J for the hardness. Comparing with Eq. 3.9, we note that J_i accounts for the negative inverse of the bare susceptibility, $J_i = -\chi_0^{-1}$, and $1/R_{ij}$ is the $1/|\mathbf{r} - \mathbf{r}'|$ contribution with which Ewald sums or Gaussian charge treatments can be applied to avoid its divergence at short distances.

We recall that the IDM is the ratio of internal to external perturbations, as in

Eq. 3.11. It can be expressed in QEq as,

$$\begin{aligned}
\epsilon^{-1}(\mathbf{R}_i, \mathbf{R}_j) &= \frac{d\phi_i^{\text{int}}}{d\phi_j^{\text{ext}}} = \frac{d\phi_i^{\text{ext}} + d\phi_i^H}{d\phi_j^{\text{ext}}} \\
&= \delta_{ij} + \sum_k \frac{d\phi_i^H}{dQ_k} \frac{dQ_k}{d\phi_j^{\text{ext}}} \\
\epsilon^{-1}(\mathbf{R}_i, \mathbf{R}_j) &= \delta_{ij} + \sum_k \frac{1}{R_{ik}} \chi_{kj},
\end{aligned} \tag{3.41}$$

where we recognize $dQ_k/d\phi_j^{\text{ext}}$ as the atom-centered analog of the density response to scalar potentials, $\delta n/\delta V_{\text{ext}}$ like in Eq. 3.5. Taking the FT of the IDM as done in Eqs. 3.14 to 3.18, we recover a form similar to the one obtained from DFPT in Eq. 3.16,

$$\begin{aligned}
\epsilon^{-1}(\mathbf{q}) &= 1 + \frac{4\pi}{q^2} \chi(\mathbf{q}), \\
\epsilon^{-1}(\mathbf{q}) &= 1 + \frac{4\pi}{q^2} \left(-J(\mathbf{q}) - \frac{4\pi}{q^2} \right)^{-1},
\end{aligned} \tag{3.42}$$

$$\epsilon(\mathbf{q}) = 1 + \frac{4\pi}{q^2} J^{-1}(\mathbf{q}). \tag{3.43}$$

This ϵ bears similarity to the DFPT-derived one in Eq. 3.18, with the bare susceptibility being the inverse of the negative hardness,

$$\chi_0(\mathbf{q}) = -J^{-1}(\mathbf{q}). \tag{3.44}$$

Hence, the behavior of $J(\mathbf{q})$ at $\mathbf{q} \rightarrow 0$ dictates the q -scaling of ϵ in a related manner to how χ_0 does. If the atomic hardnesses $J(R_{ij})$ are only determined for short interatomic distances, $J(\mathbf{q} \rightarrow 0) \approx q^{-2}$ and cannot cancel the denominator coming from the bare Coulomb term. Thus, $\epsilon(\mathbf{q})$ scales as q^{-2} regardless of the material and diverges at the macroscopic limit. Regardless of the material being modeled, this divergence leads to metallic polarization.

Getting the correct polarization behavior, whether through χ_0 or $J(\mathbf{q})$, can be addressed by modeling J_i at atom pairs to supply the long-range character of the hardness, which can be done by calculations with bond degrees of freedom [72, 87, 88]. Alternately, elements from conceptual DFT can be introduced to explicitly describe χ_0 . In the next few sections, we discuss two improvements to QEq, the split-charge equilibration (SQE) method and the atom-condensed Kohn-Sham DFT approximated to second order (ACKS2), and how they recover the proper polarization.

3.4 Split-charge equilibration (SQE)

The original idea of using bond degrees of freedom to introduce restoring forces not just on atoms but on bonds for empirical force fields began with the atom-atom charge transfer (AACT) model proposed by Chelli et al. [87]. They aimed to improve upon the shortcomings of QEq by addressing the cubic polarization and nonzero charge transfer at large interatomic distances [86]. Nistor et al. reintroduced the atomic hardnesses J_i , resulting in the split-charge equilibration (SQE) model [72].

Before discussing the extension of the QEq models, we first discuss the basic elements of moving from atom space to bond space.

3.4.1 Elements and properties of bond-space variables

The bond degrees of freedom were added by describing the atomic charge Q_i as a sum over split-charges,

$$Q_i = \sum_j L_{ij} p_{ij} = \sum_j' p_{ij}, \quad (3.45)$$

where p_{ij} is defined as *the charge transferred from atom j to i* . Antisymmetry upon switching indices is implied from this definition,

$$p_{ij} = -p_{ji}, \quad (3.46)$$

as the charge transferred from i to j is the negative of the charge transferred from j to i . The sum in Eq. 3.45 can be mediated by a topology/incidence matrix L_{ij} that maps the split charges to the corresponding atomic charge. The topology matrix can be thought of as a transformation of variables from atom-space to bond-space, and has also been called the transfer matrix [75, 88].

Through the antisymmetry condition in Eq. 3.46, L_{ij} encodes charge neutrality through a zero column sum,

$$\sum_i L_{ij} = 0.$$

As such, minimizing a Lagrangian is not necessary for solving SQE systems. More generally, charge conservation can be enforced in the SQE model by modifying Eq. 3.45 to account for reference charges Q^0 [90, 91],

$$\mathbf{Q} = \mathbf{L}\mathbf{p} + \mathbf{Q}^0, \quad (3.47)$$

$$\Delta = \mathbf{Q} - \mathbf{Q}^0 = \mathbf{L}\mathbf{p}. \quad (3.48)$$

$\Delta = \mathbf{Q} - \mathbf{Q}^0$ is the vector of atomic charge differences from their reference values, as in Eq. 3.35.

We consider the test systems visualized in Fig. 3.2. The first example is a water molecule in which charge transfer between the hydrogen atoms is not allowed. Labeling the atoms (H_0, H_1, O_2), we have the following equations for the atomic charges,

$$\begin{aligned}\Delta_0 &= p_{02}, \\ \Delta_1 &= p_{12}, \\ \Delta_2 &= p_{20} + p_{21} = -p_{02} - p_{12}.\end{aligned}$$

Due to antisymmetry⁶, the number of p needed to describe the charge transfer of the system reduces from 4 to 2. Eq. 3.45 can be cast in a matrix form to better understand L_{ij} ,

$$\mathbf{\Delta} = \mathbf{L}\mathbf{p}, \quad (3.49)$$

$$\begin{pmatrix} \Delta_0 \\ \Delta_1 \\ \Delta_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} p_{02} \\ p_{12} \end{pmatrix}. \quad (3.50)$$

For a fully connected system, the system of equations becomes,

$$\begin{aligned}\Delta_0 &= p_{01} + p_{02}, \\ \Delta_1 &= p_{10} + p_{12} = -p_{01} + p_{12}, \\ \Delta_2 &= p_{20} + p_{21} = -p_{02} - p_{12},\end{aligned}$$

and the corresponding linear system,

$$\begin{pmatrix} \Delta_0 \\ \Delta_1 \\ \Delta_2 \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & -1 \end{pmatrix} \begin{pmatrix} p_{01} \\ p_{02} \\ p_{12} \end{pmatrix}. \quad (3.51)$$

We consider a third system in which atom 1 is fully separated from the rest of the atoms, leaving only one bond,

$$\begin{aligned}\Delta_0 &= p_{02}, \\ \Delta_1 &= 0, \\ \Delta_2 &= p_{20} = -p_{02}.\end{aligned}$$

$\Delta_1 = 0$ means that the charge at atom 1 is not allowed to vary from its reference

⁶For fully connected systems with all N atoms allowed to transfer charge to one another, the maximum number of bond variables goes as $N(N-1)/2$. In most cases, there will be more bond variables than atoms, so this example is one of the few exceptions.

value. This atom contributes nothing to the energetics of the system beyond a shift in the reference. As such, the linear system is trivial,

$$\begin{pmatrix} \Delta_0 \\ \Delta_1 \\ \Delta_2 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} (p_{02}). \quad (3.52)$$

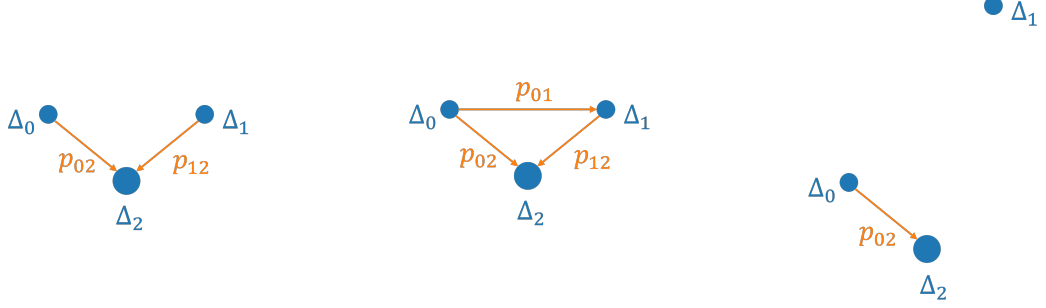


Figure 3.2: Visualization of the restricted (left), fully connected (center), and dissociated/trivial (right) systems corresponding to the linear systems in Eqs. 3.50, 3.51, and 3.52. The left and center systems lead to the same $\{\Delta_i\}$ owing to indirect charge transfer pathways. The dissociated system will have no allowed charge transfer for atom 1, thus leading to $Q_1 = Q_1^0$ and will generally have a different $\{\Delta_i\}$.

As long as atoms are connected to one another, whether directly through a single p_{ij} or indirectly through multiple connected ones, the bond-space variables will describe the same system as it belongs to the same bond topology. Different bond topologies arise from dissociated fragments of the system, between which a bond-based system will disallow charge transfer. In a general way, the conversion to bond variables already inhibits charge transfer between separated fragments, which addresses the incorrect dissociation limits in QEq.

Note that $\mathbf{L}$ in Eq. 3.51 is not full rank, which is a consequence of the charge-transfer variables forming a closed loop, leading to a nontrivial null space that corresponds to cyclic charge transport [88]. Unless the bond networks are explicitly crafted to avoid these cyclic modes, it is inevitable that $\mathbf{L}$ will have a nonzero null space and is generally noninvertible. The reverse mapping from p_{ij} to Q_i will then require pseudoinverses of the topology matrix, $\mathbf{L}^+$, and has the gauge freedom of the cyclic mode vector $\mathbf{z}$ belonging to the null space of $\mathbf{L}$ (where $\mathbf{L}\mathbf{z} = 0$),

$$\mathbf{p} = \mathbf{L}^+ (\mathbf{Q} - \mathbf{Q}^0) + \mathbf{z} = \mathbf{L}^+ \Delta + \mathbf{z}. \quad (3.53)$$

As there are almost always more bonds than atoms, $\mathbf{L}$ is not full rank and thus $\mathbf{L}^T \mathbf{L}$ is non-invertible. Getting the correct pseudoinverse would then require the use of Tikhonov/ridge regression or singular value decomposition (SVD). As an example,

we use ridge regression to provide a suitable $\mathbf{L}^+$,

$$\mathbf{L}^+ = (\mathbf{L}^T \mathbf{L} + \alpha \mathbb{I}_b)^{-1} \mathbf{L}^T, \quad (3.54)$$

where $\mathbb{I}_b$ is the identity matrix commensurate to the number of bonds, and α is a small but positive constant to allow the inversion of $\mathbf{L}^T \mathbf{L}$. Note that choosing $\mathbf{p}$ in Eq. 3.53 to recover the atomic charges $\mathbf{Q}$ incurs information loss. The regularization parameter α attenuates the eigenvalues of $\mathbf{L}$ and will be a source of an imperfect mapping when a double transformation of $\mathbf{Q}$ from Eqs. 3.48 and 3.53 is done,

$$\begin{aligned} \mathbf{Q}' &= \mathbf{L}\mathbf{p} + \mathbf{Q}^0, \\ &= \mathbf{L} (\mathbf{L}^+ (\mathbf{Q} - \mathbf{Q}^0) + \mathbf{z}) + \mathbf{Q}^0, \\ \mathbf{Q}' &= \mathbf{L}\mathbf{L}^+ \mathbf{Q} + (\mathbb{I}_a - \mathbf{L}\mathbf{L}^+) \mathbf{Q}^0, \end{aligned} \quad (3.55)$$

where $\mathbb{I}_a$ is the identity matrix with the length of the number of atoms. $\mathbf{z}$ does not contribute to the recovery of atomic charges since $\mathbf{L}\mathbf{z} = 0$. Eq. 3.55 suggests that the $\mathbf{Q}'$ obtained from gathering $\mathbf{p}$ cannot be an exact mapping of the reference charges owing to the regularized inverse $\mathbf{L}^+$ leading to an imperfect projection $\mathbf{L}\mathbf{L}^+$. Selection of α can be heuristically done to be small enough to preserve the projection as much as possible while still allowing for inverting linear systems that are bond-based. In the next section we discuss its practical use case in the SQE model.

3.4.2 SQE model

With the elements introduced in the previous section, we now introduce the extensions to the QEq model introduced by Nistor et al. [72]. The SQE energy is almost identical to E_{QEq} in Eq. 3.26, but with the bond penalty term κ_b ,

$$E_{SQE}(\{Q_i\}) = E_{QEq}(\{Q\}) + \frac{1}{2} \sum'_{b=(ij) \in \mathbf{L}} \kappa_b p_b^2, \quad (3.56)$$

$$E_{SQE}(\{Q_i\}) = \mathbf{E}^{(0)} + \mathbf{Q}^T \chi + \frac{1}{2} \mathbf{Q}^T \tilde{\mathbf{J}} \mathbf{Q} + \frac{1}{2} \mathbf{p}^T \kappa \mathbf{p}. \quad (3.57)$$

The last term on the RHS is the new addition: the energy associated with the bond-hardness of the system. We adopt the $b = (ij) \in \mathbf{L}$ bond index, where it runs over all ij atom pairs that are counted by the topology matrix. The restricted sum closely follows the one set by L_{ij} in Eq. 3.45, where bonds can be selected explicitly⁷, or

⁷In AACT [87] and the original SQE work [72], they only allow covalently bonded atoms to be part of the topology. The review of charge flow models from Jensen [40] suggests allowing p_{ij} between atoms i, j with an appreciable overlap in electron orbitals.

through a radial cutoff $R_{c,SQE}$,

$$L = \{(i, j) \mid \forall (i, j) \text{ s.t. } R_{ij} < R_{c,SQE}\}. \quad (3.58)$$

The form in Eq. 3.57 uses a mixed atom-bond representation, but numerical calculations for terms with bond-variables are typically done exclusively in atom [88, 92] or bond space [72, 73, 90]. For this, a transformation of the terms in QEq to bond space must be done by expressing the charges Q_i in terms of p_{ij} . Denoting ΔE_{SQE} as the SQE energy without the short-range terms, $E_i^{(0)}$,

$$\begin{aligned} \Delta E_{SQE}(\{p\}) &= \mathbf{Q}^T \chi + \frac{1}{2} \mathbf{Q}^T \tilde{\mathbf{J}} \mathbf{Q}, \\ &= (\mathbf{Lp})^T \chi + \frac{1}{2} (\mathbf{Lp})^T \tilde{\mathbf{J}} (\mathbf{Lp}) + \frac{1}{2} \mathbf{p}^T \boldsymbol{\kappa} \mathbf{p} \\ \Delta E_{SQE}(\{p\}) &= \mathbf{p}^T (\mathbf{L}^T \chi) + \frac{1}{2} \mathbf{p}^T (\mathbf{L}^T \tilde{\mathbf{J}} \mathbf{L}) \mathbf{p} + \frac{1}{2} \mathbf{p}^T \boldsymbol{\kappa} \mathbf{p} \\ \Delta E_{SQE}(\{p\}) &= \mathbf{p}^T \chi_{SQE} + \frac{1}{2} \mathbf{p}^T (\mathbf{J}_{SQE} + \boldsymbol{\kappa}) \mathbf{p}, \end{aligned} \quad (3.59)$$

where we define the electronegativities and the combined Coulomb and hardness kernels as,

$$\chi_{SQE} = \mathbf{L}^T \chi = \sum_{b=(ij)} \left(\sum_i L_{bi} \chi_i \right) = \sum_{ij} (\chi_i - \chi_j), \quad (3.60)$$

$$\mathbf{J}_{SQE} = \mathbf{L}^T \tilde{\mathbf{J}} \mathbf{L} = \sum_{b=(ij), b'=(i'j')} \left(\sum_{ij} L_{bi} \tilde{J}_{ij} L_{jb'} \right) = \sum_{ij, i'j'} (\tilde{J}_{ii'} - \tilde{J}_{ij'} - \tilde{J}_{ji'} + \tilde{J}_{jj'}). \quad (3.61)$$

In the three-atom, two-bond example in Eq. 3.50, χ_{SQE} looks like,

$$\chi_{SQE} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} \chi_0 \\ \chi_1 \\ \chi_2 \end{pmatrix} = \begin{pmatrix} \chi_0 - \chi_2 \\ \chi_1 - \chi_2 \end{pmatrix} = \begin{pmatrix} \chi_{02} \\ \chi_{12} \end{pmatrix},$$

where each element of the χ_{SQE} vector is just the difference between the atomic electronegativities of the bond ij , $\chi_{SQE,ij} = \chi_i - \chi_j$. χ_{SQE} describes the electronegativity difference between atoms.

The combined Coulomb-hardness (atomic and bond hardness) kernel is,

$$\mathbf{J}_{SQE} + \boldsymbol{\kappa} = \mathbf{L}^T \tilde{\mathbf{J}} \mathbf{L} = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} J_0 & V_{01} & V_{02} \\ V_{01} & J_1 & V_{12} \\ V_{02} & V_{12} & J_2 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ -1 & -1 \end{pmatrix} + \begin{pmatrix} \kappa_{02} & 0 \\ 0 & \kappa_{12} \end{pmatrix},$$

$$\tilde{\mathbf{J}}_{SQE} = \begin{pmatrix} J_0 + J_2 - 2V_{02} + \kappa_{02} & V_{01} - V_{02} - V_{12} + J_2 \\ V_{01} - V_{02} - V_{12} + J_2 & J_1 + J_2 - 2V_{12} + \kappa_{12} \end{pmatrix}.$$

The bond hardness terms are added to the diagonals of the bond-space matrix. With no guarantees that $\mathbf{J}_{SQE}$ will be invertible, one can think of the κ_{ij} as a regularizer similar to the α in getting $\mathbf{L}^+$.

From the energy term, we see the equilibration condition for split charges. In QEq, the equilibration condition says that all of the first-order derivatives of the total energy wrt each atomic charge are equal as in Eq. 3.33 and their differences should sum to 0,

$$\frac{\partial E_{QE}}{\partial Q_k} = \frac{\partial E_{QE}}{\partial Q_{k'}} \rightarrow 0 = \frac{\partial E_{QE}}{\partial Q_k} - \frac{\partial E_{QE}}{\partial Q_{k'}}.$$

The charge equilibration in bond space means that the first-order derivative of the energy wrt the split charges for all $p_{kk'}$ becomes 0 [72],

$$0 = \frac{\partial E_{SQE}}{\partial p_{kk'}},$$

$$-\chi_{kk'} = \sum_i (J_k p_{ki} - J_{k'} p_{k'i}) + \sum_{i < j} (J_{ik} - J_{ik'} - J_{jk} + J_{jk'}) p_{ij} + \kappa_{kk'} p_{kk'}, \quad (3.62)$$

$$-\chi_{SQE} = (\mathbf{J}_{SQE} + \boldsymbol{\kappa}) \mathbf{p} = \tilde{\mathbf{J}}_{SQE} \mathbf{p}. \quad (3.63)$$

The split charges can then be determined by inverting Eq. 3.63. While $\mathbf{J}_{SQE}$ is generally not invertible because it inherits the null modes of $\mathbf{L}$ ⁸, the bond hardnesses $\boldsymbol{\kappa}$ allow inversion of the system as long as they are strictly positive. The split charges can then be recovered as,

$$\mathbf{p} = \tilde{\mathbf{J}}_{SQE}^{-1} (-\chi_{SQE}). \quad (3.64)$$

Since the construction of the $\mathbf{p}$ vector can be unbiased (through the cutoff $R_{c,SQE}$),

⁸Starting from the definition that $\mathbf{z}$ belongs in the null space of $\mathbf{L}$,

$$\begin{aligned} \mathbf{L}\mathbf{z} &= 0, \\ \mathbf{J}_{SQE}\mathbf{z} &= \mathbf{L}^T \tilde{\mathbf{J}} \mathbf{L} \mathbf{z} = 0, \\ \therefore \ker(\mathbf{L}) &\subseteq \ker(\mathbf{L}^T \tilde{\mathbf{J}} \mathbf{L}), \end{aligned}$$

That is, the eigenvector $\mathbf{z}$ that corresponds to a zero eigenvalue for $\mathbf{L}$ will also provide a zero eigenvalue for $\mathbf{J}_{SQE}$.

it adds another level of arbitrariness. To get properties that QEq calculates, one can recover the atomic charges $\mathbf{Q}$ using the original definition in Eq. 3.45, keeping in mind that the double transformation is inexact owing to regularization as discussed in Eq. 3.55.

The complications brought by bond-space variables make the connections to linear response functions χ_0 and ϵ less straightforward. One way to link it is by using the reverse mapping in Eq. 3.53 to describe the bond hardness terms in atom space. In a simple case where κ is taken to be homogeneous, the contributions proportional to the bond hardness may be represented by,

$$\begin{aligned}\mathbf{p}^T \kappa \mathbf{p} &= (\mathbf{L}^+ \Delta)^T \kappa (\mathbf{L}^+ \Delta) \\ \mathbf{p}^T \kappa \mathbf{p} &= \Delta^T \left((\mathbf{L}^+)^T \kappa \mathbf{L}^+ \right) \Delta = \Delta^T \mathbf{W} \Delta,\end{aligned}\tag{3.65}$$

leading to a mapping of the bond hardness in atom space,

$$\mathbf{W} = (\mathbf{L}^+)^T \kappa \mathbf{L}^+.\tag{3.66}$$

This gives a version of SQE that is fully in atom space,

$$E_{SQE}(\Delta) = \mathbf{E}^{(0)} + \Delta^T \chi + \frac{1}{2} \Delta^T (\tilde{\mathbf{J}} + \mathbf{W}) \Delta.\tag{3.67}$$

In a more general case where κ is geometry-dependent and heterogeneous, Eqs. 3.65 and 3.66 do not hold because $\mathbf{p}$ should be determined from a minimization of the energy related to the penalties to the bonds which includes κ ,

$$E_\kappa = \frac{1}{2} \mathbf{p}^T \kappa \mathbf{p}.$$

A way to reduce the general case to the previous one (with a constant $\kappa_0 = 1$) is by rescaling $\mathbf{L}$ and $\mathbf{p}$ via,

$$\tilde{\mathbf{L}} = \mathbf{L} \kappa^{-1/2},\tag{3.68}$$

$$\tilde{\mathbf{p}} = \mathbf{p} \kappa^{1/2},\tag{3.69}$$

which then gives

$$\mathbf{W} = (\tilde{\mathbf{L}}^+)^T \tilde{\mathbf{L}}^+ = (\tilde{\mathbf{L}} \tilde{\mathbf{L}}^T)^+ = (\mathbf{L} \kappa^{-1} \mathbf{L}^T)^+.\tag{3.70}$$

Another way to look at the generic case is found in Appendix B.

SQE encounters issues whether it is solved in atom or bond space. Solving in atom space encounters difficulties in getting the correct dissociation limits as this requires

the W_{ij} elements to diverge to infinity [40]. In bond space, $\mathbf{L}$ has an abrupt behavior for included and dissociated bonds: it either recognizes that a bond is included as a variable ($L_{ij} = 1$) or not ($L_{ij} = 0$). There is no smooth transition in dissociation, and the transformation from $\kappa_{bb} \rightarrow \mathbf{W}_{ij}$ depends on $\mathbf{L}^+$, which depends on the regularization. Despite these drawbacks, SQE has been used to describe nonmetallic [72, 90] systems as well as some metallic systems [73, 92], and has been able to address the overpolarization present in QEq models.

3.5 ACKS2

Verstraelen et al. [74, 75] introduce ACKS2 as a formalization of improvements to QEq under the lens of conceptual DFT (cDFT) [41]. It relies on partitioning the charge density $n(\mathbf{r})$ into atomic populations $\mathcal{N}_i$ of each atom i ,

$$\mathcal{N}_i = \int n_i(\mathbf{r}) d\mathbf{r}. \quad (3.71)$$

$n_i(\mathbf{r})$ is the Atoms-in-Molecules (AIM) atomic density given by,

$$n_i(\mathbf{r}) = w_i(\mathbf{r})n(\mathbf{r}), \quad (3.72)$$

with the weight function $0 \leq w_i(\mathbf{r}) \leq 1$ specifying which part of the density $n(\mathbf{r})$ belongs to atom i . Different schemes, such as the Bader, Becke, and Hirshfeld partitionings, all decompose the electronic density $n(\mathbf{r})$ into atomic populations $\mathcal{N}$. The total energy of the system, E_{pop} , can then be defined by constraining the density to atomic populations,

$$E(\{\mathcal{N}_i\}) = \min_{\substack{n \\ \mathcal{N}_i = \int w_i(\mathbf{r})n(\mathbf{r})d\mathbf{r}}} E_\nu[n], \quad (3.73)$$

where $E_\nu[n]$ is the energy functional for a given external potential⁹, ν . The ground state energy is then determined variationally like DFT by optimizing a Lagrangian with N constraints for each atom instead of a single multiplier μ ,

$$\mathcal{L} = \max_{\lambda_1, \dots, \lambda_N} \min_n \left(E[n] - \sum_i \lambda_i \left(\int w_i(\mathbf{r})n(\mathbf{r})d\mathbf{r} - \mathcal{N}_i \right) \right). \quad (3.74)$$

λ_i are the chemical potentials for each partition.

⁹External and KS potentials, V_{ext} and V_{KS} , are written as ν and u like in [75] for brevity.

3.5.1 QEq from cDFT

From cDFT, we can define second-order expansions of the energy with respect to $\{\mathcal{N}\}$ as is done in QEq with atomic charges. We first define reference densities and energies,

$$n^{(0)}(\mathbf{r}) = n(\mathcal{N}_1^{(0)}, \dots, \mathcal{N}_N^{(0)}; \mathbf{r}), \quad (3.75)$$

$$E^{(0)} = E(\mathcal{N}_1^{(0)}, \dots, \mathcal{N}_N^{(0)}) = E_\nu[n^{(0)}], \quad (3.76)$$

where reference populations relate to $\mathcal{N}_i$ with,

$$\mathcal{N}_i = \mathcal{N}_i^{(0)} + \Delta_i, \quad (3.77)$$

where Δ_i are the relative variations of the populations. These Δ_i relate to the variable charges in Eq. 3.35 with a sign flip¹⁰. Densities and energies can then be expanded around these references,

$$n(\{\mathcal{N}_i^{(0)} + \Delta_i\}; \mathbf{r}) \approx n^{(0)}(\mathbf{r}) + \sum_i \left. \frac{\partial n(\mathbf{r})}{\partial \mathcal{N}_i} \right|_{\mathcal{N}^{(0)}} \Delta_i = n^{(0)}(\mathbf{r}) + \sum_i f_i(\mathbf{r}) \Delta_i, \quad (3.78)$$

where the derivative is evaluated at the reference value, $\mathcal{N}^{(0)} = (\mathcal{N}_1^{(0)}, \dots, \mathcal{N}_N^{(0)})$. The variation of the density with the changes in atomic populations is defined as the AIM Fukui function,

$$f_i(\mathbf{r}) = \left. \frac{\partial n(\mathbf{r})}{\partial \mathcal{N}_i} \right|_{\mathcal{N}^{(0)}}. \quad (3.79)$$

Linearized density perturbations are sufficient to expand the energy to second order [69],

$$E(\{\mathcal{N}_i^{(0)} + \Delta_i\}) \approx E_{\text{pop}}(\{\mathcal{N}_i^{(0)}\}) + \sum_i \left. \frac{\partial E}{\partial \mathcal{N}_i} \right|_{\mathcal{N}^{(0)}} \Delta_i + \frac{1}{2} \sum_{ij} \Delta_i \left. \frac{\partial^2 E}{\partial \mathcal{N}_i \partial \mathcal{N}_j} \right|_{\mathcal{N}^{(0)}} \Delta_j. \quad (3.80)$$

¹⁰From the definition of the atomic charge with Z_i as the nuclear charge,

$$Q_i = Z_i - \mathcal{N}_i = Z_i - (\mathcal{N}_i^{(0)} + \Delta_i) = Q_i^{(0)} - \Delta_i.$$

The derivatives are the chemical potential (negative electronegativity) and the combined atomic hardness and Coulomb kernel,

$$-\chi_i = \frac{\partial E}{\partial \mathcal{N}_i} \Big|_{\mathcal{N}^{(0)}} = - \int \chi [n^{(0)}] (\mathbf{r}) f_i(\mathbf{r}) d\mathbf{r} \quad (3.81)$$

$$\tilde{J}_{ij} = \frac{\partial^2 E}{\partial \mathcal{N}_i \partial \mathcal{N}_j} \Big|_{\mathcal{N}^{(0)}} = \int J [n^{(0)}] (r, r') f_i(\mathbf{r}) f_j(r') d\mathbf{r} dr' = J_i + V_{ij}. \quad (3.82)$$

The integrands $\chi [n^{(0)}]$ and $J [n^{(0)}]$ are calculated with HK-DFT,

$$\chi [n^{(0)}] (\mathbf{r}) = \int \frac{n^{(0)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{txc} [n^{(0)}] (\mathbf{r}) + V(\mathbf{r}) \quad (3.83)$$

$$J [n^{(0)}] (\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + J_{txc} [n^{(0)}] (\mathbf{r}, \mathbf{r}'), \quad (3.84)$$

with V_{txc} and J_{txc} being the first- and second-order derivatives of the combined kinetic energy and exchange-correlation functionals, $E_{txc} [n]$,

$$V_{txc} [n^{(0)}] = \frac{\partial E_{txc} [n]}{\partial n(\mathbf{r})} \Big|_{n^{(0)}}, \quad (3.85)$$

$$J_{txc} [n^{(0)}] = \frac{\partial^2 E_{txc} [n]}{\partial n(\mathbf{r}) \partial n(\mathbf{r}')} \Big|_{n^{(0)}}. \quad (3.86)$$

Note that Eq. 3.80 is similar to the QEq expansions in Eqs. 3.26 and 3.36. In fact, the exchange-correlation contributions are ignored for QEq and $J [n^{(0)}]$ resolves to a form similar to the hardness and the Coulomb kernel, and would share the same pathologies of QEq models in Sec. 3.3.

3.5.2 ACKS2: explicitly adding kinetic energy

ACKS2 treats the kinetic energy separately from the exchange-correlation energy. We re-express the total energy functional as a sum of terms that either explicitly or implicitly depend on n ,

$$E_\nu [n] = E^{\text{exp}} [n] + T_s [n] + \int n(\mathbf{r}) \nu(\mathbf{r}) d\mathbf{r}. \quad (3.87)$$

The kinetic energy, T_s , implicitly depends on the density through the KS orbitals¹¹,

$$T_s [n] = -\frac{1}{2} \sum_{n \in \text{occ.}} \int \psi_n^*(\mathbf{r}) \nabla^2 \psi_n(\mathbf{r}) d\mathbf{r}, \quad (3.88)$$

¹¹Following atomic units, so $\hbar = e = 4\pi\epsilon_0 = 1$.

where n runs over the occupied KS orbitals. The explicit functional is just the universal functional in Eq. 3.2 without T_s ,

$$E^{\text{exp}}[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]. \quad (3.89)$$

While contributions from exchange and correlation effects are still neglected, separating out the kinetic energy allows an extension of E_{QE} with T_{ACKS2} ,

$$E_{\text{ACKS2}}(\{\Delta_i\}) = \sum_i \left(E_i^{(0)} - \chi_i \Delta_i + \frac{1}{2} \sum_j \Delta_i \tilde{J}_{ij} \Delta_j \right) + T_s(\{\Delta_i\}). \quad (3.90)$$

To understand what T_{ACKS2} looks like, we minimize the KS energy functional from Eq. 3.7,

$$E_0^{KS}[u, N] \leq \left(T_s[n] + \int n(\mathbf{r})u(\mathbf{r})d\mathbf{r} \right), \quad (3.91)$$

where u is the auxiliary potential. The crucial step is taking the Legendre transformation of the KS energy functional $E^{KS}[u, N]$ to include u as the dual variable, and combing through all possible trial KS potentials u to find the maximum¹²,

$$T_s[u; n] = \max_u \left(E_0^{KS}[u, N] - \int n(\mathbf{r})u(\mathbf{r})d\mathbf{r} \right). \quad (3.92)$$

The variations of u needed to maximize the RHS of Eq. 3.92 can be linearized,

$$u(\mathbf{r}) = u^{(0)}(\mathbf{r}) + \sum_i U_i w_i(\mathbf{r}). \quad (3.93)$$

$u^{(0)}(\mathbf{r})$ is the KS potential needed to obtain the reference charge density, $n^{(0)}$, w_i are the atomic weight functions from the schemes in Eq. 3.72, and U_i are the variations in the potential felt by the electrons in the i -th atom. The constraint $\sum_i U_i = 0$ excludes a trivial overall shift in the potential. Since T_s is determined from a maximization of the RHS, the linearization and limited basis expansions will systematically underestimate its contribution. We express the kinetic energy perturbation, $\delta T_s = T_s - T_s^{(0)}$ as a perturbation of the density and auxiliary potentials¹³ using Eqs. 3.78 and 3.93,

$$\begin{aligned} \delta T_s(\{\Delta_i\}, \{U_i\}) &= \sum_i \frac{\partial E_0^{KS}}{\partial U_i} U_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 E_0^{KS}}{\partial U_i \partial U_j} U_i U_j \\ &+ \sum_i \left(\frac{\partial E_u}{\partial \mathcal{N}_i} \Delta_i + \frac{\partial E_u}{\partial U_i} U_i \right) + \sum_{ij} \frac{\partial^2 E_u}{\partial \mathcal{N}_i \partial U_j} \Delta_i U_j, \end{aligned} \quad (3.94)$$

¹²While it is safer to use the supremum, the population density n was already determined from a constrained Lagrangian optimization in Eq. 3.74, ensuring ν -representability.

¹³No second derivatives of E_u with respect to u or n are present due to the linear coupling.

where E_u is the integral of the coupling of the density $n(\mathbf{r})$ to the KS potentials $u(\mathbf{r})$,

$$E_u(u, n) = \int n(\mathbf{r})u(\mathbf{r})d\mathbf{r}.$$

We expand each of the derivatives in Eq. 3.94 starting with E_0^{KS} , which only relies on U_i ,

$$\begin{aligned} \sum_i \frac{\partial E_0^{KS}}{\partial U_i} U_i &= \sum_i U_i \int \left. \frac{\partial E_0^{KS}}{\partial u(\mathbf{r})} \right|_{n^{(0)}} \frac{\partial u(\mathbf{r})}{\partial U_i} d\mathbf{r} = \sum_i U_i \int n^{(0)}(\mathbf{r}) w_i(\mathbf{r}) d\mathbf{r} \\ \sum_i \frac{\partial E_0^{KS}}{\partial U_i} U_i &= \sum_i U_i \mathcal{N}_i^0 \end{aligned} \quad (3.95)$$

$$\frac{1}{2} \sum_{ij} \frac{\partial^2 E_0^{KS}}{\partial U_i \partial U_j} U_i U_j = \frac{1}{2} \sum_{ij} U_i U_j \int \frac{\partial^2 E_0^{KS}}{\partial u(\mathbf{r}) \partial u(\mathbf{r}')} w_i(\mathbf{r}) w_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}' = \frac{1}{2} \sum_{ij} U_i X_{ij} U_j, \quad (3.96)$$

with the X_{ij} , called the KS linear response kernel, expanded in terms of the atomic weight basis,

$$X_{ij} = \int \chi_0[u^{(0)}](\mathbf{r}, \mathbf{r}') w_i(\mathbf{r}) w_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (3.97)$$

This kernel can be shown to be negative semidefinite, and has a zero eigenvalue corresponding to the eigenvector of all ones [74]. Note that the second derivative of E_0^{KS} with respect to u provides the bare susceptibility. The integrand relates to the bare response χ_0 as,

$$\chi_0[u^{(0)}](\mathbf{r}, \mathbf{r}') = \frac{\delta^2 E_0^{KS}}{\delta u(\mathbf{r}) \delta u(\mathbf{r}')} = \chi_0(r, r'). \quad (3.98)$$

For the derivatives of E_u ,

$$\begin{aligned} \sum_i \frac{\partial E_u}{\partial \mathcal{N}_i} \Delta_i &= \sum_i \int \left. \frac{\partial E_u}{\partial n(\mathbf{r})} \right|_{u^{(0)}} \frac{\partial n(\mathbf{r})}{\partial \mathcal{N}_i} \Delta_i d\mathbf{r} = \sum_i \Delta_i \int u^{(0)}(\mathbf{r}) f_i(\mathbf{r}) d\mathbf{r} \\ \sum_i \frac{\partial E_u}{\partial \mathcal{N}_i} \Delta_i &= \sum_i (-\chi_{s,i}) \Delta_i, \end{aligned} \quad (3.99)$$

where $\chi_{s,i}$ is the KS contribution to the atomic electronegativity [74],

$$\chi_{s,i} = - \int f_i(\mathbf{r}) u^{(0)}(\mathbf{r}) d\mathbf{r}. \quad (3.100)$$

For the first derivative with respect to U ,

$$\begin{aligned}\sum_i \frac{\partial E_u}{\partial U_i} U_i &= \sum_i U_i \int \frac{\partial E_u}{\partial u(\mathbf{r})} \bigg|_{n^{(0)}} \frac{\partial u(\mathbf{r})}{\partial U_i} d\mathbf{r} = \sum_i U_i \int n^{(0)}(\mathbf{r}) w_i(\mathbf{r}) d\mathbf{r} \\ \sum_i \frac{\partial E_u}{\partial U_i} U_i &= \sum_i U_i \mathcal{N}_i^0.\end{aligned}\tag{3.101}$$

The $U_i \mathcal{N}_i^0$ term is just a shift in the reference population, but the terms in Eqs. 3.95 and 3.101 (E_u enters with a minus sign in T_s) cancel out. For the mixed derivative,

$$\begin{aligned}\sum_{ij} \frac{\partial^2 E_u}{\partial \mathcal{N}_i \partial U_j} \Delta_i U_j &= \sum_{ij} \Delta_i U_j \frac{\partial}{\partial \mathcal{N}_i} \int \frac{\partial E_u}{\partial u(\mathbf{r}')} \bigg|_{n^{(0)}} \frac{\partial u(\mathbf{r}')}{\partial U_j} d\mathbf{r}' \\ &= \sum_{ij} \Delta_i U_j \frac{\partial}{\partial \mathcal{N}_i} \int n^{(0)}(\mathbf{r}') w_j(\mathbf{r}') d\mathbf{r}' \\ \sum_{ij} \frac{\partial^2 E_u}{\partial \mathcal{N}_i \partial U_j} \Delta_i U_j &= \sum_i \Delta_i U_i,\end{aligned}\tag{3.102}$$

where we have used the independence of atomic partitions from each other (see Eqs. 24–27 of [74]),

$$\frac{\partial}{\partial \mathcal{N}_i} \int n^{(0)}(\mathbf{r}') w_j(\mathbf{r}') d\mathbf{r}' = \int \frac{\partial n_j(\mathbf{r}')}{\partial \mathcal{N}_i} d\mathbf{r}' = \delta_{ij}.\tag{3.103}$$

Collecting all of the terms gives us the expression of T_s in Eq. 3.92 in terms of the basis expansions of u, n ,

$$T_s(\{\Delta_i\}, \{U_i\}) = \max_{\substack{U_* \\ \sum_i U_i=0}} \left(\frac{1}{2} \sum_{ij} U_i X_{ij} U_j - \sum_i U_i \Delta_i \right) = \max_{\mathbf{U}} \left(\frac{1}{2} \mathbf{U}^T \mathbf{X} \mathbf{U} - \mathbf{U}^T \mathbf{\Delta} \right).\tag{3.104}$$

The $\chi_{s,i} \Delta_i$ coupling in Eq. 3.99 is not included, as it contributes to the total atomic electronegativity χ_i from QEq and can be parametrized with a single parameter. With the kinetic energy described in terms of atom-condensed variables Δ, U , the total energy of ACKS2 from Eq. 3.90 can then be described as,

$$\begin{aligned}E_{\text{ACKS2}}(\{\Delta_i\}, \{U_i\}) &= \sum_i \left(E_i^{(0)} - \chi_i \Delta_i + \frac{1}{2} J_i \Delta_i^2 + \frac{1}{2} \sum_j \Delta_i V_{ij} \Delta_j \right) \\ &\quad + \max_{\substack{U_* \\ \sum_i U_i=0}} \left(\frac{1}{2} \sum_{ij} U_i X_{ij} U_j - \sum_i U_i \Delta_i \right).\end{aligned}\tag{3.105}$$

Numerical implementations of ACKS2 [40, 74, 75] involve a Lagrangian formalism similar to QEq for both charge and potential conservation, but these are not the

focus of this work. In the succeeding section we see a deeper connection between T_{ACKS2} and the response functions.

3.5.3 ACKS2 and response functions

In this section, we try to extract expressions for the response functions determined from Secs. 3.1 and 3.3 for ACKS2. For this, we begin with the Lagrangian form of Eq. 3.87 for a constant number of particles N ,

$$\mathcal{L}_v[n, u, \mu; N] = E^{\text{exp}}[n] + E_0^{KS}[u] + \int n(\mathbf{r})(v(\mathbf{r}) - u(\mathbf{r})) d\mathbf{r} + \mu \left(\int n(\mathbf{r}) d\mathbf{r} - N \right), \quad (3.106)$$

with μ as the chemical potential for the whole system. $\mathcal{L}$ depends parametrically on N , and this dependence is omitted from this point. Taking the stationary point of the Lagrangian with respect to its variables gives,

$$\frac{\delta \mathcal{L}}{\delta n(\mathbf{r})} = \frac{\delta E^{\text{exp}}}{\delta n(\mathbf{r})} + v(\mathbf{r}) - u(\mathbf{r}) + \mu = 0, \quad (3.107)$$

$$\frac{\delta \mathcal{L}}{\delta u(\mathbf{r})} = \frac{\delta E_0^{KS}}{\delta u(\mathbf{r})} - n(\mathbf{r}) = 0, \quad (3.108)$$

$$\frac{\delta \mathcal{L}}{\delta \mu} = \int n(\mathbf{r}) d\mathbf{r} - N = 0. \quad (3.109)$$

Charge conservation is ensured in Eq. 3.109. Taking another derivative with respect to n and u gives the response functions. Starting with n ,

$$\begin{aligned} \frac{\delta^2 \mathcal{L}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} &= \frac{\delta^2 E^{\text{exp}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} + \frac{\delta v(\mathbf{r})}{\delta n(\mathbf{r}')} - \frac{\delta u(\mathbf{r})}{\delta n(\mathbf{r}')} + \frac{\delta \mu}{\delta n(\mathbf{r}')} = 0, \\ \chi(\mathbf{r}, \mathbf{r}')^{-1} &:= \frac{\delta v(\mathbf{r})}{\delta n(\mathbf{r}')} = -\frac{\delta^2 E^{\text{exp}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} + \frac{\delta u(\mathbf{r})}{\delta n(\mathbf{r}')} - \frac{\delta \mu}{\delta n(\mathbf{r}')}, \end{aligned} \quad (3.110)$$

where we define the inverse of the density response to the external potential v as $\chi^{-1}(\mathbf{r}, \mathbf{r}')$. The u derivative leads to the bare susceptibility,

$$\begin{aligned} \frac{\delta^2 \mathcal{L}}{\delta u(\mathbf{r}) \delta u(\mathbf{r}')} &= \frac{\delta^2 E_0^{KS}}{\delta u(\mathbf{r}) \delta u(\mathbf{r}')} - \frac{\delta n(\mathbf{r})}{\delta u(\mathbf{r}')} = 0, \\ \chi_0(\mathbf{r}, \mathbf{r}') &:= \frac{\delta n(\mathbf{r})}{\delta u(\mathbf{r}')} = \frac{\delta^2 E_0^{KS}}{\delta u(\mathbf{r}) \delta u(\mathbf{r}')}, \end{aligned} \quad (3.111)$$

where the density response with respect to the KS potential is the bare susceptibility. Substituting χ_0 into Eq. 3.110 and noting E^{exp} in Eq. 3.89,

$$\chi(\mathbf{r}, \mathbf{r}')^{-1} = -\frac{1}{|\mathbf{r} - \mathbf{r}'|} - f_{xc}(\mathbf{r}, \mathbf{r}') + \chi_0^{-1}(\mathbf{r}, \mathbf{r}') - \frac{\delta \mu}{\delta n(\mathbf{r}')}. \quad (3.112)$$

Using the same assumptions in Eq. 3.16 to ignore f_{xc} and noting that we are keeping the system at N particles to set μ constant¹⁴, we return to a χ that is similar to the one from DFPT in Eq. 3.9,

$$\chi(\mathbf{r}, \mathbf{r}')^{-1} \approx \chi_0^{-1}(\mathbf{r}, \mathbf{r}') - \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (3.113)$$

The bare susceptibility χ_0 is directly modeled in ACKS2 using atomic degrees of freedom $\{\Delta_i\}, \{U_i\}$ through X_{ij} from Eq. 3.98. In the next section, we see how X_{ij} is represented by the bond hardness κ .

Finally, the dielectric tensor in ACKS2 can be determined similarly by inserting the FT of the inverse of Eq. 3.113 into $\epsilon(\mathbf{q})$ in Eq. 3.15,

$$\epsilon(\mathbf{q}) \approx 1 - \frac{4\pi}{q^2} \chi_0(q),$$

with the difference being that χ_0 is parametrized by the atom-condensed X_{ij} in Eq. 3.97. Under the lens of ACKS2, we see that the explicit presence of the bare susceptibility solves the overpolarization issues present in plain QEq models. In the succeeding part, we will see how the additions of ACKS2 and SQE are related to one another, and posit that the bond-hardness terms in SQE can provide the presence of χ_0 .

3.5.4 Linking SQE to ACKS2

The connection between ACKS2 and SQE requires the mappings from atom to bond variables (and vice versa) introduced in Sec. 3.4.1. Derivations are detailed in [40, 74], but an overview is provided below.

We first have to express E_{ACKS2} purely in terms of atomic populations/charges, Δ . Eq. 3.104 requires a maximization with respect to U , which we perform by finding the extremum,

$$\begin{aligned} 0 &= \frac{\partial T_s}{\partial U} = \mathbf{X}\mathbf{U} - \Delta \\ \Delta &= \mathbf{X}\mathbf{U}. \end{aligned} \quad (3.114)$$

The corresponding $\mathbf{U}$ that maximizes T_s needs the pseudoinverse of $\mathbf{X}$, as the KS linear response kernel is generally non-invertible [74]¹⁵,

$$\mathbf{U} = \mathbf{X}^+ \Delta. \quad (3.116)$$

¹⁴For nonconserving systems, $\delta\mu/\delta n(\mathbf{r}') \neq 0$, and care must be taken when dealing with it. It is defined in [93] as the unconstrained local hardness term.

¹⁵While this is not true for metals because a constant shift may change it due to a nonzero density

This definition of $\mathbf{U}$ leads to the kinetic energy purely as a function of Δ ,

$$\begin{aligned} T_s(\Delta) &= \frac{1}{2} (\mathbf{X}^+ \Delta)^T \mathbf{X} (\mathbf{X}^+ \Delta) - (\mathbf{X}^+ \Delta)^T \Delta, \\ &= \frac{1}{2} \Delta^T (\mathbf{X}^+ \mathbf{X} \mathbf{X}^+ - 2\mathbf{X}^+) \Delta, \\ T_s(\Delta) &= -\frac{1}{2} \Delta^T \mathbf{X}^+ \Delta, \end{aligned} \quad (3.117)$$

where we have used the weak inverse condition of the pseudoinverse,

$$A^+ A A^+ = A^+.$$

From Eq. 3.105, the ACKS2 energy is then fully described by Δ ,

$$\begin{aligned} E_{\text{ACKS2}}(\{\Delta_i\}) &= \sum_i \left(E_i^{(0)} + \chi_i \Delta_i + \frac{1}{2} \sum_j \Delta_i \tilde{J}_{ij} \Delta_j \right) - \frac{1}{2} \sum_{ij} \Delta_i (X)_{ij}^+ \Delta_j, \\ &= \sum_i \left(E_i^{(0)} + \chi_i \Delta_i + \frac{1}{2} \sum_j \Delta_i \left(\tilde{J}_{ij} - (X)_{ij}^+ \right) \Delta_j \right), \\ E_{\text{ACKS2}}(\Delta) &= \mathbf{E}^{(0)} + \Delta^T \chi + \frac{1}{2} \Delta^T \left(\tilde{\mathbf{J}} - \mathbf{X}^+ \right) \Delta. \end{aligned} \quad (3.118)$$

Notice that Eq. 3.118 is equal to the generic case of the atomic version of SQE in Eq. 3.70 if,

$$\mathbf{W} = (\mathbf{L} \boldsymbol{\kappa}^{-1} \mathbf{L}^T)^+ = -\mathbf{X}^+. \quad (3.119)$$

We see that χ_0 is modeled in the SQE model through its atomic representation X_{ij} in Eq. 3.97. Jensen [40] further states that if the κ_{ij} penalty terms are included between all possible atom pairs, with values corresponding to $-X_{ij}^+$, then the ACKS2 and SQE models become equivalent. One should note that the pseudoinverse enters twice in the relation:

1. once through the inversion of the topology matrix. The pseudoinverse only maps back the eigenvectors of L_{ib} that return a neutral charge as discussed in Sec. 3.4.1, and
2. once through X_{ij}^+ , as $\mathbf{X}$ is generally non-invertible due to the row-sum condition

of states (DOS) and its derivative at the Fermi energy level,

$$\left. \frac{dn(\epsilon)}{d\epsilon} \right|_{\epsilon=\epsilon_F} \neq 0, \quad (3.115)$$

we have to consider insulating cases where the DOS *is* zero.

in Eq. 68 of the original paper [74],

$$\sum_i X_{ij} = 0,$$

ensuring that $n^{(0)}$ does not change under a constant N .

We summarize the chapter by recapping that appropriate polarization for both insulators and metals can be obtained from the correct χ_0 behavior from the discussions in DFPT, and how the absence of this ingredient in QEq leads to its pathological metallic behavior. We then show how SQE adds a penalty term for long-range charge transfer through the bond hardnesses κ . ACKS2 then provides a theoretical framework of explicitly modeling the atom-condensed susceptibility kernel X_{ij} , and is related to SQE through pseudoinverses of both $\mathbf{L}$ and $\mathbf{X}$.

The succeeding chapter provides a detailed discussion of a practical implementation of SQE in our existing in-house code.

Chapter 4

Long-range improvements to PANNA

This chapter introduces the main computational work done for this dissertation: modeling improvements to QEq through SQE, a bond-based model. We first discuss the Properties from Artificial Neural Network Architectures (PANNA) code [47, 65], as well as an improved N -body descriptor [94], which constitute the baseline short-range potentials and descriptors whose physics the ad hoc long-range descriptors extend. We then discuss the methodology of parametrizing the coefficients of QEq using short-range ingredients with electrostatic PANNA [37] as well as how it is integrated into the current architecture.

The main work in this part of the dissertation involves two parts of the code. The workflow is shown in Fig. 4.1. The main contributions are highlighted in bold, where changes to data loading, as well as training, are included.

1. Patching the original QEq routine of PANNA (PANNA long range) to adapt it to the JAX module [95], which supports just-in-time (jit) compilation, graphics processing units (GPUs), and auto-differentiation. This allows for a leaner user interface, needing only one input file compared to the original work in [47], and improves training speed by up to two orders of magnitude.
2. Implementation of the SQE model to correct the pathologies inherent in QEq. Discussions regarding the periodicity as well as code are original contributions by me. Current work uses a constant bond hardness with no deduplication to account for periodic boundary conditions. All calculations are exclusively done in bond space.

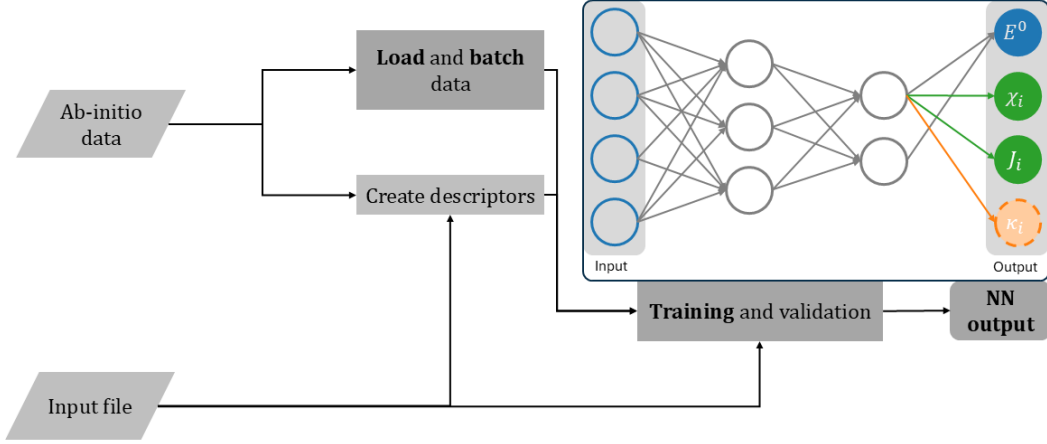


Figure 4.1: Additions to the PANNA workflow, where dissertation work is highlighted in bold. Changes to neural network output are in green for PANNA-QEq, and orange are proposed changes to future work for PANNA-SQE as the current work only implements a constant bond hardness.

4.1 Short-range MLIP and descriptor: PANNA and LATTE

PANNA [47, 65] is a Python software package that trains fully connected, feed-forward networks on *ab initio* data that originally used modified Behler-Parrinello (BP) descriptors [14, 16], which included 2-body (radial) and 3-body (angular) terms as its feature vectors. From the original work, PANNA has undergone software overhauls to use modern machine-learning backends such as JAX to allow autodifferentiation. To address the issue that descriptors beyond 3-body order are needed to generally distinguish between atomic environments [20], the Local Atomic Tensors Trainable Expansion (LATTE) [94] was also added in the code as a way to capture descriptors of arbitrary body order that respect the required invariances. Following the tensor-product method of contracting the feature vectors [21, 22], the basic element of the LATTE descriptor is a local tensor around atom i ,

$$A_{i,u}^{\alpha_1, \dots, \alpha_p}(\{R_{ij}\}) = \sum_{j \in \mathcal{N}_i} \sigma_u(s_i, s_j) f_{u,s_i}(|\mathbf{R}_{ij}|) \hat{r}_{ij}^{\alpha_1} \otimes \dots \otimes \hat{r}_{ij}^{\alpha_p}, \quad (4.1)$$

where the sum runs over all the neighbors j around atom i dictated by R_c . $\hat{r}_{ij} = \vec{r}_{ij}/|\vec{r}_{ij}|$ are versors/unit vectors corresponding to each vector up to the tensor of order p . Each tensor contraction enters as a bin in the final descriptor, which is

indexed by u . σ_u is a learnable scalar that accounts for species combinations, and the radial function f_{u,s_i} contains learnable parameters,

$$f_{u,s_i}(r) = \frac{1}{r_{u,s_i}^2} \left(\text{ReLU} \left(1 - \left(\frac{r - r_{u,s_i}}{\omega_{u,s_i}} \right)^2 \right) \right)^3. \quad (4.2)$$

The parameters $r_{u,s_i}, \omega_{u,s_i}$ are the learnable centers and widths for each bin u and species s_i , and ReLU is the Rectified Linear Unit.

Each A is then fully contracted to a final descriptor G for each atom i of bin u as,

$$G_{i,u}(\{R_{ij}\}) = \sum_{\alpha_1, \dots, \alpha_m} \prod_{k=1}^N A_{i,u_k}^{\alpha_1^k, \dots, \alpha_{p_k}^k}(\{R_{ij}\}). \quad (4.3)$$

Each bin element $G_{i,u}$ is a scalar that maintains the relevant invariances:

- translational symmetry, as relative positions $r_{ij} = r_i - r_j$ are used in $A_{i,u_k}^{\alpha_1^k, \dots, \alpha_{p_k}^k}$,
- rotational symmetry since the final contraction of versors $\hat{r}_{ij}^{\alpha_1} \otimes \dots \otimes \hat{r}_{ij}^{\alpha_p}$ transforms as a scalar under SO(3) rotations,
- inversion symmetry as each of the indices $\alpha_1, \dots, \alpha_m$ shows up twice among the α_j^k (each tensor component is contracted with each other component), and
- permutation invariance from the unordered sum in A , $\sum_{j \in \mathcal{N}_i}$.

As an example, for a 4-body descriptor of the type $100(\alpha, \alpha, \alpha\beta)$, each bin of a single atom is contracted as,

$$G_{i,u} = \sum_{\alpha, \beta} A_{i,u_1}^{\alpha} A_{i,u_2}^{\beta} A_{i,u_3}^{\alpha\alpha\beta}, \quad (4.4)$$

with u running up to 100. Further details of the LATTE descriptor may be found in the original work by Pellegrini in [94].

For all types of descriptors, PANNA uses the fully connected ANN, with each node j at the l -th layer being described by the element [58, 65],

$$a_j^l = g \left(\sum_{i=1}^{n_{l-1}} a_i^{l-1} W_{ij}^l + b_j^l \right), \quad (4.5)$$

where g is a nonlinear activation function and W is the matrix of weights. The last layer of the short-range PANNA models always has a single node to predict the short-range atomic energy $E_i^{(0)}$, which sums to the total energy $E_{\text{SR}} = \sum_i E_i^{(0)}$.

Training uses mini-batch stochastic gradient descent (SGD), which reduces memory use and speeds up training, together with the Adam optimizer [96].

4.2 PANNA-QEq

The first iteration of including long-range electrostatics in PANNA used QEq as the ad hoc solution [37]. The QEq energy is succinctly given by,

$$E_{QEq} = E_{\text{SR}} + E_{\text{Coul}}, \quad (4.6)$$

where E_{Coul} is the long-range energy given by,

$$E_{\text{Coul}} = \frac{1}{2} \sum_{i \neq j} Q_i V_{ij} Q_j, \quad (4.7)$$

where the Coulomb kernel V_{ij} is modeled by Gaussian charges as given by Eq. 3.29. The short-range energy is modified to follow the local terms from QEq in Eq. 3.26,

$$\begin{aligned} E_{\text{SR}} &= \sum_i \left[E_i^{(0)}(G_i) + \left(E_i^{(1)}(G_i) + \chi_i^0 \right) Q_i + \frac{1}{2} \left(E_i^{(2)} + J_i^0 \right) Q_i^2 \right], \\ E_{\text{SR}} &= \sum_i \left[E_i^{(0)}(G_i) + \tilde{E}_i^{(1)} Q_i + \frac{1}{2} \tilde{E}_i^{(2)} Q_i^2 \right], \end{aligned} \quad (4.8)$$

where χ_i^0, J_i^0 are offset parametrizations based on the ionization potential (IP) and electron affinity (EA) [70, 97],

$$\chi_i^0 = \frac{1}{2} (\text{IP} + \text{EA}), \quad (4.9)$$

$$J_i^0 = \text{IP} - \text{EA}. \quad (4.10)$$

The atomic electronegativity and hardness depend on local environments through the descriptors G_i , which must each be parametrized by including additional heads in the output layer. E_{Coul} is calculated through V_{ij} coming from the Ewald sums,

$$V_{ij} = \begin{cases} \frac{\text{erf}(\gamma_{ij} R_{ij})}{R_{ij}} (1 - \delta_{ij}) + \left(\frac{2\gamma_{ij}}{\sqrt{\pi}} \right) \delta_{ij}, & \text{real space,} \\ \frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{\exp(i\mathbf{G} \cdot \mathbf{R}_{ij})}{G^2} \exp\left(-\frac{G^2}{4\gamma_{ij}^2}\right), & \text{reciprocal space.} \end{cases} \quad (4.11)$$

In the original implementation [37], V_{ij} is calculated using only the reciprocal-space term of the Ewald sum for periodic systems and only the real-space term for non-periodic systems.

Forces are determined from the negative gradient of the energies with respect to positions, $F = -\nabla_R E$. We go through each of the force terms from E_{QEq} for a

particular atom l . Starting with the Q -independent term,

$$\begin{aligned} F_l^{(0)} &= -\frac{\partial E^{(0)}}{\partial R_l} = -\sum_a \sum_{ij} \left(\frac{\partial E_a^{(0)}}{\partial G_{ij}} \frac{\partial G_{ij}}{\partial R_{ij}} \right) \frac{\partial R_{ij}}{\partial R_l}, \\ F_l^{(0)} &= \sum_a \sum_{ij} \left(\frac{\partial E_a^{(0)}}{\partial G_{ij}} \frac{\partial G_{ij}}{\partial R_{ij}} \right) (\delta_{il} - \delta_{jl}). \end{aligned} \quad (4.12)$$

The index a runs through all atoms in the system. The derivatives inside the parentheses of Eq. 4.12 can be evaluated explicitly or through auto-differentiation¹, and are abbreviated as $\partial E/\partial R_{ij}$ from here on. The pair derivative is,

$$\frac{\partial R_{ij}}{\partial R_l} = \frac{\partial (R_j - R_i)}{\partial R_l} = \delta_{jl} - \delta_{il}.$$

The Q -dependent terms in E_{SR} are differentiated with respect to positions only through the coefficients, not through the charges, due to the Hellmann-Feynman theorem. Starting with the energy relating to the electronegativities, $E_\chi = \sum_a \chi_a Q_a$,

$$F_l^{(1)} = -\sum_a \sum_{ij} \frac{\partial E_\chi}{\partial E_a^{(1)}} \frac{\partial E_a^{(1)}}{\partial R_{ij}} \frac{\partial R_{ij}}{\partial R_l} = \sum_{ij} \frac{\partial}{\partial R_{ij}} \left(\sum_a Q_a E_a^{(1)} \right) \left(-\frac{\partial R_{ij}}{\partial R_l} \right). \quad (4.13)$$

For the forces related to the atomic hardness,

$$F_l^{(2)} = -\sum_a \sum_{ij} \frac{\partial E_J}{\partial E_a^{(2)}} \frac{\partial E_a^{(2)}}{\partial R_{ij}} \frac{\partial R_{ij}}{\partial R_l} = \sum_{ij} \frac{\partial}{\partial R_{ij}} \left(\sum_a Q_a^2 E_a^{(2)} \right) \left(-\frac{\partial R_{ij}}{\partial R_l} \right). \quad (4.14)$$

The long-range forces coming from E_{Coul} are calculated as,

$$F_{\text{Coul},l} = \begin{cases} \left[\frac{\text{erfc}(\gamma_{il} R_{il})}{R_{il}^3} + \frac{2\gamma_{il}}{\sqrt{\pi} R_{il}^2} \exp(-\gamma_{il}^2 R_{il}^2) \right] R_{il}, & \text{real space,} \\ \frac{4\pi}{\Omega} \sum_{G \neq 0} \frac{\sin(\mathbf{G} \cdot \mathbf{R}_{il})}{G^2} \exp\left(-\frac{G^2}{4\gamma_{il}^2}\right) G_l, & \text{reciprocal space.} \end{cases} \quad (4.15)$$

The charge equilibration condition is similar to Eq. 3.31 with charge conservation imposed,

$$\frac{\partial E_{QE}}{\partial Q_i} = \sum_j \left[\tilde{E}_i^{(2)} \delta_{ij} + V_{ij} (1 - \delta_{ij}) \right] Q_j + \tilde{E}_i^{(1)}(G_i) + \lambda = 0, \quad (4.16)$$

where λ is the Lagrange multiplier/chemical potential of the system needed for charge conservation, and the matrix equation to be solved is in Eq. 3.34. Solving this yields the charges $\mathbf{Q}$, which enter the energies, the forces, and eventually the loss. The

¹In PANNA, modified BP descriptors explicitly evaluate these derivatives, while derivatives of LATTE descriptors are calculated through auto-differentiation.

short-range PANNA model can be regressed on energies and forces with Tikhonov or L^2 regularization, but PANNA-QEq also allows the option to regress on atomic charges as reflected by its loss function,

$$\mathcal{L} = \gamma_E \mathcal{L}^E + \gamma_F \mathcal{L}^F + \gamma_Q \mathcal{L}^Q + \gamma_R \mathcal{L}^R, \quad (4.17)$$

where the γ weight the importance of each property in the regression, and the losses are,

$$\mathcal{L}^E(\mathbf{W}) = \sum_{c \in \text{batch}} (E_c^{\text{ref}} - E_{\text{tot},c}(\mathbf{W}))^2, \quad (4.18)$$

$$\mathcal{L}^F(\mathbf{W}) = \sum_{c \in \text{batch}} \frac{1}{3N_c} \sum_{i=1}^{N_c} |\mathbf{F}_i^{\text{ref}} - \mathbf{F}_i(\mathbf{W})|^2, \quad (4.19)$$

$$\mathcal{L}^Q(\mathbf{W}) = \sum_{c \in \text{batch}} \frac{1}{N_c} \sum_{i=1}^{N_c} (Q_i^{\text{ref}} - Q_i(\mathbf{W}))^2, \quad (4.20)$$

$$\mathcal{L}^R(\mathbf{W}) = \frac{|\mathbf{W}|^2}{2}. \quad (4.21)$$

$\mathbf{W}$ is the (flattened) vector of weights from the network and N_c is the number of atoms in structure c . The workflow can be seen in Fig. 4.2. It has been shown in the original

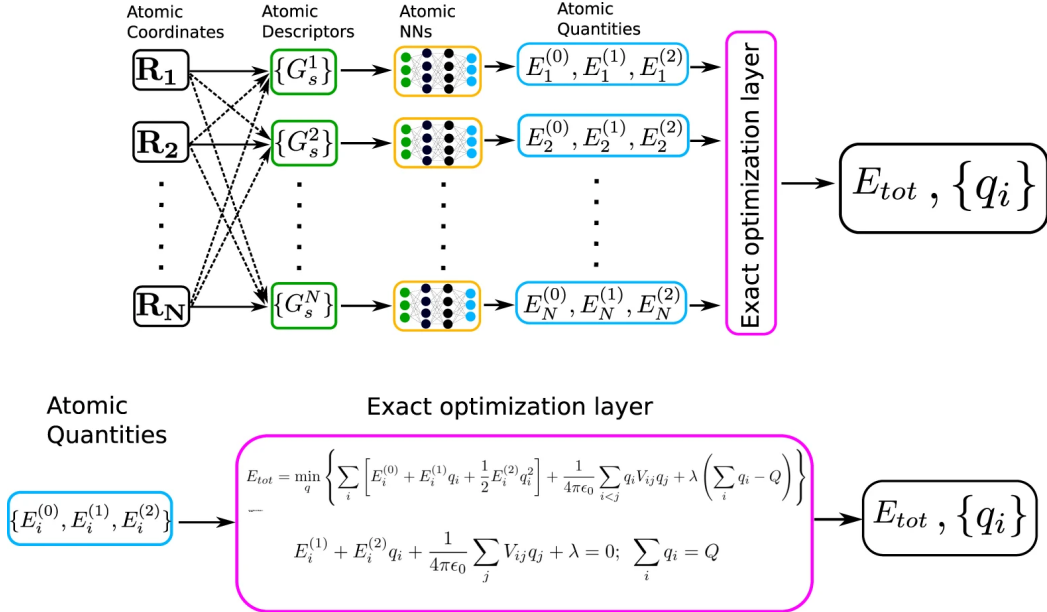


Figure 4.2: Workflow for the PANNA-QEq model. Graphic from original work in [37].

work [37] and other studies [32, 98] that regression on atomic charges is not necessary, and can even be detrimental as it depends on a particular partitioning/atom-condensing of atomic charges from electronic densities (see Sec. 3.5 for another discussion).

4.3 PANNAJAX-QEq

As mentioned at the start of this chapter, the third iteration of PANNA (PANNAJAX-QEq) uses the `JAX` module as the backend (with `tensorflow` being used for data loading), and uses the LATTE descriptor. The training is also accelerated due to auto-differentiation which allows for a much faster evaluation of the chain-rule terms in Eq. 4.12. This means that factors of the form,

$$\sum_{a,ij} \frac{\partial E_a}{\partial G_{ij}} \frac{\partial G_{ij}}{\partial R_{ij}} \rightarrow \sum_{a,ij} \frac{\partial E_a}{\partial R_{ij}}, \quad (4.22)$$

can be differentiated without explicitly calculating derivatives relating to G_{ij} ². A test to verify the improvements in PANNAJAX-QEq is found in Appendix C.

Despite improvements in code performance and descriptors, the pathological shortcomings of QEq from earlier classical force fields persist in MLIP codes [38, 39]. These studies have also shown the QEq problems to persist despite using message-passing equivariant neural networks [23, 24]. Using an improved charge-flow model over QEq [40] instead of the standard MLIP elements may be considered as another way to improve the long-range description of MLIPs. We discuss in the succeeding section a property that, for some systems, is correctly represented with the appropriate electrostatics: phonons.

4.4 Long-range forces and phonon dispersions

The main physical quantities this chapter aims to tackle are the phonon dispersions, particularly the splitting of the longitudinal optical (LO) and transverse optical (TO) normal modes in ionic crystals such as magnesium oxide (MgO). We show that, more than getting nonzero long-range forces, the correct response functions are needed to manifest this splitting. We briefly review some concepts in lattice dynamics.

4.4.1 Phonon dispersions

The energy of a lattice system in equilibrium as a function of its displacements can be represented as a second-order Taylor expansion [99],

$$E(\mathbf{R}) = E_0 + \frac{1}{2} \sum_{i\alpha,j\beta} C_{\alpha\beta}(\mathbf{R}_i, \mathbf{R}_j) R_{i\alpha} R_{j\beta}. \quad (4.23)$$

²Numerically, it involves taking the gradient with respect to the neighbor lists from the data loading.

$C_{\alpha\beta}$ is the matrix of interatomic force constants (IFC) that indicates how the system responds to displacements and can be likened to a stiffness matrix.

It is convenient to represent properties in periodic systems in reciprocal space to utilize their translational symmetries. We introduce the dynamical matrix $D_{i\alpha,j\beta}(\mathbf{q})$ as the lattice Fourier transform of $C_{i\alpha,j\beta}$,

$$D_{i\alpha,j\beta} = \frac{1}{\sqrt{m_i m_j}} \sum_l C_{\alpha\beta} \left(\mathbf{R}_i^{(l)}, \mathbf{R}_j^{(0)} \right) e^{-i\mathbf{q} \cdot (\mathbf{R}_i^{(l)} - \mathbf{R}_j^{(0)})}. \quad (4.24)$$

Solving the eigenvalue problem of Eq. 4.24 gives the phonon frequencies of the system,

$$D(\mathbf{q}) \cdot \mathbf{e} = \omega_\nu^2(\mathbf{q}) \cdot \mathbf{e}, \quad (4.25)$$

where $\nu = 1, \dots, 3N$ indexes the $3N$ phonon branches.

Phonon dispersions can be determined from force fields by building the IFCs first through a finite difference/“frozen phonon” method, where the positions of the nuclei are clamped to allow the electronic degrees of freedom to relax. As an example, the forces $\mathbf{F}(\mathbf{R})$ determined from a trained MLIP can be used to build an approximated $C_{i\alpha,j\beta}$ through,

$$C_{i\alpha,j\beta} = -\frac{\partial F_{i\alpha}}{\partial R_{j\beta}} \approx -\frac{F_{i\alpha}(\mathbf{R}_j + \Delta) - F_{i\alpha}(\mathbf{R}_j - \Delta)}{2\Delta}. \quad (4.26)$$

The dynamical matrix at a particular wave vector $\mathbf{q}$ is then calculated from a system with a cell size commensurate to it using Eq. 4.24 and subsequently diagonalized to get the phonon bands. To calculate finer phonon resolutions, the use of larger and larger supercells is needed³ for the finite displacement method.

Larger supercells have interatomic distances that will exceed the radial cutoff chosen for constructing the neighbor lists of the force field. Because of this, phonon dispersions coming from long-range interactions will be absent: the q close to the high symmetry points will not be calculated. We next discuss a simple model where electrostatics manifests in lattice dynamics.

4.4.2 Phonons from long-range electrostatics

If the system responds to electric fields through the presence of charges, we can add it as an additional degree of freedom for its total energy. We can express the generic

³This is in contrast to DFPT where $D(\mathbf{q})$ are directly calculated in reciprocal space for an arbitrary $\mathbf{q}$ without the need for supercells.

quadratic form for the energy of a (cubic) system as [99, 100],

$$E(\mathbf{R}, \boldsymbol{\mathcal{E}}) = E_0 + \frac{1}{2} \sum_{i\alpha, j\beta} C_{i\alpha, j\beta} R_{i\alpha} R_{j\beta} + q \sum_{i\alpha\beta} R_{i\alpha} Z_{i\alpha\beta}^* \boldsymbol{\mathcal{E}}_\beta - \frac{\Omega}{8\pi} \sum_{\alpha\beta} \epsilon_{\alpha\beta} \boldsymbol{\mathcal{E}}_\alpha \boldsymbol{\mathcal{E}}_\beta. \quad (4.27)$$

Ω is the unit cell volume, $\epsilon_{\alpha\beta}$ is the dielectric tensor, and the coupling between the displacements $\mathbf{R}$ and $\boldsymbol{\mathcal{E}}$ is the Born effective charge of the ions, Z^* . The last two terms of Eq. 4.27 provide couplings to the electric field due to the presence of charges. We use the Hamilton equations of motion for momentum $p_{i\alpha}$ to determine the additional effect of the electric field on the phonons,

$$\frac{dp_{i\alpha}}{dt} = - \sum_{j\beta} C_{i\alpha, j\beta} R_{j\beta} - q \sum_{\beta} Z_{i\alpha\beta}^* \boldsymbol{\mathcal{E}}_\beta. \quad (4.28)$$

In the absence of free charges, $\boldsymbol{\mathcal{E}}$ and the electric displacement $\boldsymbol{\mathcal{D}}$ follow the Maxwell equations,

$$\nabla \times \boldsymbol{\mathcal{E}} \sim i\mathbf{q} \times \boldsymbol{\mathcal{E}} = 0, \quad \nabla \cdot \boldsymbol{\mathcal{D}} \sim i\mathbf{q} \cdot \boldsymbol{\mathcal{D}} = 0. \quad (4.29)$$

These two fields are related by the polarization vector $\boldsymbol{\mathcal{P}}$,

$$\boldsymbol{\mathcal{D}} = \boldsymbol{\mathcal{E}} + 4\pi\boldsymbol{\mathcal{P}}. \quad (4.30)$$

We take the derivative of Eq. 4.27 with respect to the electric field,

$$\frac{\partial E(\{\mathbf{R}\}, \boldsymbol{\mathcal{E}})}{\partial \boldsymbol{\mathcal{E}}_\beta} = q \sum_{i\alpha} R_{i\alpha} Z_{i\alpha\beta}^* - \frac{\Omega}{4\pi} \sum_{\alpha\beta} \epsilon_{\alpha\beta} \boldsymbol{\mathcal{E}}_\alpha. \quad (4.31)$$

Rearranging Eq. 4.31 provides expressions for the electric displacement and polarization,

$$\boldsymbol{\mathcal{D}}_\beta = -\frac{4\pi q}{\Omega} \sum_{i\alpha} R_{i\alpha} Z_{i\alpha\beta}^* + \sum_{\alpha\beta} \epsilon_{\alpha\beta} \boldsymbol{\mathcal{E}}_\alpha, \quad (4.32)$$

$$\boldsymbol{\mathcal{P}}_\beta = -\frac{q}{\Omega} \sum_{i\alpha} R_{i\alpha} Z_{i\alpha\beta}^* + \sum_{\alpha\beta} \frac{\epsilon_{\alpha\beta} - \delta_{\alpha\beta}}{4\pi} \boldsymbol{\mathcal{E}}_\alpha. \quad (4.33)$$

Differentiation with respect to $\mathbf{R}$ and $\boldsymbol{\mathcal{E}}$ provides expressions for the dielectric constant and the Born effective charges in terms of polarization,

$$\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + 4\pi \frac{d\boldsymbol{\mathcal{P}}_\beta}{d\boldsymbol{\mathcal{E}}_\alpha}, \quad Z_{i\alpha\beta}^* = -\frac{\Omega}{q} \frac{d\boldsymbol{\mathcal{P}}_\beta}{dR_{i\alpha}}. \quad (4.34)$$

Since $\mathcal{D}$ is divergence-free, we can express $\mathbf{q} \cdot \mathcal{D} = 0$ as,

$$-\frac{4\pi q}{\Omega} \sum_{i\alpha} R_{i\alpha} Z_{i\alpha\beta}^* \hat{\mathbf{q}}_\beta + \sum_{\alpha\beta} \hat{\mathbf{q}}_\alpha \epsilon_{\alpha\beta} \hat{\mathbf{q}}_\beta (\hat{\mathbf{q}} \cdot \mathcal{E}) = 0. \quad (4.35)$$

Isolating the electric field provides,

$$\mathcal{E} = \hat{\mathbf{q}} \frac{4\pi q}{\Omega} \sum_{k\beta} \frac{\sum_\gamma Z_{k\beta}^* \hat{\mathbf{q}}_\gamma}{\sum_{\alpha\beta} \hat{\mathbf{q}}_\alpha \epsilon_{\alpha\beta} \hat{\mathbf{q}}_\beta} R_{k\beta}. \quad (4.36)$$

Upon substitution into Eq. 4.28 we get an expression for the long-range contribution to the dynamical matrix,

$$D_{i\alpha,j\beta} = D_{i\alpha,j\beta}^{\text{an}} + D_{i\alpha,j\beta}^{\text{na}}, \quad (4.37)$$

where,

$$D_{i\alpha,j\beta}^{\text{na}} = \frac{4\pi}{\Omega} \frac{(\mathbf{q} \cdot \mathbf{Z}_i^*)_\alpha (\mathbf{q} \cdot \mathbf{Z}_j^*)_\beta}{\mathbf{q} \cdot \epsilon^\infty \cdot \mathbf{q}}. \quad (4.38)$$

It is labeled as non-analytic because Eq. 4.38 has an undefined limit at the Γ point, $\mathbf{q} = 0$. This term affects the phonon branches differently: transverse modes have $\mathcal{E}_T \perp \mathbf{q}$ so $\mathcal{E}_T = 0$ and will be unaffected by the electric field. In longitudinal modes, $\mathcal{E}_L \parallel \mathbf{q}$ thus affecting ω_L . At the zone center, the frequencies are given as,

$$\omega_T^2 = \omega_0^2, \quad (4.39)$$

$$\omega_L^2 = \omega_0^2 + \frac{4\pi(Z^*)^2}{\Omega \epsilon_\infty M}, \quad (4.40)$$

where ω_0 are the phonon frequencies obtained from $D_{i\alpha,j\beta}^{\text{an}}$. The longitudinal modes in Eq. 4.40 rely on the dielectric constant ϵ_∞ , which depends on a proper description of the susceptibility as discussed in Ch. 3.

4.4.3 Phonons for short-range and QEq models

To illustrate this effect, we train a short-range (PANNAJAX) and a charge equilibration (PANNAJAX-QEq) model on $2 \times 2 \times 2$ supercells of MgO in the conventional cell, with a lattice parameter $a \approx 8.4$ Å. SCF calculations were performed with the PBEsol exchange-correlation functional using the projector augmented-wave (PAW) method. We take around 1200 structures, of which 400 are sampled at 100, 300, 500 K each, and a few structures at a higher temperature at 1000 K to allow for variations in the displacements. The data are split 90:10 into training and validation sets.

As for the model, we use a LATTE descriptor with 150 bins each for the 2- and 3-body descriptors, and 50 bins for the 4-body contractions. The architecture chosen was $64 : 32 : M$, where $M = 1, 3$ for the short-range and QEq models, respectively. A

neural network cutoff of $R_c = 4.0 \text{ \AA}$ was used. Fig. 4.3 shows the coverage of the radial cutoff used, noting that only a fraction of the interactions contributing to the forces can be covered. The phonon dispersions for both models are shown in Fig. 4.4. DFPT

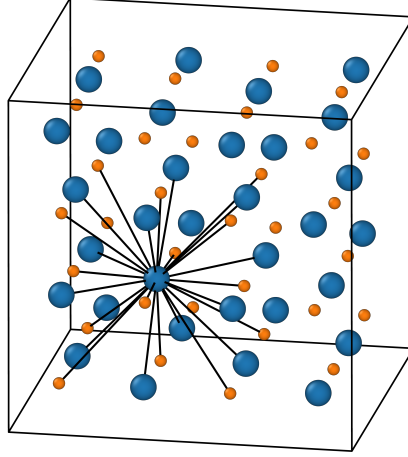


Figure 4.3: Sample structure for the MgO supercell showing an atom with its connected neighbors with $R_c = 4.0 \text{ \AA}$.

results are obtained from a $\text{nq1}, \text{nq2}, \text{nq3}=4, 4, 4$ grid mesh, which explicitly evaluates $\mathbf{q}$ points halfway along the $\Gamma \rightarrow X \rightarrow L$ path. From the finite displacement method, it is expected that larger supercells are able to capture commensurate $\mathbf{q}$ points closer to Γ from the X point and exhibit the LO-TO splitting. It is worth noting that even if ϵ_∞ and Z^* can be calculated from DFT, the model is only explicitly regressed in energies and forces.

Results show that the dispersions are independent of the supercell size. This is expected in the short-range model, as an $R_c = 4.0 \text{ \AA}$ cutoff will not be able to see most of the atoms beyond the unit cell as shown in Fig. 4.3. That the QEq model shows a virtually identical dispersion to its short-range counterpart may be attributed to the fact that a metallic ϵ_∞ effectively suppresses the difference in the LO and TO modes as $\omega_L^2 - \omega_T^2 \propto 1/\epsilon_\infty$ from Eqs. 4.39–4.40⁴. As discussed in Sec. 3.3, improvements in the QEq model are needed to temper the screening of ϵ . We will see in the following section how the SQE model is implemented in PANNA, and how well it performs in training and phonons.

⁴It is also possible that the solution reached by the QEq model provides atomic charges that are very close to 0, making it effectively a short-range model.

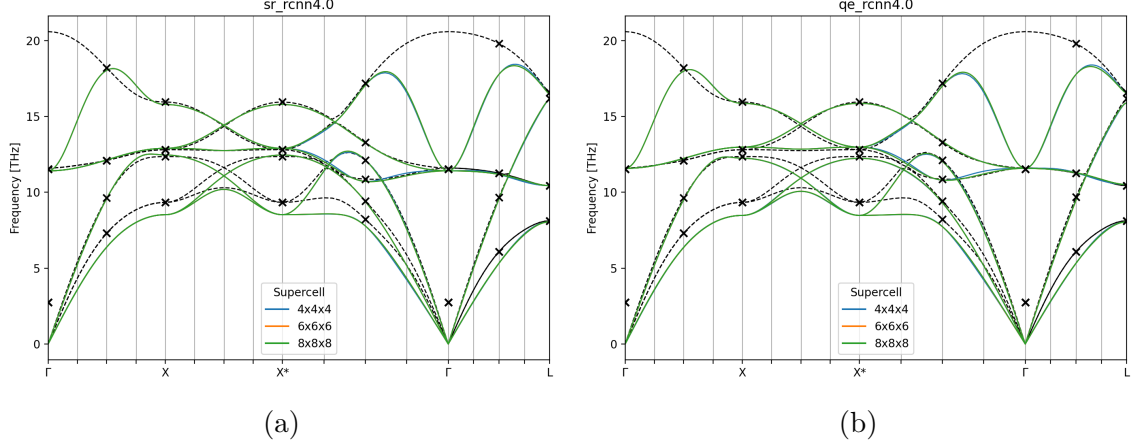


Figure 4.4: Phonon dispersions evaluated at different supercell sizes for (a) short-range and (b) QEq models. DFPT results are shown in black dashed lines with x markers indicating non-interpolated results.

4.5 PANNAJAX-SQE

Following Sec. 3.4, the SQE model extends from QEq by adding a bond penalty term shown in Eq. 3.56,

$$E_{SQE}(\{Q_i\}) = E_{QEq}(\{Q\}) + \frac{1}{2} \sum'_{b=(ij) \in \mathbf{L}} \kappa_b p_b^2.$$

The bond hardness term works similarly to the atomic hardness terms J_i , but corresponds to how likely a charge is allowed to stay between the orbitals of the two atoms that share it. While it is ideal that we allow the model to fully parametrize κ_b for all present bonds in the system, the current implementation of SQE is done with a constant hardness as a hyperparameter.

4.5.1 Creating the L_{ib} matrix

The fundamental element to be added in the SQE implementation is the topology matrix, L_{ib} . To allow for an unbiased method of selecting the bonds, we create $\mathbf{L}$ based on a cutoff, $R_{c,SQE}$, distinct from the neural network cutoff (see Eq. 3.58),

$$L_{ib} = \{b = (i, j) \mid \forall (i, j > i) \text{ s.t. } R_{ij} < R_{c,SQE}\}.$$

Details in the code implementation are discussed in Appendix C.2. With $\mathbf{L}$ created, we then discuss the peculiarities of solving the SQE system: the ill-conditioned nature of solving in bond space⁵, and what p_{ij} represents for periodic systems. We discuss

⁵Solving in atom space carries its own problems, namely not getting the dissociation limits (discussed in the Supplementary Material of [40]) and the off-diagonal elements of W_{ij} diverging to

both in the succeeding sections.

4.5.2 Bond variables are ill-conditioned

Following the discussion from Sec. 3.4.1, bond variable-based models carry the issue of generally being overcomplete: most of the time, *the number of bonds is much larger than the number of atoms*. The number of atoms in a structure is a well-defined property, whereas there are multiple ways to define a set of bonds connecting the atoms. Because of this, models that use bond variables almost always encounter linear systems with matrices that are ill-conditioned [40, 88]. That is, solutions of linear systems are very sensitive to its parameters. We revisit the L_{ib} of the fully connected system in Eq. 3.51,

$$L_{ib} = \begin{pmatrix} 1 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & -1 \end{pmatrix}.$$

The columns of the matrix are not linearly independent ($\text{col0} + \text{col2} = \text{col1}$), consistent with the fact that this system has a cyclic flow⁶. Generally, pseudoinverses are needed either when projecting back to atom space (Eq. 3.55) or the inversion of the SQE kernel to solve for p (Eq. 3.64). The current implementation in PANNAJAX-SQE uses ridge regression instead of truncated SVD, as the addition of bond-hardnesses κ or the regularization α act as ridge regularizers rather than abrupt truncations.

4.5.3 Periodic p_b are renormalized

The elements of L_{ib} have a direct meaning in non-periodic systems: there will be as many rows as there are atoms in the system, and the columns indicate all the permitted bonds $b = (ij)$ from $\mathbf{L}$. A more careful approach must be taken for periodic systems. Consider a simple periodic system with two atoms as shown in Fig. 4.5. The worst-case scenario (memory-wise) is to include all possible bonds. For the time being, let us introduce a notation on the split charges to determine from which cell the charge may be transferred, $p_{ij}^{(c \leftarrow c')}$. $c \leftarrow c'$ means the atom i from cell c (which is always the original cell indexed at 0) receives a charge from neighbor j at cell c' . We only consider split charges of the type $0 \leftarrow c'$ since only atoms in the unit cell are considered. From here we simplify the set of bonds b considered for periodic systems. First, interactions within the unit cell, $p_{ij}^{(0 \leftarrow 0)}$, are always included (solid orange line), as is done in

infinity for dissociating bonds.

⁶Three distinct bonds connecting three atoms create the simplest possible cyclic flow. More complex cyclic flows can be present (e.g., benzene rings), but 3-bond cyclic flow sets are very common in bond topologies that are unbiased/not dictated explicitly.

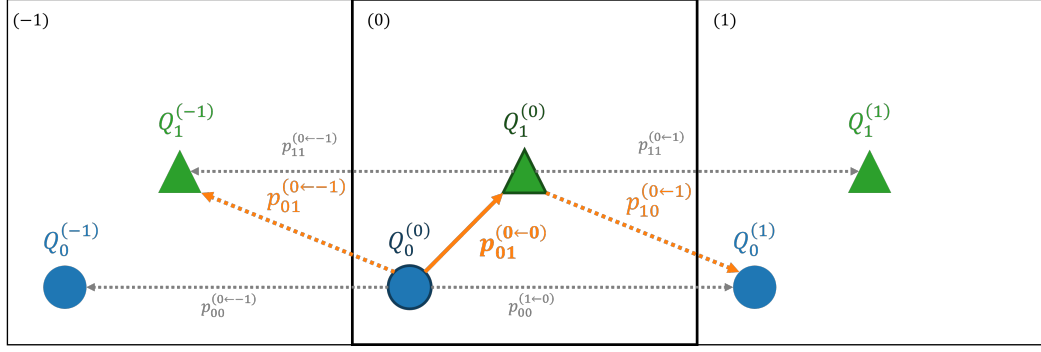


Figure 4.5: A sample periodic system with two atoms. The gray lines indicate a connection of the atom to its own periodic image, which constitutes a cyclic flow (overall charge transfer 0) and should not be included in L_{ib} . After considering redundant p_b /columns in L_{ib} , only a single independent variable, $p_{01}^{(0\leftarrow 0)}$, is left. This can be understood as the renormalized interaction between atom 0 and atom 1 and all its periodic images within the neighborhood of 0.

non-periodic systems. The first simplification comes from bonds referring to atoms that receive charges from their own replicas, $p_{ii}^{(0\leftarrow c)}$ (gray lines). These contribute a net zero charge transfer, and thus a cyclic flow, as periodicity dictates that it will receive the same charge that it gives. Secondly, interactions between different atoms at different replicas, $p_{ij}^{(0\leftarrow c)}$ (orange dotted lines), cannot be easily disregarded but show redundancies when represented in the topology matrix. From Fig. 4.5 we see that these two interactions are antisymmetric pairs of each other,

$$p_{01}^{(0\leftarrow -1)} = -p_{10}^{(0\leftarrow 1)}.$$

This leaves us with the remaining bonds $p_{01}^{(0\leftarrow 0)}$ and $p_{01}^{(0\leftarrow -1)}$,

$$L_{ib} = \begin{matrix} & p_{01}^{(0\leftarrow 0)} & p_{01}^{(0\leftarrow -1)} \\ \begin{matrix} Q_0 \\ Q_1 \end{matrix} & \begin{pmatrix} 1 & 1 \\ -1 & -1 \end{pmatrix} \end{matrix} \rightarrow L_{ib} = \begin{pmatrix} 1 \\ -1 \end{pmatrix},$$

which leads to identical columns, suggesting that these bond variables are redundant. Thus, there is only one independent variable in the system which is the sum of the two $p_{01} = p_{01}^{(0\leftarrow 0)} + p_{01}^{(0\leftarrow -1)}$, leading to a topology matrix that only considers the connections within a unit cell.

Having one independent p_{ij} for this system does not mean that the interactions from other cells are ignored. For periodic systems, it implies that p_{ij} accounts for a collective charge transfer: coming into atom i from its neighbors j as well as all its

periodic replicas⁷,

$$p_{b,\text{eff}} = \sum_{b \in (ij)} p_b. \quad (4.41)$$

This also means that the hardnesses κ_b that are coupled to the corresponding split charges p_b may be represented with an effective hardness,

$$\kappa_{b,\text{eff}} = \left(\sum_{b \in (ij)} \frac{1}{\kappa_b} \right)^{-1}. \quad (4.42)$$

The regularization methods discussed in Sec. 3.4.2 still allow the SQE linear system to be inverted even in the presence of repeated bonds. Nevertheless, future implementations should reduce as many redundancies in the topology matrix, collapsing all contributions to a collective flow and hardness with a procedure to obtain the effective quantities. A proposed algorithm is discussed in Appendix C.2.

4.6 Phonon dispersions in SQE

We now try to see if the long-range forces coming from the SQE models are able to produce the correct response in the phonons.

Like in Fig. 4.4, we plot the phonons in an ionic crystal, MgO, that has LO-TO splitting at the zone center using trained SQE models with a constant bond-hardness.

4.6.1 SQE parameters

The hyperparameters to be optimized for the SQE model are both the constant hardness $\kappa_b \rightarrow \kappa$ and the cutoff for the topology matrix, $R_{c,\text{SQE}}$. κ was chosen from a uniform logarithmic grid running from 10^0 to 10^{-9} , with a higher κ imposing a stronger penalty for charge transfer. The selected $R_{c,\text{SQE}}$ were 2.2, 3.0, and 5.0 Å corresponding to capturing the first-nearest neighbors, second-nearest neighbors, and a range that captures most of the cell and some periodic images.

4.6.2 Results

The training curves corresponding to the parameter sweeps are found in Fig. 4.7. We select $R_{c,\text{SQE}} = 5.0$ Å and $\kappa = 10^{-6}$ as the reference hyperparameters. Also included are the short-range and QEq models as black solid and dashed lines. That both models achieve similar errors in energies and forces hints that the QEq potential may have resulted in atomic charges close to zero, reverting to a short-range model. We

⁷From here on we drop the superscript ($0 \leftarrow c$).

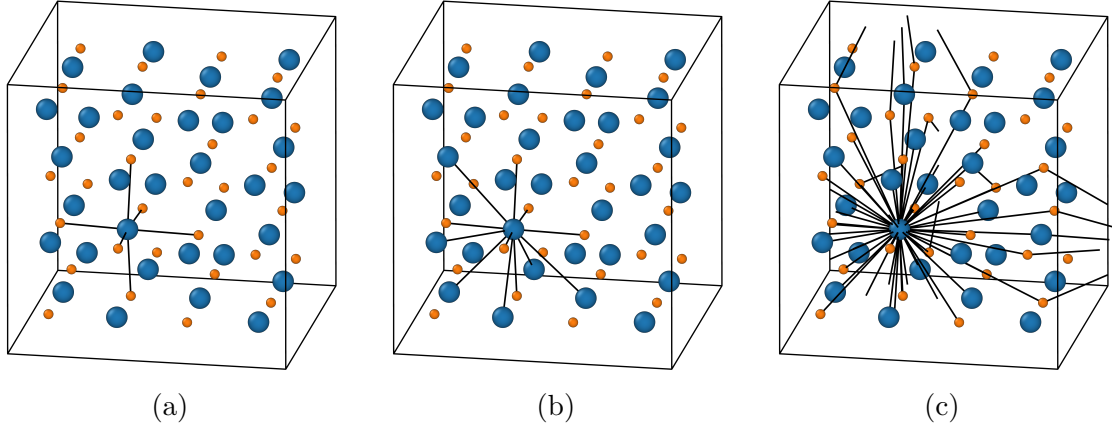


Figure 4.6: Connections of an Mg atom in a $2 \times 2 \times 2$ MgO supercell at different cutoffs used for dictating L_{ib} . From left to right: $R_{c,SQE} = 2.2, 3.0, 5.0$ Å.

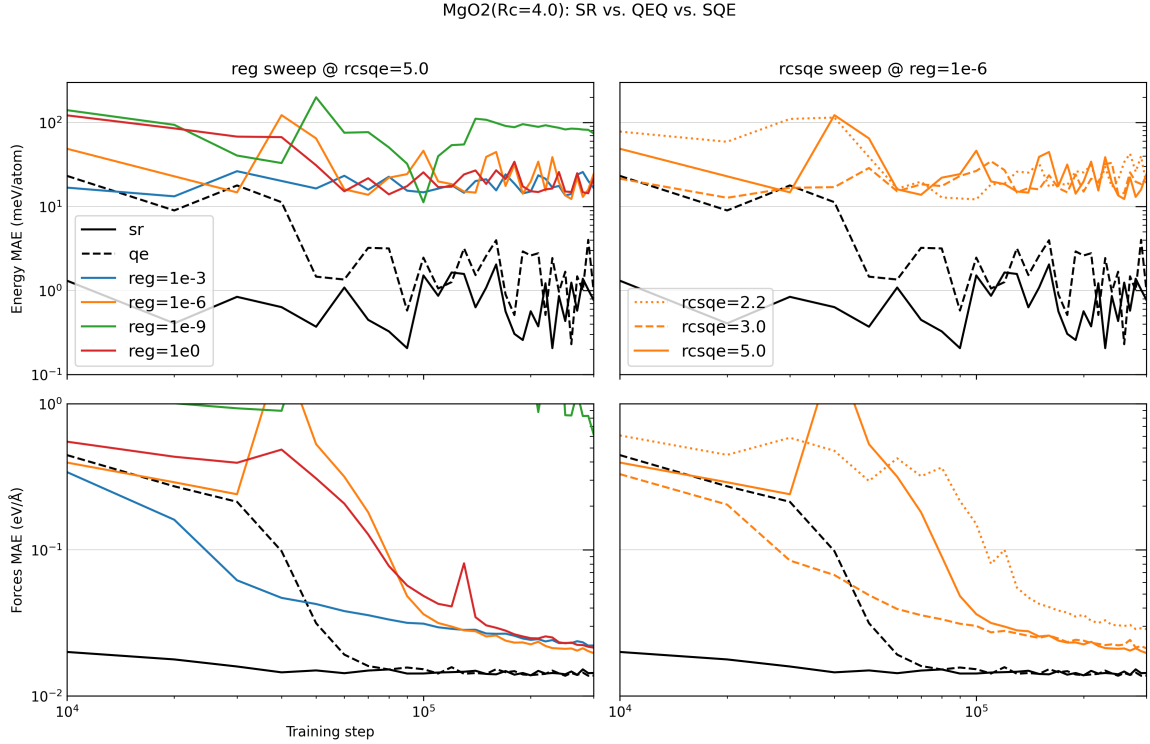


Figure 4.7: Training curves for different hyperparameter combinations of κ_b , $R_{c,SQE}$. For reference, solid and dashed black lines indicate the short-range and QEq models, respectively.

also see that the SQE models are sensitive to the hyperparameters, and almost always have higher errors than the SR and QEq models. The almost one order of magnitude difference in the energy can be attributed to the fact that the bond hardness is kept uniform and constant throughout, restricting the capability of the SQE models to achieve lower bounds. The smaller difference in the force errors is due to the constant bond hardness contributing nothing to the derivatives with respect to the neural network vectors.

Despite the poorer performance relative to the other two models, the energy (~ 20 meV/atom) and force (~ 30 meV/Å) errors still lead to stable phonon dispersions in Fig. 4.8. Promisingly, we see that larger supercells, whose commensurate $\mathbf{q}$ points lie closer to Γ , bring the LO-TO splitting closer to the DFPT results. While this is already different from the SR and QEq dispersions in Fig. 4.4, we also see that the phonons from the SQE model consistently underestimate the DFPT results. As stated earlier, the forces from the geometry-dependence of κ_b are notably absent as it was set to be constant⁸. We also plot the difference in squares of the LO and TO modes

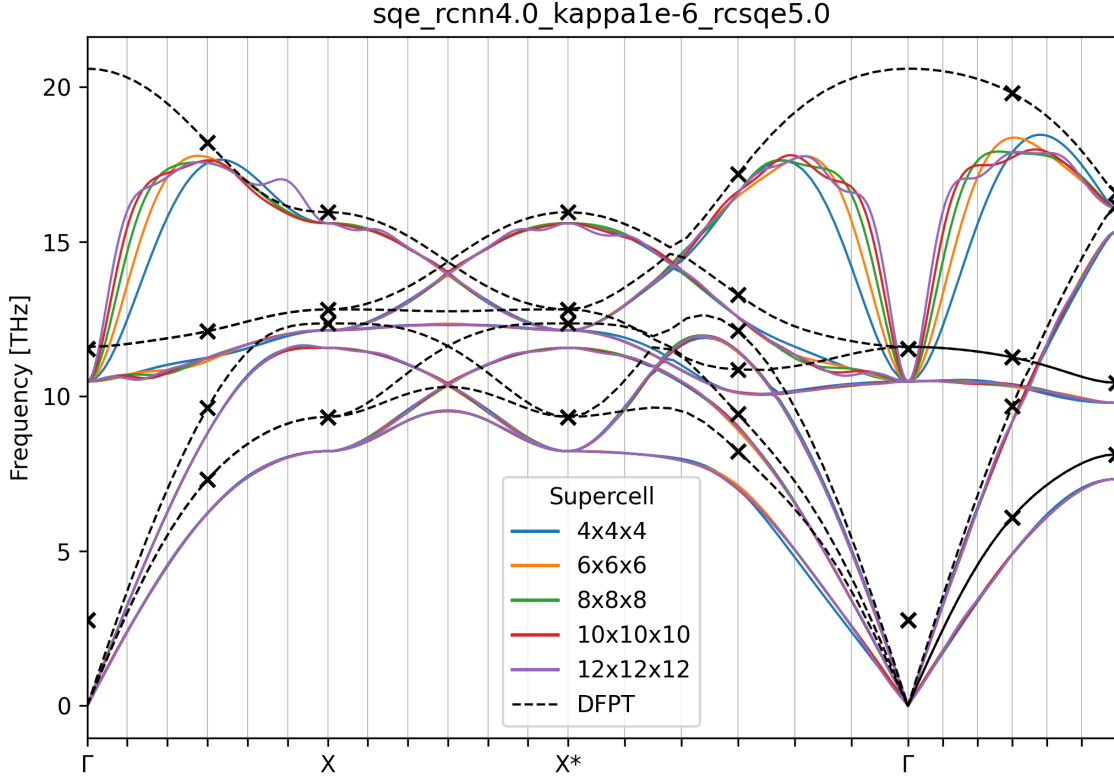


Figure 4.8: Phonon dispersion curves for a selected SQE model using the finite displacement method. The actual phonon calculations from commensurate $\mathbf{q}$ points are marked by black crosses, whereas phonon interpolation is shown by the dashed lines.

at the $\Gamma \rightarrow X$ branch in Fig. 4.9 as this is proportional to the ratio of $(Z^*)^2/\epsilon_\infty$. We highlight all the commensurate $\mathbf{q}$ from all the supercell sizes and see that, near Γ , the difference tends to a value of about 125 THz^2 as opposed to the DFPT value of 289 THz^2 . Coming back to Eqs. 4.39–4.40, we can provide values for the ratio from the difference,

$$\frac{(Z^*)^2}{\epsilon_\infty} = \frac{M\Omega}{4\pi} (\omega_L^2 - \omega_T^2). \quad (4.43)$$

With a lattice parameter $a = 4.22 \text{ Å}$, the estimated ratio from the SQE models has

⁸Studies on the linear response kernel [82, 101] indicate that X_{ij} are distance dependent and relate to the overlap of the orbitals between two atoms, and X_{ij} is linked to κ as discussed in Sec. 3.5.4.

$(Z^*)^2/\epsilon_\infty \approx 0.51$ as compared to the DFPT value of 1.18. While the ratio is less than half of the expected value, we already see that an approximate SQE model with a constant hardness is able to produce a qualitative difference of $\Delta(\omega^2)$ with various supercell sizes, which may be attributed to the dielectric constant ϵ_∞ being finite leading to a less metallic behavior.

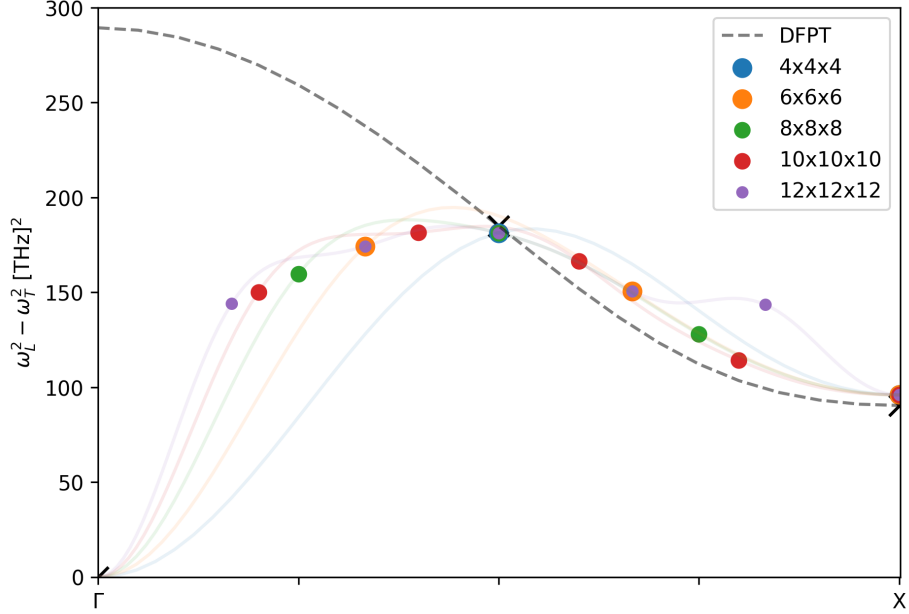


Figure 4.9: Difference of squared LO and TO modes $\omega_L^2 - \omega_T^2$ from $\Gamma \rightarrow X$. Reference DFPT values are marked with x, with interpolated values in dashed lines. Lightly colored lines are the interpolated differences for the various supercell sizes.

We can further improve the results via (a) data by training on larger supercells and (b) model by a proper parametrization of κ_b . For the data, even extending to $4 \times 4 \times 4$ supercells allows for finer commensurate $\mathbf{q}$ points (e.g., having $X/4, 3X/4$ calculated in the path $\Gamma \rightarrow X$) to get a splitting that is more consistent with the DFPT results. While this may be more computationally expensive, one can train not directly on DFT data but on data from a model that is cheaper but still captures the important physical phenomena [102]. For the model, a parametrizable and heterogeneous κ_b allows for greater flexibility and a fuller description of the forces coming from the geometry-dependence of the bond-hardness terms.

Chapter 5

Summary and outlook

This thesis investigates two ways in which representations of atomic environments affect the performance of MLIPs. In particular, we look into the convergence of body-ordered basis functions in the short-range regime and improvements to the ad hoc treatments of long-range electrostatics.

The ACE family of MLIPs takes advantage of an explicit body-ordered construction of their descriptors, and we try to answer the question, **“Do body-ordered basis functions converge to an effective lower-order (pair) interaction?”** We hoped that if it does, there is a way to employ truncation methods to make the descriptors more efficient. The self-interactions inherent in the unrestricted tensor products make it difficult to decorrelate the contributions of different orders K from each other, and only through the application of purification methods from Ho et al. [55] as well as a laborious training procedure of elemental systems do signatures of convergence in the coefficients manifest. Moreover, we confirm through tight-binding experiments in simple and symmetric systems that the canonical many-body expansion does not converge in general. Our study of body-order convergence suggests that the success of body-ordered potentials in describing quantum mechanical effects does not necessarily stem from capturing the lower-order energetics correctly, as they fail to do so even for simple systems.

We have also implemented a split-charge equilibration model in the PANNA MLIP as a way to address the metallic screening inherent in charge-equilibration schemes. For this part we endeavored to answer the question: **“Can a split-charge model be integrated into the MLIP pipeline to describe signatures of long-range interactions, namely the LO-TO splitting?”** We show that a more realistic representation of the bare susceptibility χ_0 is needed to provide finite dielectric behavior, and the SQE model is able to correct this behavior by dictating a bond topology through which atoms are allowed to transfer charge to one another. Despite not yet parametrizing the bond hardnesses κ_b , the SQE models are able to distinguish phonon dispersions calculated using the finite difference method at different supercell sizes,

and estimate a nonzero ratio of the $(Z^*)^2/\epsilon_\infty$ where the short-range and QEq models failed to do so. To the best of our knowledge, there has not been an extensive study of phonon dispersions with the SQE model, which is why we prioritized this initial test.

We envision further developments in each of the investigations. While we have seen that the canonical many-body expansion is conditionally convergent, it may be worth looking at situations in which the expansion may be re-expressed in a way that can be truncated early. Techniques similar to Haydock [103] may be used as motivation. It is worth noting that not only are 3-body descriptors insufficient [20] in differentiating more complicated geometries, but a recent study by Domina and Ceriotti [104] has also shown that even descriptors up to $K = 7$ result in degeneracies in describing atomic environments. While converging the energetics order by order may seem like a good direction in making the descriptors used by MLIPs more interpretable, it may be a futile effort to find efficient truncation methods as more complicated structures do not converge in body order even in the canonical expansion, which is itself difficult to construct.

Tests of the SQE extension of PANNA are ongoing and suggest multiple avenues for improvement:

1. Data: using much larger or asymmetric (e.g., $2 \times 2 \times 16$) supercells allows the models to be trained at commensurate $\mathbf{q}$ points closer to the Γ point.
2. Model construction: κ_b can be fully parametrized, which can reduce the training errors of the SQE models. Additionally, the topology matrix L_{ib} only has $0, \pm 1$ as its entries, and modifying them to be distance-dependent may allow for a smoother behavior at the dissociation limits.
3. Training targets: Calculations for the dielectric constants have been studied by Nistor and Muser [73] for NaCl, and having an expression for ϵ_∞ calculated from SQE elements can be leveraged as an additional target as $\epsilon_{\alpha\beta}$ can be readily calculated from DFT.
4. Different physical tests: SQE has also been studied to get proper dissociation behavior [86, 90] in molecular systems.

The SQE models are also related to other charge-flow models as discussed by Jensen [40]: ACKS2 as discussed in Ch. 3 and bond capacity models [89, 105]. These models are atom-centered and have the advantage of not using bond degrees of freedom, which almost always result in overdetermined systems as we have shown. Moving forward, we want to see how these charge flow models compare to state-of-the-art long-range MLIPs [106, 107] which have ingredients inspired by conceptual DFT.

With the advent of foundation or universal MLIPs, training bespoke models, while more time-consuming, has distinct merits in understanding how these surrogate models work so well. By having a greater amount of control in the MLIP construction pipeline, one has greater flexibility to probe and better understand how different descriptor architectures learn atomic environments, whether local or long-ranged.

Appendix A

Supplementary information for the body-order convergence project

A.1 Simulation parameters

For all runs: The cutoff is set to 5 Å for both the force and neighbor list cutoffs. The potential does not use the nonlinear version of the Finnis-Sinclair potential which is enabled by default in the pacemaker package. The radial basis is the Chebyshev expansion with cosine cutoff function. The energy-force cost balancing is set so that the RMSE for forces is weighted 50 times more than the energies. The optimizer is set to BFGS with a maximum of 3000 iterations and a batch size of 100. Details about the input files may be found in the [documentation](#) of pacemaker.

Table [A.1](#) lists the training parameters used for the dimer curves presented in Chapter 2.

Table A.1: Simulation parameters for dimer curve experiments

Training set	Descriptor label	Train steps	Validation set	nmax	lmax
Dimer 124	$K = 2, N_f = 45$	3000	val_dimer 123	100	0
	$K = 3, N_f = 90$	3000	val_dimer 123	45/8	0/2
	$K = 4, N_f = 250$	3000	val_dimer 123	45/5/4	0/2/2
Diamond 1000	$K = 2, N_f = 45$	3000	val_diverse 123	100	0
	$K = 3, N_f = 90$	3000	val_diverse 123	45/8	0/2
	$K = 4, N_f = 250$	3000	val_diverse 123	45/5/4	0/2/2
Diverse 1000	$K = 2, N_f = 45$	3000	val_diverse 1000	100	0
	$K = 3, N_f = 90$	3000	val_diverse 1000	45/8	0/2
	$K = 4, N_f = 250$	3000	val_diverse 1000	45/5/4	0/2/2
	$K = 4, N_f = 493$	3000	val_diverse 1000	45/8/4	0/3/3
	$K = 4, N_f = 930$	3000	val_diverse 1000	45/9/5	0/6/3
	$K = 5, N_f = 793$	3000	val_diverse 1000	45/8/4/3	0/3/3/2
Diverse 50000	$K = 4, N_f = 250$	3000	val_diverse 1000	45/5/4	0/2/2
	$K = 4, N_f = 493$	810	val_diverse 1000	45/8/4	0/3/3
	$K = 4, N_f = 930$	418	val_diverse 1000	45/9/5	0/6/3
	$K = 5, N_f = 793$	1151	val_diverse 1000	45/8/4/3	0/3/3/2

A.2 Additional plots

A.2.1 Force plots between DFT and dimer-trained potential

Fig. A.1 shows the force values from the reference DFT data (blue scatter) as compared with the values predicted by the NNP (orange line) at the short-range region for the dimer-trained potential with $K = 4$ and $N_f = 250$. We see that despite low relative errors (maximum at 13%), the absolute force errors are large, which contributes to the large validation errors at the overfitting region.

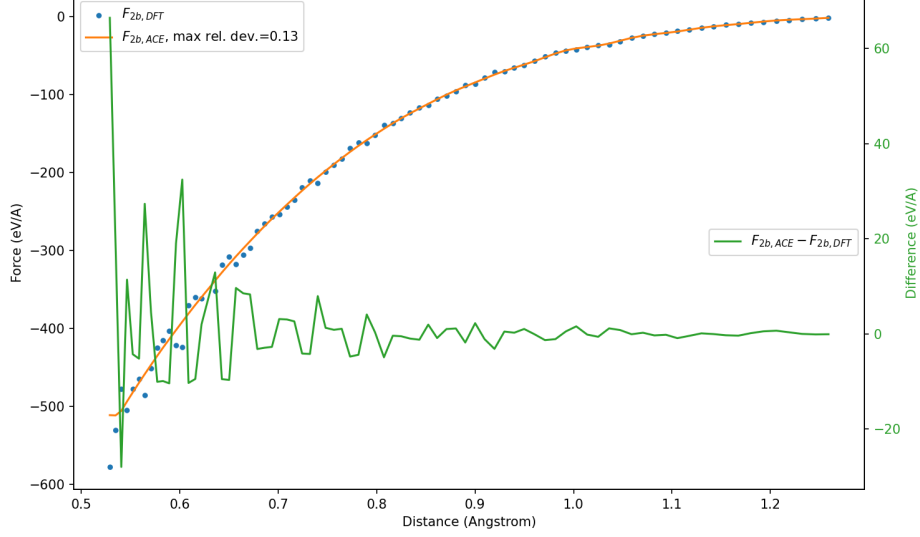


Figure A.1: Forces at the short-range region for the dimer-trained potential and the difference between the forces of the DFT and the dimer-trained potential (green, right y-axis).

A.2.2 Loss analysis of diverse dataset dimer curves

Fig. A.2 (top) shows the loss $\mathcal{L}$ vs. number of functions N_f for the potential trained on the diverse dataset and (bottom) the corresponding dimer curves at the terminal N_f for each body-order K . We see from the loss curves that opening the channel for more complex basis functions by increasing K does help improve training. Further evidence of this comes from the faint lines, which are loss data from potentials still trained with $K = 2$ (or $K = 3$) but with the same number of functions as the next higher K . Nevertheless, the dimer curve shows a more prominent qualitative change going from $K = 2$ to $K = 3$ than from $K = 3$ to $K = 4$, even though the drop in losses is smaller. From here we see that the parameters at which the loss converges do not indicate that the curves have already converged.

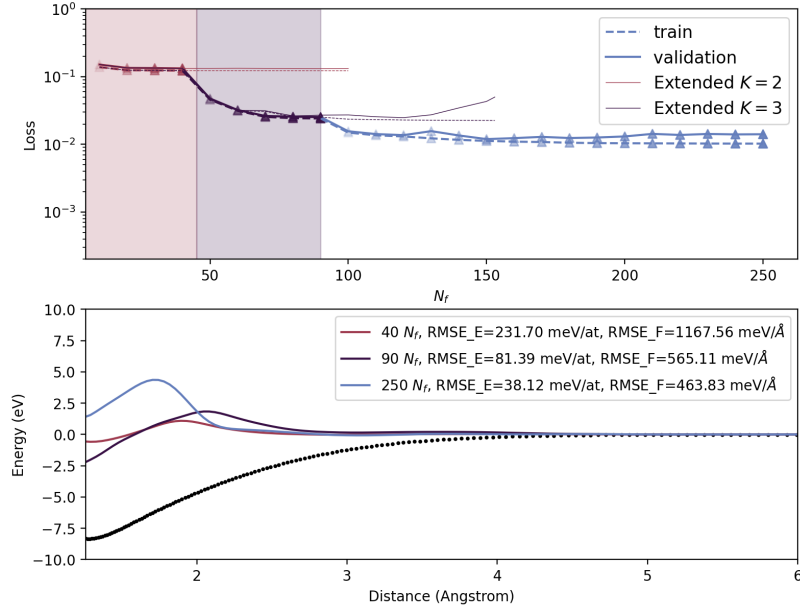


Figure A.2: $\mathcal{L}$ vs. N_f (top) and dimer curves (bottom) for the diverse dataset. Orange and pink plots correspond to potentials with only $K=2$ and up to $K=3$ functions, respectively, while purple curves include $K=4$ functions. The x-values of the dimer curve start at the minimum distance found in the diverse dataset.

A.2.3 Biasing the diverse dataset with dimer data

Fig. A.3 shows the effect of biasing the diverse dataset with an increasing number of dimer structures. These tests were done to verify that the linear ACE potentials are fully capable of learning the correct interaction curve if sufficient data is provided. We show that once around 10% of the dataset is composed of dimer structures, the potential is able to approach the DFT data. We also added an additional potential trained on the dataset with 50 dimers added but initialized with a different seed to ensure that initialization effects are minimal.

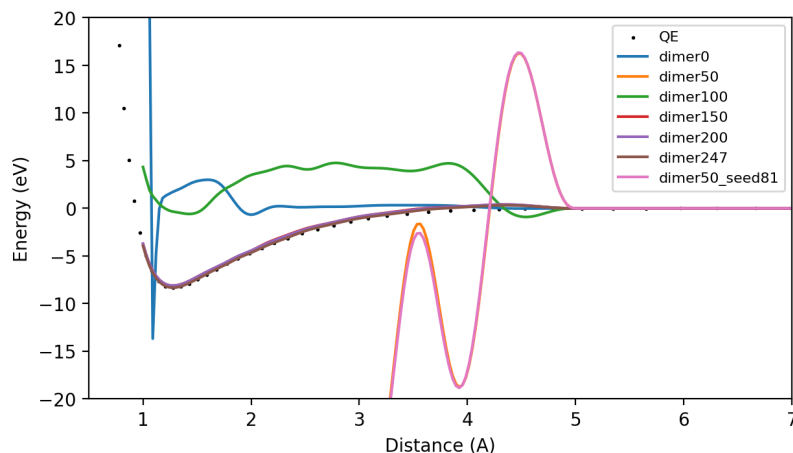


Figure A.3: Dimer curves of potentials trained from the mixture of the 1000 structures from the diverse dataset with an increasing number of structures from the dimer dataset. An additional potential was also trained on the dataset with 50 dimers added but initialized with a different seed to check the initialization effects. Prominent oscillations at short range are due to the absence of bond pairs in structures in the dataset at the sub-1 Å distance region.

A.2.4 Learning curves of diverse dataset runs

Figs. A.4 and A.5 show the learning curves for the diverse dataset with 1000 and 50000 structures, respectively. The different colors indicate the descriptor sets of varying complexity and body-order as controlled by K and N_f . In general, we see that the potentials trained on the dataset with fewer structures approach the overfitting regions much faster, which indicates that less complex descriptor sets, which have fewer parameters, are less susceptible to overfitting. On the other hand, the potentials trained with 50 times as much data have still not overfit. Both learning curves have losses around the same order of magnitude, which indicates that the larger dataset benefits from the more complex descriptor sets¹.

¹We did not train for longer as it would be computationally expensive without the promise that the losses and dimer curves would have improved by then.

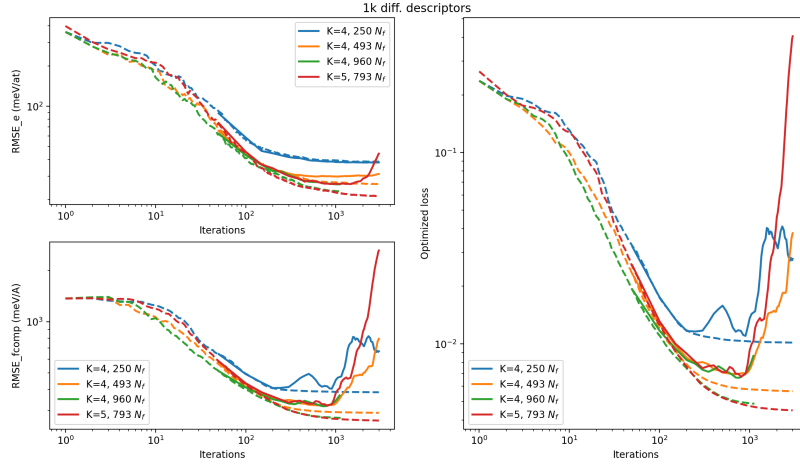


Figure A.4: Learning curves for (upper left) energy, (lower left) force, and (right) total for the diverse dataset with 1000 structures. Different colors indicate different descriptor sets with varying K and N_f .

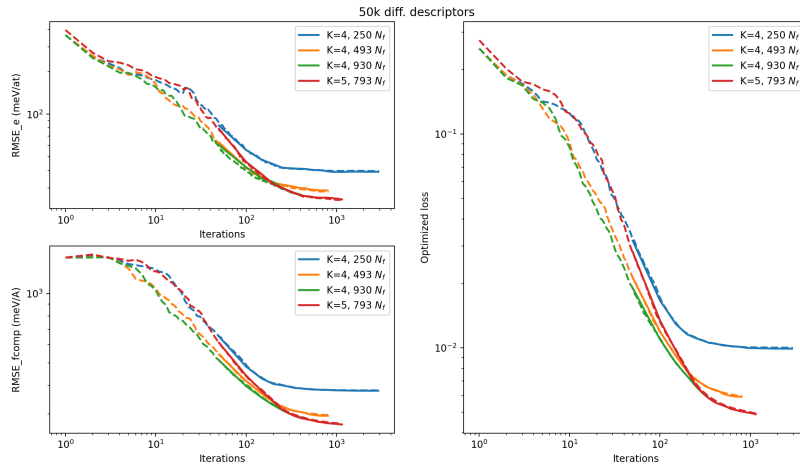


Figure A.5: Learning curves for (upper left) energy, (lower left) force, and (right) total for the diverse dataset with 50000 structures.

A.2.5 Learning curves and dimer curves for 5k and 10k runs

Figs. A.6 and A.7 show the learning curves for the diverse dataset with 5000 and 10000 structures, respectively. The different colors indicate the descriptor sets of varying complexity and body-order as controlled by K and N_f . Less prominent overfitting is observed in the 5000 dataset as compared to the learning curve of the potentials trained on the 1000-structure dataset. The learning curves of the 10000 dataset do not show any signs of overfitting after the runs were completed. Their corresponding dimer curves in Figs. A.8 and A.9 show behavior similar to that of the potentials trained on the 1000 and 50000 structures in that the dimer curves do not approach a defined curve as higher K basis functions are introduced in the descriptor set.

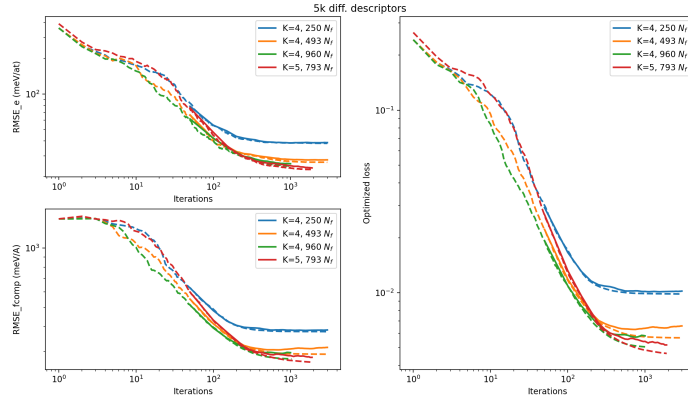


Figure A.6: Learning curves for (upper left) energy, (lower left) force, and (right) total for the diverse dataset with 5000 structures. Different colors indicate different descriptor sets with varying K and N_f .

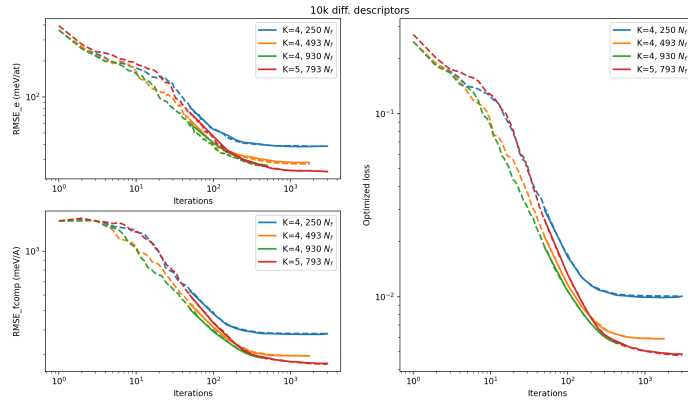


Figure A.7: Learning curves for (upper left) energy, (lower left) force, and (right) total for the diverse dataset with 10000 structures.

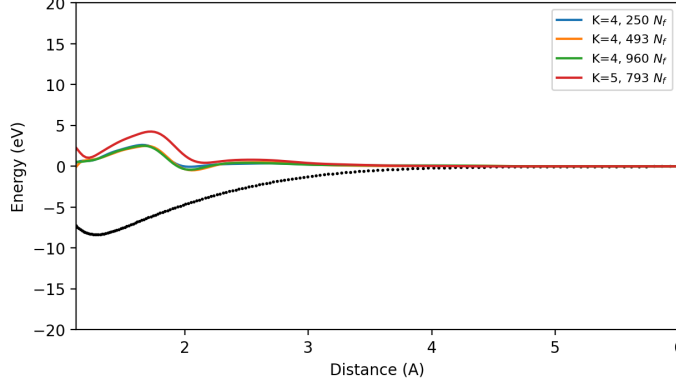


Figure A.8: Dimer curves for the diverse dataset with 5000 structures. Different colors indicate different descriptor sets with varying K and N_f .

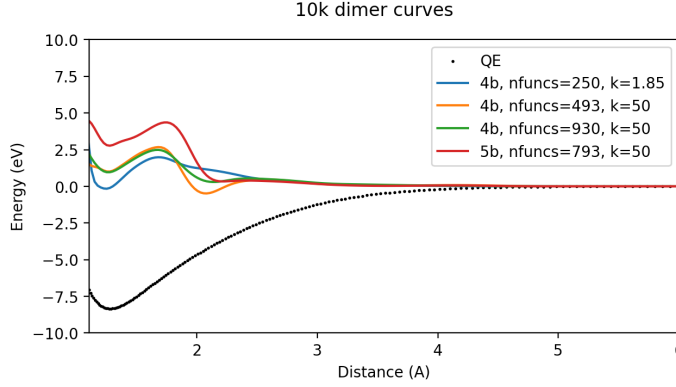


Figure A.9: Dimer curves for the diverse dataset with 10000 structures. Different colors indicate different descriptor sets with varying K and N_f .

A.3 Derivation of the symmetric tight-binding result

At the tight-binding level of theory, we already see that the higher orders of the many-body/cluster expansion may not necessarily converge. We look at symmetric systems of N hydrogen atoms, i.e., systems in which all the pairwise $V^{(K=2)}$ interactions are equal to each other, and likewise for higher orders up to the highest possible order, $K = N$. The shortened form of Eq. 2.14 is,

$$E^{(N)} = \sum_{K=0}^N \sum_{i_1 < i_2 < \dots < i_K} V^{(K)}(\mathbf{R}_{i_1}, \mathbf{R}_{i_2}, \dots, \mathbf{R}_{i_K}). \quad (\text{A.1})$$

We examine a highly symmetric case wherein all the interactions $V^{(K)}$ are identical for a particular body order K due to highly symmetrized systems C_N . Physically realizable systems run from $K = 0$ to 4, where C_0 refers to the background energy,

and C_4 the regular tetrahedron². The sum over indices $\{i_k\}$ in Eq. A.1 simplifies to a combinatoric factor,

$$E^{(N)} = \sum_{K=0}^N \binom{N}{K} V^{(K)}. \quad (\text{A.2})$$

All $V^{(K)}$ of a given order are identical, and each order appears with a combinatoric multiplicity. The corresponding Schrödinger equation in matrix form is,

$$HU = \begin{pmatrix} 0 & t & \dots & t \\ t & 0 & \ddots & t \\ \vdots & \ddots & \ddots & t \\ t & \dots & t & 0 \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \\ \vdots \\ U_N \end{pmatrix} = \varepsilon U. \quad (\text{A.3})$$

Before we continue, we list the properties we expect of our solutions:

Wishlist

1. In a system of N particles with a particle removed, we want the energy to go from $E_N \rightarrow E_{N-1}$.
2. In the eigenvalue level occupation for the tight-binding case, the a -th eigenvalue is,

$$\varepsilon_a = \begin{cases} (N-1)t, & a = 0 \\ -t, & a = 1, \dots, N-1, \end{cases} \quad (\text{A.4})$$

with $t < 0$. One can show this by induction starting from the $N = 2, 3$ symmetric Hamiltonians as before. This should hold except when $N = 0$ as the vacuum energy is defined to be 0.

3. The K -th subcluster is obtained by isolating the lower-order subclusters,

$$V^{(N)} = E^{(N)} - \sum_{K=0}^{N-1} \binom{N}{K} V^{(K)}, \quad (\text{A.5})$$

and should be,

$$V^{(K)} = (-1)^K K t, \quad K \geq 2. \quad (\text{A.6})$$

Hamiltonians of the form in Eq. A.3 have eigenvectors which are cyclic. This

²While it is difficult to realize symmetric geometries for $K \geq 5$, clusters wherein all the interactions between each permutation of bonds are symmetric are possible.

suggests an ansatz $U_{a,j}$ where³,

$$U_{a,j} = \frac{1}{\sqrt{N}} e^{i2\pi aj/N}. \quad (\text{A.7})$$

Looking at the j -th row of the LHS,

$$\begin{aligned} (HU_a)_j &= \sum_{l=1}^N H_{jl} U_{a,l}, \\ &= \sum_{l=1}^N H_{jl} \left(\frac{1}{\sqrt{N}} e^{i2\pi al/N} \right), \\ &= \sum_{l=1}^N t(1 - \delta_{jl}) \frac{1}{\sqrt{N}} e^{i2\pi al/N}, \\ (HU_a)_j &= \frac{t}{\sqrt{N}} \left(\sum_{l=1}^N e^{i2\pi al/N} - e^{i2\pi aj/N} \right). \end{aligned} \quad (\text{A.8})$$

Because of the cyclic nature of the solution, the sum on the RHS goes to 0 unless $a = 0$,

$$\begin{aligned} (HU_a)_j &= \frac{t}{\sqrt{N}} (N\delta_{a0}(1) - e^{i2\pi aj/N}), \\ &= \frac{t}{\sqrt{N}} (N\delta_{a0}(e^{i2\pi aj/N}) - e^{i2\pi aj/N}), \\ (HU_a)_j &= t(N\delta_{a0} - 1)U_{a,j}, \end{aligned} \quad (\text{A.9})$$

where we declare $\delta_{a0} = \delta_{a0}(e^{i2\pi aj/N})$. Eq. A.9 satisfies the second item in the wishlist corresponding to the a -th eigenenergy, in particular the nondegenerate ε_0 ,

$$\varepsilon_0 = (N - 1)t, \quad N \geq 1. \quad (\text{A.10})$$

By induction and reviewing the equilateral trimer case in Eqs. 2.24–2.26 we know that the rest of the eigenvalues will be degenerate. Since the full trace must be zero, all of the other eigenvalues must be $-t$, which validates the second case of wishlist item 2.

Since the system is nonmagnetic, two electrons will always occupy the lowest energy level ε_0 , and the remaining $N - 2$ electrons occupy the degenerate $-t$ levels. As an example, we calculate the trimer energy and $V^{(3)}$ subclusters using Eqs. A.10

³ a is the eigenvalue index and j is the component of the solution.

and 2.25,

$$\begin{aligned}
E^{(3)} &= 2\varepsilon_0 + (3 - 2)\varepsilon_{(a \neq 0)} \\
E^{(3)} &= 2(2t) + (-t) = 3t, \\
V^{(3)} &= E^{(3)} - \binom{3}{2}V^{(2)} - \binom{3}{1}V^{(1)} - \binom{3}{0}V^{(0)}, \\
V^{(3)} &= 3t - 3(2t) - 0 - 0 = -3t,
\end{aligned}$$

which confirms the equilateral trimer results from Eqs. 2.25–2.26. Doing so again for the tetramer and pentamer,

$$\begin{aligned}
E^{(4)} &= 2\varepsilon_0 + (4 - 2)\varepsilon_{(a \neq 0)} \\
E^{(4)} &= 2(3t) + 2(-t) = 4t, \\
V^{(4)} &= E^{(4)} - \binom{4}{3}V^{(3)} - \binom{4}{2}V^{(2)} \\
V^{(4)} &= 4t - 4(-3t) - 6(2t) = 4t.
\end{aligned}$$

$$\begin{aligned}
E^{(5)} &= 2(4t) + 3(-t) = 5t, \\
V^{(5)} &= E^{(5)} - \binom{5}{4}V^{(4)} - \binom{5}{3}V^{(3)} - \binom{5}{2}V^{(2)} \\
V^{(5)} &= 5t - 5(4t) - 10(-3t) - 10(2t) = -5t.
\end{aligned}$$

By induction, we notice a general trend for the subclusters of symmetric systems in Wishlist item 3, Eq. A.6. This expression also confirms the result from [42].

Finally, we confirm wishlist item 1: that we recover consistent energetics when a particle is removed from the system. We denote the energy of the highly symmetric system of originally N atoms with one atom removed as $E_{\text{extract}}^{(N)}$. The goal is to show,

$$E_{\text{extract}}^{(N)} = E^{(N-1)}.$$

We look at the trimer case as an example. An intuitive way of looking at this term is,

$$\begin{aligned}
E_{\text{extract}}^{(3)} &= E^{(3)} - \text{“energy added by including a 3rd atom in the two-particle case.”} \\
&= E^{(3)} - V^{(3)} - 2V^{(2)} \\
E_{\text{extract}}^{(3)} &= 3t - (-3t) - 2(2t) = 2t = E^{(2)}.
\end{aligned}$$

For the tetramer case, we calculate using a form similar to Eq. A.5,

$$\begin{aligned} E_{\text{extract}}^{(4)} &= E^{(4)} - V^{(4)} - \left[\binom{4}{3} - \binom{3}{3} \right] V^{(3)} - \left[\binom{4}{2} - \binom{3}{2} \right] V^{(2)}, \\ E_{\text{extract}}^{(4)} &= 3t = E^{(3)}, \end{aligned}$$

where the prefactor in brackets indicates “the number of K -terms when there are 4 particles minus the number of terms when one particle is removed”. Both the $N = 3$ and 4 cases show that the tight-binding cases for symmetric systems follow wishlist item 1, which provides a reasonable model in describing the many-body expansion.

A general expression for the total energy of a symmetric system with one particle removed may be given as,

$$E^{(N-1)} = E^{(N)} - V^{(N)} - \sum_{K=2}^{N-1} \left[\binom{N}{K} - \binom{N-1}{K} \right] V^{(K)}. \quad (\text{A.11})$$

From here we verify the expected behavior that a removal of a single particle from a structure of N particles will have the energy of a system with $N - 1$ particles.

Appendix B

Generic case for the atom-space mapping of SQE

We thank the reviewer, Federico Grasselli, for pointing out the subtlety in properly representing the split charge variable $\mathbf{p}$ in transforming it back to atom space. Below we detail an alternate discussion of what was presented from the referee review.

As seen from Eq. 3.53,

$$\mathbf{p} = \mathbf{L}^+ \mathbf{\Delta} + \mathbf{z} = \mathbf{p}_0 + \mathbf{z},$$

the reverse mapping of $\mathbf{p}$ should include the cycle mode vectors $\mathbf{z}$ to indicate the gauge freedom. The contributions of bond-hardness in atom space as presented in Eq. 3.66 only work coincidentally in the case of homogeneous hardness $\boldsymbol{\kappa}$ as discussed in the main body of the thesis. A more careful atomic representation of the energy related to the bond penalty requires finding $\mathbf{p}$ that minimizes,

$$E_{\kappa} = \frac{1}{2} \mathbf{p}^T \boldsymbol{\kappa} \mathbf{p} = \frac{1}{2} (\mathbf{p}_0 + \mathbf{z})^T \boldsymbol{\kappa} (\mathbf{p}_0 + \mathbf{z}).$$

Getting the right $\mathbf{p}$ can be done through a constrained minimization of E_{κ} . We minimize a Lagrangian of the following form,

$$F(\mathbf{z}, \lambda) = \frac{1}{2} (\mathbf{p}_0 + \mathbf{z})^T \boldsymbol{\kappa} (\mathbf{p}_0 + \mathbf{z}) - \lambda^T (\mathbf{L} \mathbf{z}), \quad (\text{B.1})$$

where the constraint is ensuring that $\mathbf{L} \mathbf{z} = 0$, or that $\mathbf{z}$ belongs to the kernel of $\mathbf{L}$. Minimizing F wrt. $\mathbf{z}$,

$$\begin{aligned} \frac{\partial F}{\partial \mathbf{z}} &= \frac{1}{2} \mathbf{p}_0 \boldsymbol{\kappa} \mathbf{p}_0 + \mathbf{p}_0^T \boldsymbol{\kappa} \mathbf{z} + \frac{1}{2} \mathbf{z}^T \boldsymbol{\kappa} \mathbf{z} - (\mathbf{L}^T \lambda)^T \mathbf{z} \\ 0 &= \boldsymbol{\kappa} (\mathbf{p}_0 + \mathbf{z}) - \mathbf{L}^T \lambda \\ \mathbf{p} &= \boldsymbol{\kappa}^{-1} \mathbf{L}^T \lambda. \end{aligned} \quad (\text{B.2})$$

Acting $\mathbf{L}$ on $\mathbf{p}$ gives the Lagrange multiplier,

$$\begin{aligned}\mathbf{L}\mathbf{p} &= \mathbf{\Delta} = \mathbf{L}(\boldsymbol{\kappa}^{-1}\mathbf{L}^T\lambda) \\ \lambda &= (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{\Delta},\end{aligned}\tag{B.3}$$

where we use a pseudoinverse since $\mathbf{L}$ is generally non-invertible. We substitute λ to get the appropriate value for $\mathbf{p}$,

$$\mathbf{p} = \boldsymbol{\kappa}^{-1}\mathbf{L}^T (\mathbf{L}\boldsymbol{\kappa}\mathbf{L}^T)^+ \mathbf{\Delta},\tag{B.4}$$

and subsequently plug in $\mathbf{p}$ to the bond energy to get the correct $\mathbf{W}$,

$$\begin{aligned}E_\kappa &= \frac{1}{2}(\boldsymbol{\kappa}^{-1}\mathbf{L}^T (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{\Delta})^T \boldsymbol{\kappa}(\boldsymbol{\kappa}^{-1}\mathbf{L}^T (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{\Delta}) \\ &= \frac{1}{2}\mathbf{\Delta}^T (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{L}\boldsymbol{\kappa}^{-1}\boldsymbol{\kappa}\boldsymbol{\kappa}^{-1}\mathbf{L}^T (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{\Delta} \\ &= \frac{1}{2}\mathbf{\Delta}^T (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{\Delta} \\ E_\kappa &= \frac{1}{2}\mathbf{\Delta}^T (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+ \mathbf{\Delta} = \frac{1}{2}\frac{1}{2}\mathbf{\Delta}^T \mathbf{W}\mathbf{\Delta}.\end{aligned}\tag{B.5}$$

We then recognize the generic $\mathbf{W}$ as,

$$\mathbf{W} = (\mathbf{L}\boldsymbol{\kappa}^{-1}\mathbf{L}^T)^+.\tag{B.6}$$

Appendix C

Additional information for PANNA code implementation

C.1 Carbon chain test

A test run was done to see if the extension of PANNA-QEq to use upgraded libraries and auto-differentiation provides the same advantages as discussed in [37]. To verify consistency with the original model, tests were done on the carbon chain dataset from [27] for two similar structures, $\text{C}_{10}\text{H}_3^+$ and C_{10}H_2 , visualized in Fig. C.1. A cutoff radius of $R_c = 4.23 \text{ \AA}$ was chosen, as shown in Fig. C.1. The validation error

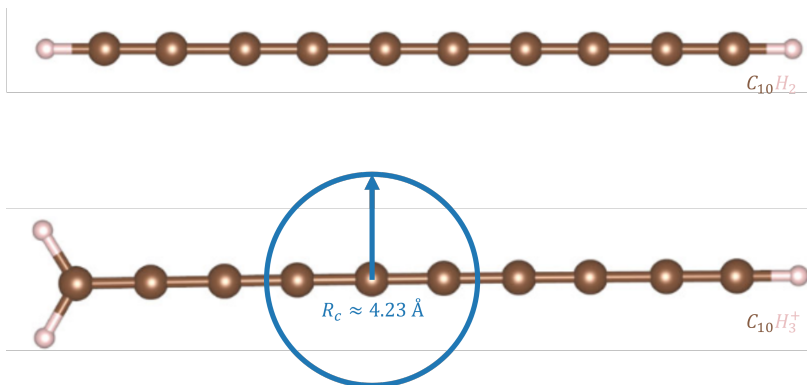


Figure C.1: Carbon chain structures, $\text{C}_{10}\text{H}_3^+$ and C_{10}H_2 . The chosen cutoff radius, $R_c = 4.23 \text{ \AA}$, is shown.

curves of the different versions of the models are shown in Fig. C.2. We see that the PANNAJAX-QEq model is able to achieve the same losses as a bespoke PANNA-QEq model and the reference values. The short-range model does not go below $100 \text{ meV/\AA}$ unless the cutoff radius is doubled, at the cost of poorer scaling of the neighbor lists in training time and memory. We also show that the PANNAJAX-QEq model trains adequately whether charges were regressed or not.

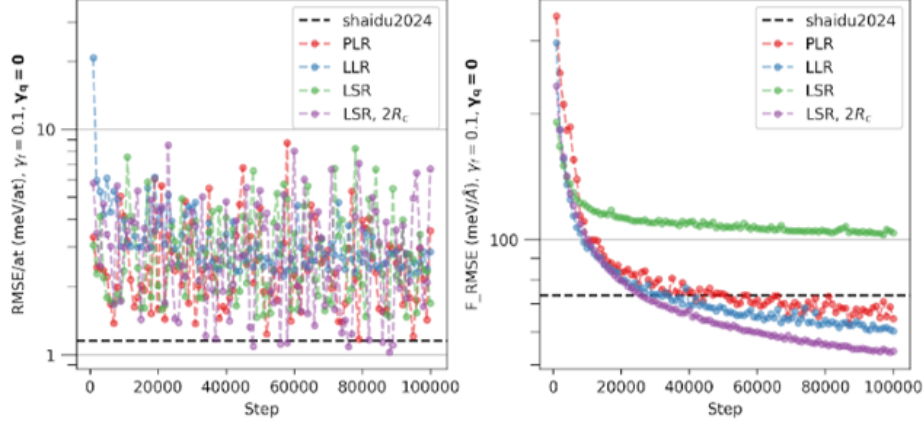


Figure C.2: Validation curves for energy (left), force components (center), and charges (right) for different models. The different models are PANNA-QEq (red), PANNAJAX-QEq (blue), and a short-range model (green). An additional model for a doubled R_c (purple) is included. Dashed lines are reference values from [37]. All models were trained without regressing on charges, $\gamma_q = 0$.

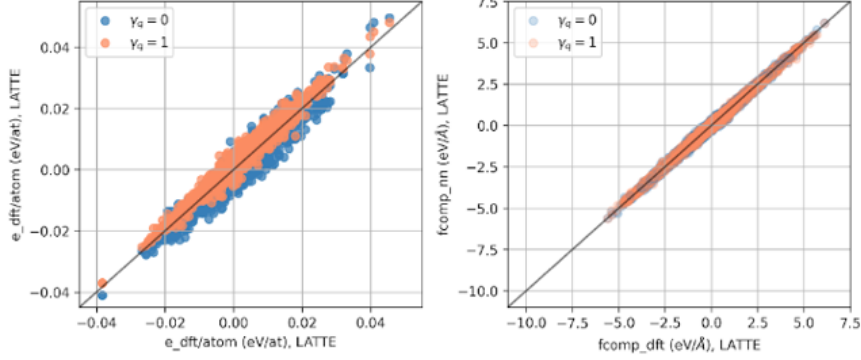


Figure C.3: Parity plot for energies (left) and forces (right) for the PANNAJAX-QEq models regressed (orange) and not regressed (blue) on charges.

C.2 Creating the topology matrix

The process for creating the topology matrix is written below¹.

1. Fill the neighbor list for neighbors j for each atom i ,

$$\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i, \quad (\text{C.1})$$

where $\mathbf{R}_j$ runs over all neighbors in the unit cell and periodic images that are within the cutoff $R_{c,\text{SQE}}$.

2. Concatenating `inda_sqe` and `indb_sqe` gives the `row` indices, which record each time an atom appears in the split-charge variables. Each pair ij appears twice: the second time from its antisymmetric ji counterpart (Eq. 3.46).

¹The same process is done for getting the neighbor list for the neural networks, except the indices do not need to be unique (i.e., it includes both (0,1) and (1,0)).

3. The columns represent all the relevant bonds, which are ordered the same way as `(inda_sqe, indb_sqe)`. In the index tuple, each bond will appear twice (i.e., p_{10} is implicitly included as a -1 in $\mathbf{L}$). To ensure this, the `range(nbonds)` function is entered twice for the `col` indices.
4. $\mathbf{L}$ will always have an equal number of 1 and -1 entries due to charge conservation. The `L_elem` list has the right number of these elements, with all the positive entries first before the negative ones, in correspondence to `col`.
5. Scatter `L_elem` into $\mathbf{L}$ at `(row,col)`.

Code

```
def build_L(inda_sqe, indb_sqe, nats):

    nb = len(inda_sqe) # no. of bonds
    # rows collect all of the times atom appears in a bond.
    # second half is negative as atom enters in 2nd index.
    rows = np.concatenate([inda_sqe, indb_sqe])
    cols = np.concatenate([np.arange(nb), np.arange(nb)])
    L_elem = np.concatenate([np.ones(nb), -1*np.ones(nb)])
    L = np.zeros((nats, nb)).astype(np.float32)
    L[rows, cols] = L_elem
    assert np.allclose(np.sum(L,axis=0),0), "L colsum must be 0"

    return L
```

Note that this version of the code does not have the deduplication procedure for periodic systems yet, but I propose the following high-level implementation:

1. A code that collects all of the bond vectors chosen by $\mathbf{L}$ via the indices `inda_sqe` and `indb_sqe` and puts it in a list.
2. Pass the bond vector list as an argument of `build_L`. Let the function flag any duplicate instances (whenever the index tuple is identical), and search from the bond vector list the lengths of these vectors. This works as the current implementation identically orders the indices and the bond vectors.
3. Collect the duplicate bonds and calculate for p_{eff} and κ_{eff} from Eqs. 4.41-4.42. Replace all the columns relating to a particular ij pair with a single column representing p_{eff} with a corresponding k_{eff} .

C.3 Parameterizing bond hardness

There is currently a code that pulls from the 4th head κ_i as shown in Fig. 4.1 the atomic outputs of the network distinct from atomic hardnesses J_i , and uses them as inputs to create the bond hardnesses κ_{ij} . The function is shown below,

Code

```
def kij_func(E3, inda_s, indb_s, func='sum'):
    if func == 'sum': # kij = k[i] + k[j]
        return E3[inda_s]+E3[indb_s]
    if func == 'harmonic': # kij = k[i]*k[j]/(k[i]+k[j])
        return E3[inda_s]*E3[indb_s]/(E3[inda_s]+E3[indb_s])
    if func == 'geom': # kij = (k[i]*k[j])**0.5
        return (E3[inda_s]*E3[indb_s])**0.5
    raise ValueError("Unsupported func: {}".format(func))
```

`inda_s` and `indb_s` are the atom, neighbor indices of the bonds selected by the topology matrix $\mathbf{L}$, and the tuple `(inda_s,indb_s)` should list all of the relevant bond variables chosen. This is the mechanism that produces the bond-specific κ_b from atomic outputs. We ensure positivity of the bond hardness by applying a softplus function to the κ_i .

Unfortunately, this method is not used in the current implementation of the code as the differentiation wrt atomic positions such as in Eq. 4.22,

$$\sum_{a,ij} \frac{\partial E_a}{\partial G_{ij}} \frac{\partial G_{ij}}{\partial R_{ij}} \rightarrow \sum_{a,ij} \frac{\partial E_a}{\partial R_{ij}},$$

needs care when dealing with bond-variables.

Bibliography

- [1] Apolinario Miguel Tan, Franco Pellegrini, and Stefano De Gironcoli. Convergence of Body-Orders in Linear Atomic Cluster Expansions. *The Journal of Physical Chemistry A*, 129(31):7229–7237, August 2025.
- [2] Martin H. Müser, Sergey V. Sukhomlinov, and Lars Pastewka. Interatomic potentials: Achievements and challenges. *Advances in Physics: X*, 8(1):2093129, December 2023.
- [3] Murray S. Daw and M. I. Baskes. Semiempirical, Quantum Mechanical Calculation of Hydrogen Embrittlement in Metals. *Physical Review Letters*, 50(17):1285–1288, April 1983.
- [4] Murray S. Daw and M. I. Baskes. Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals. *Physical Review B*, 29(12):6443–6453, June 1984.
- [5] Frank H. Stillinger and Thomas A. Weber. Computer simulation of local order in condensed phases of silicon. *Physical Review B*, 31(8):5262–5271, April 1985.
- [6] A. D. Mitrakis, N. Flytzanis, and S. C. Farantos. Potential model for silicon clusters. *Physical Review B*, 39(2):1212–1218, January 1989.
- [7] J. Tersoff. New empirical approach for the structure and energy of covalent systems. *Physical Review B*, 37(12):6991–7000, April 1988.
- [8] J. Tersoff. Modeling solid-state chemistry: Interatomic potentials for multicomponent systems. *Physical Review B*, 39(8):5566–5568, March 1989.
- [9] D. Pettifor. New many-body potential for the bond order. *Physical Review Letters*, 63(22):2480–2483, November 1989.
- [10] D.W. Brenner. The Art and Science of an Analytic Potential. *physica status solidi (b)*, 217(1):23–40, January 2000.
- [11] F. Ercolessi, M. Parrinello, and E. Tosatti. Simulation of gold in the glue model. *Philosophical Magazine A*, 58(1):213–226, July 1988.

- [12] R Drautz, M Fähnle, and J M Sanchez. General relations between many-body potentials and cluster expansions in multicomponent systems. *Journal of Physics: Condensed Matter*, 16(23):3843–3852, June 2004.
- [13] R. Car and M. Parrinello. Unified Approach for Molecular Dynamics and Density-Functional Theory. *Physical Review Letters*, 55(22):2471–2474, November 1985.
- [14] Jörg Behler and Michele Parrinello. Generalized Neural-Network Representation of High-Dimensional Potential-Energy Surfaces. *Physical Review Letters*, 98(14):146401, April 2007.
- [15] Jörg Behler. Atom-centered symmetry functions for constructing high-dimensional neural network potentials. *The Journal of Chemical Physics*, 134(7):074106, February 2011.
- [16] J. S. Smith, O. Isayev, and A. E. Roitberg. ANI-1: An extensible neural network potential with DFT accuracy at force field computational cost. *Chemical Science*, 8(4):3192–3203, 2017.
- [17] E. Prodan and W. Kohn. Nearsightedness of electronic matter. *Proceedings of the National Academy of Sciences*, 102(33):11635–11638, August 2005.
- [18] Albert P. Bartók, Risi Kondor, and Gábor Csányi. On representing chemical environments. *Physical Review B*, 87(18):184115, May 2013.
- [19] Albert P. Bartók, Mike C. Payne, Risi Kondor, and Gábor Csányi. Gaussian Approximation Potentials: The Accuracy of Quantum Mechanics, without the Electrons. *Physical Review Letters*, 104(13):136403, April 2010.
- [20] Sergey N. Pozdnyakov, Michael J. Willatt, Albert P. Bartók, Christoph Ortner, Gábor Csányi, and Michele Ceriotti. Incompleteness of Atomic Structure Representations. *Physical Review Letters*, 125(16):166001, October 2020.
- [21] Alexander V. Shapeev. Moment Tensor Potentials: A class of systematically improvable interatomic potentials. *Multiscale Modeling & Simulation*, 14(3):1153–1173, January 2016.
- [22] Ralf Drautz. Atomic cluster expansion for accurate and transferable interatomic potentials. *Physical Review B*, 99(1):014104, January 2019.
- [23] Ilyes Batatia, Dávid Péter Kovács, Gregor N. C. Simm, Christoph Ortner, and Gábor Csányi. MACE: Higher Order Equivariant Message Passing Neural Networks for Fast and Accurate Force Fields, January 2023.

- [24] Ilyes Batatia, Philipp Benner, Yuan Chiang, Alin M. Elena, Dávid P. Kovács, Janosh Riebesell, Xavier R. Advincula, Mark Asta, Matthew Avaylon, William J. Baldwin, Fabian Berger, Noam Bernstein, Arghya Bhowmik, Filippo Bigi, Samuel M. Blau, Vlad Cărare, Michele Ceriotti, Sanggyu Chong, James P. Darby, Sandip De, Flaviano Della Pia, Volker L. Deringer, Rokas Elijošius, Zakariya El-Machachi, Edvin Fako, Fabio Falcioni, Andrea C. Ferrari, John L. A. Gardner, Mikołaj J. Gawkowski, Annalena Genreith-Schriever, Janine George, Rhys E. A. Goodall, Jonas Grandel, Clare P. Grey, Petr Grigorev, Shuang Han, Will Handley, Hendrik H. Heenen, Kersti Hermansson, Cheuk Hin Ho, Stephan Hofmann, Christian Holm, Jad Jaafar, Konstantin S. Jakob, Hyunwook Jung, Venkat Kapil, Aaron D. Kaplan, Nima Karimitari, James R. Kermode, Panagiotis Kourtis, Namu Kroupa, Jolla Kullgren, Matthew C. Kuner, Dantas Kuryla, Guoda Liepuoniute, Chen Lin, Johannes T. Margraf, Ioan-Bogdan Magdău, Angelos Michaelides, J. Harry Moore, Aakash A. Naik, Samuel P. Niblett, Sam Walton Norwood, Niamh O'Neill, Christoph Ortner, Kristin A. Persson, Karsten Reuter, Andrew S. Rosen, Louise A. M. Rosset, Lars L. Schaaf, Christoph Schran, Benjamin X. Shi, Eric Sivonxay, Tamás K. Stenczel, Christopher Sutton, Viktor Svahn, Thomas D. Swinburne, Jules Tilly, Cas Van Der Oord, Santiago Vargas, Eszter Varga-Umbrich, Tejs Vegge, Martin Vondrák, Yangshuai Wang, William C. Witt, Thomas Wolf, Fabian Zills, and Gábor Csányi. A foundation model for atomistic materials chemistry. *The Journal of Chemical Physics*, 163(18):184110, November 2025.
- [25] Felix Musil, Andrea Grisafi, Albert P. Bartók, Christoph Ortner, Gábor Csányi, and Michele Ceriotti. Physics-Inspired Structural Representations for Molecules and Materials. *Chemical Reviews*, 121(16):9759–9815, August 2021.
- [26] Daan Frenkel and Berend Smit. *Understanding Molecular Simulation: From Algorithms to Applications*. Elsevier Academic Press, S.l., third edition, 2023.
- [27] Tsz Wai Ko, Jonas A. Finkler, Stefan Goedecker, and Jörg Behler. A fourth-generation high-dimensional neural network potential with accurate electrostatics including non-local charge transfer. *Nature Communications*, 12(1):398, January 2021.
- [28] Federico Grasselli, Kevin Rossi, Stefano de Gironcoli, and Andrea Grisafi. Long-range electrostatics in atomistic machine learning: A physical perspective, February 2026.
- [29] Andrea Grisafi and Michele Ceriotti. Incorporating long-range physics in atomic-scale machine learning. *The Journal of Chemical Physics*, 151(20):204105, November 2019.

- [30] Andrea Grisafi, Jigyasa Nigam, and Michele Ceriotti. Multi-scale approach for the prediction of atomic scale properties. *Chemical Science*, 12(6):2078–2090, 2021.
- [31] Bingqing Cheng. Latent Ewald summation for machine learning of long-range interactions. *npj Computational Materials*, 11(1):80, March 2025.
- [32] Peichen Zhong, Dongjin Kim, Daniel S. King, and Bingqing Cheng. Machine learning interatomic potential can infer electrical response. *npj Computational Materials*, 11(1):384, December 2025.
- [33] Dongjin Kim, Daniel S. King, Yoonjae Park, Roya Savoj, Sebastien Hamel, Xiaoyu Wang, and Bingqing Cheng. *Polarizable Atomic Multipoles for Learning Long-Range Electrostatics*, May 2026.
- [34] Ang Gao and Richard C. Remsing. Self-consistent determination of long-range electrostatics in neural network potentials. *Nature Communications*, 13(1):1572, March 2022.
- [35] Linfeng Zhang, Han Wang, Maria Carolina Muniz, Athanassios Z. Panagiotopoulos, Roberto Car, and Weinan E. A deep potential model with long-range electrostatic interactions. *The Journal of Chemical Physics*, 156(12):124107, March 2022.
- [36] S. Alireza Ghasemi, Albert Hofstetter, Santanu Saha, and Stefan Goedecker. Interatomic potentials for ionic systems with density functional accuracy based on charge densities obtained by a neural network. *Physical Review B*, 92(4):045131, July 2015.
- [37] Yusuf Shaidu, Franco Pellegrini, Emine Küçükbenli, Ruggero Lot, and Stefano De Gironcoli. Incorporating long-range electrostatics in neural network potentials via variational charge equilibration from shortsighted ingredients. *npj Computational Materials*, 10(1):47, March 2024.
- [38] Martin Vondrák, Karsten Reuter, and Johannes T. Margraf. Pushing charge equilibration-based machine learning potentials to their limits. *npj Computational Materials*, 11(1):288, September 2025.
- [39] Martin Vondrák, William J Baldwin, Gábor Csányi, Karsten Reuter, and Johannes T Margraf. *Integrating Charge Equilibration with Equivariant Machine-Learning Interatomic Potentials*, February 2026.
- [40] Frank Jensen. Unifying Charge-Flow Polarization Models. *Journal of Chemical Theory and Computation*, 19(13):4047–4073, July 2023.

- [41] Robert G. Parr and Yang Weitao. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press, January 1995.
- [42] Sanggyu Chong, Tong Jiang, Michelangelo Domina, Filippo Bigi, Federico Grasselli, Joonho Lee, and Michele Ceriotti. Resolving the body-order paradox of machine learning interatomic potentials. *The Journal of Chemical Physics*, 164(6):064121, February 2026.
- [43] J.M. Sanchez, F. Ducastelle, and D. Gratias. Generalized cluster description of multicomponent systems. *Physica A: Statistical Mechanics and its Applications*, 128(1-2):334–350, November 1984.
- [44] R. Biswas and D. R. Hamann. New classical models for silicon structural energies. *Physical Review B*, 36(12):6434–6445, October 1987.
- [45] L. G. Ferreira, Su-Huai Wei, and Alex Zunger. First-principles calculation of alloy phase diagrams: The renormalized-interaction approach. *Physical Review B*, 40(5):3197–3231, August 1989.
- [46] Linfeng Zhang, Jiequn Han, Han Wang, Roberto Car, and Weinan E. Deep Potential Molecular Dynamics: A Scalable Model with the Accuracy of Quantum Mechanics. *Physical Review Letters*, 120(14):143001, April 2018.
- [47] Ruggero Lot, Layla Martin-Samos, Stefano De Gironcoli, and Anne Hemeryck. Developing a Neural Network potential to investigate interface phenomena in solid-phase epitaxy. In *2021 IEEE 16th Nanotechnology Materials and Devices Conference (NMDC)*, pages 1–5, Vancouver, BC, Canada, December 2021. IEEE.
- [48] M. Domina, J. W. Abbott, P. Pegolo, F. Bigi, and M. Ceriotti. How Unconstrained Machine-Learning Models Learn Physical Symmetries. *PRX Intelligence*, 1(1):013013, August 2026.
- [49] Genevieve Dusson, Markus Bachmayr, Gabor Csanyi, Ralf Drautz, Simon Etter, Cas van der Oord, and Christoph Ortner. Atomic cluster expansion: Completeness, efficiency and stability. *Journal of Computational Physics*, 454, 2022.
- [50] Dávid Péter Kovács, Cas Van Der Oord, Jiri Kucera, Alice E. A. Allen, Daniel J. Cole, Christoph Ortner, and Gábor Csányi. Linear Atomic Cluster Expansion Force Fields for Organic Molecules: Beyond RMSE. *Journal of Chemical Theory and Computation*, 17(12):7696–7711, December 2021.
- [51] Yury Lysogorskiy, Cas Van Der Oord, Anton Bochkarev, Sarath Menon, Matteo Rinaldi, Thomas Hammerschmidt, Matous Mrovec, Aidan Thompson, Gábor

- Csányi, Christoph Ortner, and Ralf Drautz. Performant implementation of the atomic cluster expansion (PACE) and application to copper and silicon. *npj Computational Materials*, 7(1):97, June 2021.
- [52] Anton Bochkarev, Yury Lysogorskiy, Sarath Menon, Minaam Qamar, Matous Mrovec, and Ralf Drautz. Efficient parametrization of the atomic cluster expansion. *Physical Review Materials*, 6(1):013804, January 2022.
- [53] Minaam Qamar, Matous Mrovec, Yury Lysogorskiy, Anton Bochkarev, and Ralf Drautz. Atomic Cluster Expansion for Quantum-Accurate Large-Scale Simulations of Carbon. *Journal of Chemical Theory and Computation*, 19(15):5151–5167, August 2023.
- [54] William C. Witt, Cas Van Der Oord, Elena Gelžinytė, Teemu Järvinen, Andres Ross, James P. Darby, Cheuk Hin Ho, William J. Baldwin, Matthias Sachs, James Kermode, Noam Bernstein, Gábor Csányi, and Christoph Ortner. ACE-potentials.jl: A Julia implementation of the atomic cluster expansion. *The Journal of Chemical Physics*, 159(16):164101, October 2023.
- [55] Cheuk Hin Ho, Timon S. Gutleb, and Christoph Ortner. Atomic cluster expansion without self-interaction. *Journal of Computational Physics*, 515:113271, 2024.
- [56] Sanggyu Chong, Filippo Bigi, Federico Grasselli, Philip Loche, Matthias Kellner, and Michele Ceriotti. Prediction rigidities for data-driven chemistry. *Faraday Discussions*, 256:322–344, 2025.
- [57] Ilyes Batatia, Simon Batzner, Dávid Péter Kovács, Albert Musaelian, Gregor N. C. Simm, Ralf Drautz, Christoph Ortner, Boris Kozinsky, and Gábor Csányi. The design space of E(3)-equivariant atom-centred interatomic potentials. *Nature Machine Intelligence*, 7(1):56–67, January 2025.
- [58] Yusuf Shaidu. *Interatomic Potential for Li-C Systems from Cluster Expansion to Artificial Neural Network Techniques*. PhD thesis, Scuola Internazionale Superiore di Studi Avanzati, Trieste, October 2020.
- [59] Artem R. Oganov and Mario Valle. How to quantify energy landscapes of solids. *The Journal of Chemical Physics*, 130(10):104504, March 2009.
- [60] Yusuf Shaidu, Emine Küçükbenli, Ruggero Lot, Franco Pellegrini, Efthimios Kaxiras, and Stefano De Gironcoli. A systematic approach to generating accurate neural network potentials: The case of carbon. *npj Computational Materials*, 7(1):52, April 2021.

- [61] Yuval Eldar, Michael Lindenbaum, Moshe Porat, and Yehoshua Zeevi. The Farthest Point Strategy for Progressive Image Sampling. *IEEE Transactions on Image Processing*, 6(9):1305–1315, 1997.
- [62] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano De Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Sclauszero, Ari P Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M Wentzcovitch. QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21(39):395502, September 2009.
- [63] Riccardo Sabatini, Tommaso Gorni, and Stefano De Gironcoli. Nonlocal van der Waals density functional made simple and efficient. *Physical Review B*, 87(4):041108, January 2013.
- [64] Ask Hjorth Larsen, Jens Jørgen Mortensen, Jakob Blomqvist, Ivano E Castelli, Rune Christensen, Marcin Dułak, Jesper Friis, Michael N Groves, Bjørk Hammer, Cory Hargus, Eric D Hermes, Paul C Jennings, Peter Bjerre Jensen, James Kermode, John R Kitchin, Esben Leonhard Kolsbjerg, Joseph Kubal, Kristen Kaasbjerg, Steen Lysgaard, Jón Bergmann Maronsson, Tristan Maxson, Thomas Olsen, Lars Pastewka, Andrew Peterson, Carsten Rostgaard, Jakob Schiøtz, Ole Schütt, Mikkel Strange, Kristian S Thygesen, Tejs Vegge, Lasse Vilhelmsen, Michael Walter, Zhenhua Zeng, and Karsten W Jacobsen. The atomic simulation environment—a Python library for working with atoms. *Journal of Physics: Condensed Matter*, 29(27):273002, July 2017.
- [65] Franco Pellegrini, Ruggero Lot, Yusuf Shaidu, and Emine Küçükbenli. PANNA 2.0: Efficient neural network interatomic potentials and new architectures. *The Journal of Chemical Physics*, 159(8):084117, August 2023.
- [66] Simon Batzner, Albert Musaelian, Lixin Sun, Mario Geiger, Jonathan P. Mailoa, Mordechai Kornbluth, Nicola Molinari, Tess E. Smidt, and Boris Kozinsky. E(3)-equivariant graph neural networks for data-efficient and accurate interatomic potentials. *Nature Communications*, 13(1):2453, May 2022.
- [67] Bingqing Cheng, Guglielmo Mazzola, Chris J. Pickard, and Michele Ceriotti.

- Evidence for supercritical behaviour of high-pressure liquid hydrogen. *Nature*, 585(7824):217–220, September 2020.
- [68] Andreas Hermann, Robert P. Krawczyk, Matthias Lein, Peter Schwerdtfeger, I. P. Hamilton, and James J. P. Stewart. Convergence of the many-body expansion of interaction potentials: From van der Waals to covalent and metallic systems. *Physical Review A*, 76(1):013202, July 2007.
 - [69] Stefano Baroni, Stefano De Gironcoli, Andrea Dal Corso, and Paolo Giannozzi. Phonons and related crystal properties from density-functional perturbation theory. *Reviews of Modern Physics*, 73(2):515–562, July 2001.
 - [70] Anthony K. Rappe and William A. Goddard. Charge equilibration for molecular dynamics simulations. *The Journal of Physical Chemistry*, 95(8):3358–3363, April 1991.
 - [71] Gabriele Coiana and Stefano De Gironcoli. Title Pending. 2026.
 - [72] Razvan A. Nistor, Jeliasko G. Polihronov, Martin H. Müser, and Nicholas J. Mosey. A generalization of the charge equilibration method for nonmetallic materials. *The Journal of Chemical Physics*, 125(9):094108, September 2006.
 - [73] Razvan A. Nistor and Martin H. Müser. Dielectric properties of solids in the regular and split-charge equilibration formalisms. *Physical Review B*, 79(10):104303, March 2009.
 - [74] T. Verstraelen, P. W. Ayers, V. Van Speybroeck, and M. Waroquier. ACKS2: Atom-condensed Kohn-Sham DFT approximated to second order. *The Journal of Chemical Physics*, 138(7):074108, February 2013.
 - [75] Toon Verstraelen, Steven Vandenbrande, and Paul W. Ayers. Direct computation of parameters for accurate polarizable force fields. *The Journal of Chemical Physics*, 141(19):194114, November 2014.
 - [76] Richard M. Martin. *Electronic Structure: Basic Theory and Practical Methods*. Cambridge University Press, 2 edition, August 2020.
 - [77] Robert M. Pick, Morrel H. Cohen, and Richard M. Martin. Microscopic Theory of Force Constants in the Adiabatic Approximation. *Physical Review B*, 1(2):910–920, January 1970.
 - [78] R. Resta. Local-field effects and phonon screening in polar semiconductors. *Physical Review B*, 27(6):3620–3630, March 1983.

- [79] Stefano Baroni and Raffaele Resta. *Ab Initio* calculation of the macroscopic dielectric constant in silicon. *Physical Review B*, 33(10):7017–7021, May 1986.
- [80] Paul W. Ayers. Strategies for computing chemical reactivity indices. *Theoretical Chemistry Accounts*, 106(4):271–279, September 2001.
- [81] E. K. U. Gross and Walter Kohn. Local density-functional theory of frequency-dependent linear response. *Physical Review Letters*, 55(26):2850–2852, December 1985.
- [82] Nick Sablon, Frank De Proft, Paul W. Ayers, and Paul Geerlings. Computing Second-Order Functional Derivatives with Respect to the External Potential. *Journal of Chemical Theory and Computation*, 6(12):3671–3680, December 2010.
- [83] Nick Sablon, Frank De Proft, and Paul Geerlings. The linear response kernel of conceptual DFT as a measure of electron delocalisation. *Chemical Physics Letters*, 498(1-3):192–197, September 2010.
- [84] Stephen L. Adler. Quantum Theory of the Dielectric Constant in Real Solids. *Physical Review*, 126(2):413–420, April 1962.
- [85] Nathan Wiser. Dielectric Constant with Local Field Effects Included. *Physical Review*, 129(1):62–69, January 1963.
- [86] G. Lee Warren, Joseph E. Davis, and Sandeep Patel. Origin and control of superlinear polarizability scaling in chemical potential equalization methods. *The Journal of Chemical Physics*, 128(14):144110, April 2008.
- [87] Riccardo Chelli, Piero Procacci, Roberto Righini, and Salvatore Califano. Electrical response in chemical potential equalization schemes. *The Journal of Chemical Physics*, 111(18):8569–8575, November 1999.
- [88] Jiahao Chen, Dirk Hundertmark, and Todd J. Martínez. A unified theoretical framework for fluctuating-charge models in atom-space and in bond-space. *The Journal of Chemical Physics*, 129(21):214113, December 2008.
- [89] Pier Paolo Poier and Frank Jensen. Describing Molecular Polarizability by a Bond Capacity Model. *Journal of Chemical Theory and Computation*, 15(5):3093–3107, May 2019.
- [90] Toon Verstraelen, Ewald Pauwels, Frank De Proft, Veronique Van Speybroeck, Paul Geerlings, and Michel Waroquier. Assessment of Atomic Charge Models for Gas-Phase Computations on Polypeptides. *Journal of Chemical Theory and Computation*, 8(2):661–676, February 2012.

- [91] M. H. Müser. The chemical hardness of molecules and the band gap of solids within charge equilibration formalisms: Toward force field-based simulations of redox reactions. *The European Physical Journal B*, 85(4):135, April 2012.
- [92] Mykhaylo Krykunov, Christopher Demone, Jason W.-H. Lo, and Tom K. Woo. *A New Split Charge Equilibration Model and REPEAT Electrostatic Potential Fitted Charges for Periodic Frameworks with a Net Charge*. *Journal of Chemical Theory and Computation*, 13(6):2858–2869, June 2017.
- [93] Rogelio Cuevas-Saavedra, Nataly Rabi, and Paul W. Ayers. The unconstrained local hardness: An intriguing quantity, beset by problems. *Physical Chemistry Chemical Physics*, 13(43):19594, 2011.
- [94] Franco Pellegrini, Stefano de Gironcoli, and Emine Kucukbenli. LATTE: An atomic environment descriptor based on Cartesian tensor contractions, May 2023.
- [95] James Bradbury, Roy Frostig, Peter Hawkins, Matthew James Johnson, Chris Leary, Dougal Maclaurin, George Necula, Adam Paszke, Jake VanderPlas, Skye Wanderman-Milne, and Qiao Zhang. JAX: Composable transformations of Python+NumPy programs, 2018.
- [96] Diederik P. Kingma and Jimmy Ba. Adam: A Method for Stochastic Optimization, January 2017.
- [97] Max Berkowitz and Robert G. Parr. Molecular hardness and softness, local hardness and softness, hardness and softness kernels, and relations among these quantities. *The Journal of Chemical Physics*, 88(4):2554–2557, February 1988.
- [98] Dongjin Kim and Bingqing Cheng. Long-range electrostatics for machine learning interatomic potentials is easier than we thought. *The Journal of Chemical Physics*, 164(6):060901, February 2026.
- [99] Max Born and Kun Huang. *Dynamical Theory of Crystal Lattices*. The International Series of Monographs on Physics. Clarendon press, Oxford, 1985.
- [100] Andrea Dal Corso. Density Functional Perturbation Theory for Electric Fields, 2022.
- [101] Nick Sablon, Frank De Proft, and Paul Geerlings. The Linear Response Kernel: Inductive and Resonance Effects Quantified. *The Journal of Physical Chemistry Letters*, 1(8):1228–1234, April 2010.

- [102] Gabriele Coiana, Johannes Lischner, and Paul Tangney. Breakdown of phonon band theory in MgO. *Physical Review B*, 109(1):014310, January 2024.
- [103] Roger Haydock. The recursive solution of the Schrödinger equation. *Computer Physics Communications*, 20(1):11–16, September 1980.
- [104] Michelangelo Domina and Michele Ceriotti. Using large language models to probe the limits of atom-centered structural descriptors, July 2026.
- [105] Thomas Froitzheim, Marcel Müller, Andreas Hansen, and Stefan Grimme. The Bond Capacity Electronegativity Equilibration Charge Model (EEQBC) for the Elements Z=1–103, March 2025.
- [106] Bhupalee Kalita, Roman Zubatyuk, Dylan M. Anstine, Maike Bergeler, Volker Settels, Conrad Stork, Sebastian Spicher, and Olexandr Isayev. AIMNet2-NSE: A Transferable Reactive Neural Network Potential for Open-Shell Chemistry. *Angewandte Chemie International Edition*, 65(5):e16763, January 2026.
- [107] Ilyes Batatia, William J. Baldwin, Domantas Kuryla, Joseph Hart, Elliott Kassoar, Alin M. Elena, Harry Moore, Mikołaj J. Gawkowski, Benjamin X. Shi, Venkat Kapil, Panagiotis Kourtis, Ioan-Bogdan Magdău, and Gábor Csányi. MACE-POLAR-1: A Polarisable Electrostatic Foundation Model for Molecular Chemistry, February 2026.