QM/MM METHODS FOR CRYSTALLINE DEFECTS. PART 3:
MACHINE-LEARNED MM MODELS

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Abstract. We develop and analyze a framework for consistent QM/MM (quantum/classic) hybrid models of crystalline defects, which admits general atomistic interactions including traditional off-the-shell interatomic potentials as well as state of art “machine-learned interatomic potentials”. We (i) establish an \textit{a priori} error estimate for the QM/MM approximations in terms of matching conditions between the MM and QM models, and (ii) demonstrate how to use these matching conditions to construct practical machine learned MM potentials specifically for QM/MM simulations.

1. Introduction

Quantum mechanics and molecular mechanics (QM/MM) coupling methods have been widely used in multiscale modeling and simulations of large systems in materials science and biology [4, 14, 23, 25, 40, 44]. The region of primary interest (e.g., a defect core) is described by a QM model, which is embedded in an ambient environment (e.g., bulk crystal) described by an MM model. In principle, QM/MM coupling methods promise (near-)QM accuracy at (near-)MM computational cost for large-scale atomistic simulations. To achieve this in practice, the two key approximation parameters that must be controlled are the size of the QM region and the choice of MM model. The purpose of this paper is to devise a framework for constructing \textit{minimal} MM models matching the QM model in a way that results in explicit convergence rates.

QM/MM methods for material simulations originate in the need for large-scale simulations due to long-ranged elastic or electric fields that are strongly coupled to material defects. For example, the long-range fields give rise to an interaction between far-away defects, and classical continuum theories are typically sufficient to describe this. On the other hand, the resultant effect of these long-range fields on the motion of a defect (e.g., diffusion of point defects towards a crack tip, or dislocation dynamics) strongly depends on the core structure and details of the chemistry of bond breaking. These general ideas only motivate our own work, hence we refer to other sources for deeper introductions and further references on the applications of QM/MM schemes [4, 14, 25, 26, 38].

Our own interest is in the question how to design QM/MM schemes in a way that allows rigorous error control, at least in principle. To that end, we focus on a simpler but instructive setting of a single defect embedded in a homogeneous host crystal, where a rigorous numerical analysis approach is feasible. The atomistic equilibration problem in this context is a well-defined variational problem, and properties of equilibrium configurations are precisely characterised [18, 7, 8]. With this information in hand it is possible to specify conditions on MM models and QM/MM coupling schemes under which the schemes converge as the QM radius increases [4, 6, 10, 27, 43]. For example in [10] it was shown that the rate of convergence in terms of the QM
region radius is determined by clearly specified matching conditions on the Taylor expansion coefficients in the QM and MM interaction laws around a reference state. This observation is the starting point for the present work.

The key ingredient in the construction of a QM/MM scheme is the choice of MM model (given a high-fidelity QM reference model to be used for the QM region). Traditionally, empirical or even analytical interatomic potentials have been used in this context, since they more than adequately describe the elastic far-field, and are computationally inexpensive. The crux is that they generally do not match the QM interaction at all, which leads to the difficult problem of constructing coupling schemes that alleviate that mismatch.

An entirely different approach, developed outside of the QM/MM context and in fact intended to replace QM/MM models altogether, are machine-learned interatomic potentials (MLIPs) \[3, 44, 5, 1, 16, 39\]. Their defining feature is that they employ universal approximators as their parameterisation and aim to approximate a reference QM potential energy landscape to within arbitrary accuracy on a large training set. We will leverage this technology in order to construct MM schemes that satisfy the precise matching conditions identified in \[10\] that guarantee a QM/MM scheme that is consistent with the reference pure QM model.

To that end, we will first generalize the error analysis of \[10\] to obtain error estimates in terms a quantity that incorporates the matching conditions and, most importantly, can be easily incorporated into a loss function for training an MLIP. We will then train various ACE MLIPs \[16, 1\] using different variations of our general idea. The most promising candidates are those potentials where we replace fully atomistic matching conditions with a suitable continuum limit, while retaining a fully controllable error.

Outline. In Section 2, we review a rigorous framework for modelling the geometry equilibration of crystalline defects. In Section 3, we construct a QM/MM coupling method for crystalline defects, and give a priori general error estimates for both energy-mixing and force-mixing schemes, with errors quantified in terms of certain matching conditions between the MM and QM models. In Section 4.1, we discuss how to apply our theory to construct an MLIP from the given QM model, and present the NRL tight binding model and ACE interatomic potential as examples that we will use in our tests. In Section 4, we perform the numerical experiments for some real materials with point defect and dislocation. Finally, some concluding remarks are given. For simplicity of the presentations, the details of the proofs are given in appendices.

Notation. For the sake of brevity, we will denote \(A\backslash\{a\}\) by \(A\backslash a\), and \(\{b \mid a \in A\}\) by \(A - a\). We will use the symbol \(\langle \cdot, \cdot \rangle\) to denote an abstract duality pair between a Banach space and its dual space. The symbol \(|\cdot|\) normally denotes the Euclidean or Frobenius norm, while \(\|\cdot\|\) denotes an operator norm. For functional \(E \in C^2(X)\), the first and second variations are denoted by \(\langle \delta E(u), v \rangle\) and \(\langle \delta^2 E(u)v, w \rangle\) for \(u, v, w \in X\), respectively. For \(j \in \mathbb{N}\), \(g \in (\mathbb{R}^d)^A\), and \(V \in C^j((\mathbb{R}^d)^A)\), we define the notation

\[
V_{\rho}(g) := \frac{\partial^j V(g)}{\partial g_{\rho_1} \cdots \partial g_{\rho_j}} \quad \text{for} \quad \rho = (\rho_1, \ldots, \rho_j) \in A^j.
\]

The symbol \(C\) denotes generic positive constant that may change from one line of an estimate to the next. When estimating rates of decay or convergence, \(C\) will always remain independent of the system size, the lattice configuration and the test functions. The dependence of \(C\) will be clear from the context or stated explicitly.
2. Equilibration of crystalline defects

A rigorous framework for modelling the geometric equilibrium of crystalline defects has been developed in [18] for finite-range interaction models (interatomic potentials) and extended in [8] to a range of ab initio interaction models. These two works formulate the equilibrium of crystal defects as a variational problem in a discrete energy space and establishes qualitatively sharp far-field decay estimates for the corresponding equilibrium configuration. We will review the framework as important background for our own work.

2.1. Displacement space. Let \( d \in \{2, 3\} \) be the (effective) dimension of the system. We consider a single defect embedded in an infinite homogeneous crystalline bulk. Both point defects and straight line dislocations will be studied in this paper.

A homogeneous crystal reference configuration is given by the Bravais lattice \( \Lambda^h = AZ^d \), for some non-singular matrix \( A \in \mathbb{R}^{d \times d} \). The reference configuration for a system with defect is a set \( \Lambda \subset \mathbb{R}^d \) satisfying

\[
(\text{RC}) \quad \exists \ B_{\text{DEF}} > 0, \text{ such that } \Lambda \setminus B_{\text{DEF}} = \Lambda^h \setminus B_{\text{DEF}} \text{ and } \Lambda \cap B_{\text{DEF}} \text{ is finite.}
\]

The deformed configuration of the infinite lattice \( \Lambda \) is a map \( y : \Lambda \to \mathbb{R}^d \). We can decompose the configuration \( y \) into

\[
y(\ell) = y_0(\ell) + u(\ell) = x_0(\ell) + u_0(\ell) + u(\ell) \quad \forall \ \ell \in \Lambda,
\]

where \( y_0 = x_0 + u_0 \) is a predictor prescribing the far-field boundary condition and \( u \) is the corrector. We require in [2.7] that the configuration \( y_0(\ell) \) is “near equilibrium” far from the defect core: For point defects we achieve this by simply taking \( u_0(\ell) = 0 \ \forall \ \ell \in \Lambda \). The derivation of \( u_0 \) for straight dislocations is reviewed in Appendix A. The precise details, including a precise definition of the “near equilibrium” requirement is unimportant for the present work, but can be found in [8, 18].

We collect the settings for point defects and dislocations in the following conditions (P) and (D) respectively.

(P) \( d \in \{2, 3\}; \Lambda \) satisfies (RC); \( x_0(\ell) = \ell \ \forall \ \ell \in \Lambda; u_0(\ell) = 0 \ \forall \ \ell \in \Lambda \).

(D) \( \Lambda = AZ^2; x_0(\ell) = P(\ell) \) for any \( \ell \in \Lambda \) with \( P \) given by (A.1); \( u_0 \) is given by (A.2).

The set of possible atomic configurations is

\[
\text{Adm}_0(\Lambda) := \bigcup_{m > 0} \text{Adm}_m(\Lambda) \quad \text{with}
\]

\[
\text{Adm}_m(\Lambda) := \left\{ y : \Lambda \to \mathbb{R}^d, \ |y(\ell) - y(m)| > m|\ell - m| \ \forall \ \ell, m \in \Lambda \right\},
\]

where the parameter \( m > 0 \) prevents the accumulation of atoms.

For \( \ell \in \Lambda \) and \( \rho \in \Lambda - \ell \), we define the finite difference \( D_\rho u(\ell) := u(\ell + \rho) - u(\ell) \). For a subset \( \mathcal{R} \subset \Lambda - \ell \), we define \( D_{\mathcal{R}} u(\ell) := (D_\rho u(\ell))_{\rho \in \mathcal{R}} \), and we consider \( D u(\ell) := D_{\Lambda - \ell} u(\ell) \) to be a finite-difference stencil with infinite range. For a stencil \( D u(\ell) \), we define the stencil norms

\[
(2.2) \quad |Du(\ell)|_{\mathcal{N}} := \left( \sum_{\rho \in \mathcal{N}(\ell) - \ell} |D_\rho u(\ell)|^2 \right)^{1/2} \quad \text{and} \quad \|Du\|_{\mathcal{N}}^2 := \left( \sum_{\ell \in \Lambda} |Du(\ell)|_{\mathcal{N}}^2 \right)^{1/2},
\]

where \( \mathcal{N}(\ell) \) is the set containing nearest neighbours of site \( \ell \)

\[
(2.3) \quad \mathcal{N}(\ell) := \left\{ m \in \Lambda \setminus \ell \ | \exists a \in \mathbb{R}^d \text{ s.t. } |a - \ell| = |a - m| \leq |a - k| \ \forall \ k \in \Lambda \right\}.
\]
We can then define the corresponding functional space of finite-energy displacements
\[ \mathcal{U}^{1,2}(\Lambda) := \{ u : \Lambda \to \mathbb{R}^d \mid \| Du \|_{\ell^2(\Lambda)} < \infty \} \]
with the associated semi-norm \( \| Du \|_{\ell^2(\Lambda)} \). We also define the following subspace of compact displacements
\[ \mathcal{U}(\Lambda) := \{ u : \Lambda \to \mathbb{R}^d \mid \| Du \|_{\ell^2(\Lambda)} < \infty \} . \]
Then the associated class of admissible displacements is given by
\[ \mathcal{A}(\Lambda) := \{ u \in \mathcal{U}^{1,2}(\Lambda) : y_0 + u \in \text{Adm}_0(\Lambda) \} . \]

2.2. Site potential. The site potential represents the local energy contributed from each atomic site. It specifies the physical model used in the simulations. Interatomic potentials are usually defined in terms of a site potential, incorporating the modelling assumption that interaction are local. QM models are defined in terms of total energies, but a site energy can still be constructed in some cases. Here, we review the construction and analysis of \([9, 22]\).

Let \( \Lambda \) be the reference configuration satisfying (RC) with \( \Lambda^h \) the corresponding homogeneous lattice. Denote \( \Lambda^h := \Lambda^h - 0 \) and \( x_0^h : \Lambda^h \to \mathbb{R}^d \), \( x_0^h(\ell) = \ell \) \( \forall \ell \in \Lambda^h \) the predictor on the homogeneous lattice. We consider the site potential to be a collection of mappings \( V_\ell : (\mathbb{R}^d)^{\Lambda - \ell} \to \mathbb{R} \), which represent the energy distributed to each atomic site. We make the following assumptions on the regularity and locality of the site potentials, which has been justified for some basic quantum mechanic models \([7, 9, 11, 34]\). We refer to \([8, \S 2.3 \text{ and } \S 4]\) for discussions of more general site potentials.

**RL** Regularity and locality: For all \( \ell \in \Lambda \), \( V_\ell(Du(\ell)) \) possesses partial derivatives up to \( n \)-th order with \( n \geq 3 \). For \( j = 1, \ldots, n \), there exist constants \( C_j \) and \( \eta_j \) such that
\[ |V_{\ell, \rho}(Du(\ell))| \leq C_j \exp \left( -\eta_j \sum_{l=1}^{j} |\rho_l| \right) \]
for all \( \ell \in \Lambda \) and \( \rho \in (\Lambda - \ell)^j \).

When \( \Lambda = \Lambda^h \) then we denote the site potential by \( V^h : (\mathbb{R}^d)^{\Lambda^h} \to \mathbb{R} \), which can be thought of to model interaction far from the defect core. Since the periodicity of the lattice implies that for \( u : \Lambda^h \to \mathbb{R}^d \), the stencils \( Du(\ell) \) are dependent on \( \ell \in \Lambda^h \), and hence the site potential \( V^h : (\mathbb{R}^d)^{\Lambda^h} \to \mathbb{R} \) is independent of \( \ell \in \Lambda^h \).

Although the site potentials are defined on infinite stencils \((\mathbb{R}^d)^{\Lambda - \ell}\), the setting also applies to finite systems or to finite range interactions. It is only necessary to assume in this case that the potential \( V_\ell(g) \) does not depend on the reference sites \( g_\rho \) outside the interaction range. In particular, we will denote by \( V^\Omega_\ell \) the site potential of a finite system with the reference configuration lying in \( \Lambda \cap \Omega \).

2.3. Geometry equilibration. Let \( \Lambda \) satisfy (RC) and the site potential satisfy the assumptions (S). Then we have from \([8, \text{ Theorem 2.1}]\) that the energy-difference functional
\[ \mathcal{E}(u) := \sum_{\ell \in \Lambda} \left( V_\ell (Du_0(\ell) + Du(\ell)) - V_\ell (Du_0(\ell)) \right), \]
after an elementary renormalisation, is well-defined on the admissible displacements set $\mathcal{A}(\Lambda)$ and is $(n-1)$-times continuously differentiable with respect to the $\|D\cdot\|_{\mathcal{E}_N}$ norm, for both point defects and dislocations.

We can now rigorously formulate the variational problem for the equilibrium state as

\[
\bar{u} \in \arg \min \left\{ \mathcal{E}(u), u \in \mathcal{A} \right\},
\]

where “arg min” is understood as the set of local minimisers. The minimizer $\bar{u}$ satisfies the following first and second order optimality conditions

\[
\langle \delta \mathcal{E}(\bar{u}), v \rangle = 0, \quad \langle \delta^2 \mathcal{E}(\bar{u})v, v \rangle \geq 0, \quad \forall \ v \in \mathcal{H}^{1,2}(\Lambda).
\]

For the purpose of an approximation error analysis we will need a stronger stability condition, which we formulate as an assumption:

**S** (Strong stability): $\exists \ c > 0$ s.t. $\langle \delta^2 \mathcal{E}(\bar{u})v, v \rangle \geq c\|Dv\|^2_{\mathcal{E}_N} \quad \forall \ v \in \mathcal{H}^{1,2}(\Lambda)$.

The next result gives the decay estimates for the equilibrium state for point defects and dislocations [8, Theorem 3.2 and 3.7]: Suppose that either **(P)** or **(D)** is satisfied, if $\bar{u} \in \mathcal{A}(\Lambda)$ is a strongly stable solution to (2.8) satisfying **(S)**, then there exists $C > 0$ depending on $\bar{u}$ such that

\[
|D\bar{u}(\ell)|_{\mathcal{N}} \leq C(1 + |\ell|)^{-d} \log(2 + |\ell|),
\]

where $t = 0$ for **(P)** and $t = 1$ for **(D)**.

Instead of energy minimization, we may alternatively consider the force equilibrium formulation (that corresponds to the first part of (2.9)):

\[
\text{Find } \bar{u} \in \mathcal{A}(\Lambda), \text{ s.t. } \mathcal{F}_{\ell}(\bar{u}) = 0, \quad \forall \ \ell \in \Lambda,
\]

where $\mathcal{F}_{\ell} := -\nabla_{\ell}\mathcal{E}(u)$ represents the force on the atomic site $\ell$. Note that any of the minimizers of (2.8) also solves (2.11). For $u^h \in \mathcal{A}(\Lambda^h)$ on a homogeneous lattice $\Lambda^h$, the force on each atomic site $\ell$ satisfies $\mathcal{F}_{\ell}(u^h) = \mathcal{F}^h(u^h(\cdot - \ell))$ with some homogeneous force $\mathcal{F}^h$ that does not depend on site $\ell$.

3. QM/MM Coupling Methods with MLIPs

QM/MM coupling schemes can be categorized into energy- and force-mixing schemes methods: energy-based methods construct a hybrid total energy functional and seek a local minimizer of that functional, while force-based methods solve the force balance equation with QM and MM contributions. We will review both kinds of schemes in more detail, investigate error estimates and then derive the main theoretical results of this paper. Towards that end we first need to discuss the domain partitioning and provide a framework to quantify how well an MM model matches the reference QM model.

In QM/MM simulations, the reference configuration $\Lambda$ is partitioned into three disjoint sets $\Lambda = \Lambda^{QM} \cup \Lambda^{MM} \cup \Lambda^{FF}$, where $\Lambda^{QM}$ denotes the QM region containing the defect core, $\Lambda^{MM}$ denotes the MM region, and $\Lambda^{FF}$ denotes the far-field region with atomic positions frozen in the simulations. In addition to reduce spurious interface effects, we define a buffer region $\Lambda^{BUF} \subset \Lambda^{MM}$ surrounding $\Lambda^{QM}$ such that all atoms in $\Lambda^{BUF} \cup \Lambda^{QM}$ are involved in the QM calculations (to evaluate the site potentials in $\Lambda^{QM}$) but do not directly contribute to the hybrid energies of forces. For the sake of simplicity, we use balls centred at the defect core to decompose the domain $\Lambda$ with $R^{QM}$, $R^{MM}$ and $R^{BUF}$, respectively (cf. Figure 3.1).
3.1. Accuracy of the interatomic potentials. The QM/MM coupling schemes can give good equilibrium state approximations only if, in the MM region, the MM site potential provides an accurate approximation to the QM site potential. The decay of the displacement of equilibrium state \((2.10)\) implies that, far from the defect core, the Taylor expansion of the QM site potential on homogeneous lattice (see \((B.1)\) or \([10]\)) will provide an excellent approximation. This observation motivates us to introduce matching conditions between the QM and MM models in terms of Taylor expansion coefficients for the QM and MM potentials on the homogeneous lattice.

Let \(V^\text{h}\) and \(V^\text{MM}\) be the QM and MM homogeneous site potentials respectively, and assume both satisfy \((\text{RL})\). Then we define the \(j\)th order site potential error by

\[
\varepsilon^E_j := \left| \delta^j V^\text{h}(0) - \delta^j V^\text{MM}(0) \right|_{w_j^{-1}} := \left( \sum_{\rho=(\rho_1, \ldots, \rho_j) \in (\Lambda^*_h)^j} |V^\text{h}_\rho(0) - V^\text{MM}_\rho(0)|^2 w_j^{-1}(\rho) \right)^{1/2}
\]

for \(j = 1, \cdots, n\), where \(V^\text{h}_\rho(0)\) and \(V^\text{MM}_\rho(0)\) are defined by \((1.1)\), and for \(\gamma > 0\), \(w_j : (\Lambda^*_h)^j \rightarrow \mathbb{R}\) is a weight function given by

\[
w_j(\rho) := \prod_{i=1}^j w(|\rho_i|) \quad \text{with} \quad w(|\rho|) = e^{-2\gamma|\rho|}.
\]

We do not have to introduce \(\varepsilon^E_0\) since adding a constant to the site potentials will not affect the equilibrium state, nor the energy differences. The choice of \(\gamma\) only has a mild effect on the constant that is independent of the model parameters in our analysis. In practice we determine \(\gamma\) in a way that matches the locality of the site potentials \((\text{RL})\).

Note that there is always some interaction range cutoff for an MM model, such that the interactions between two atoms with distance larger than the cutoff radius \(R_{\text{cut}}\) is ignored within the MM calculations. The choice of \(R_{\text{cut}}\) is important to determine the accuracy and computational cost of the MM model. The error from the neglected interactions is automatically included in \(\varepsilon^E_j\) since \(V^\text{MM}_\rho(0) = 0\) when \(|\rho_i| > R_{\text{cut}}\) in \((3.1)\).

Alternatively, we can consider the measurements on the accuracy of the forces. We introduce the following error indicators comparing the \(j\)th order derivatives of the MM force \(F^\text{MM}\) and
QM force $F^h$ on the homogeneous lattice

$$
\varepsilon^F_j := \left| \delta^j F^h(0) - \delta^j F^{MM}(0) \right|_{w_j^{-1}} := \left( \sum_{t=(\ell_1, \ldots, \ell_d) \in (\Lambda^h)^d} \left| F^h_{\ell}(0) - F^{MM}_{\ell}(0) \right|^2 w_j^{-1}(\ell) \right)^{1/2}
$$

for $j = 1, \ldots, n - 1$, where $F^h_{\ell}(0)$ and $F^{MM}_{\ell}(0)$ are the $j$-th order derivatives of the QM and MM forces respectively, and $w_j$ is given by (3.2). Note that the forces vanish on the homogeneous lattice $\Lambda^h$ for both QM and MM models due to point symmetry, and therefore $\varepsilon^F_0$ is not required. Similar to the discussions for site potentials, the error from the truncation of interaction range cut-off $R_{cut}$ is again implicitly included.

We will show below that fitting an MM potential such that $\varepsilon^F_j$ or $\varepsilon^F$ are small up to some order leads can lead to excellent QM/MM models. However, ensuring a good fit for high matching orders turns out to be very challenging. We will therefore propose also an alternative construction that sacrifices some accuracy on $\varepsilon^F_j$ or $\varepsilon^F$ but instead demands accurate fits of virials.

The motivation for this is that this would incorporate continuum nonlinear elasticity which has been shown to provide an excellent model for atomistic interaction far from defect cores [33, 17].

Thus, we briefly review the Cauchy-Born rule [33, 17], which relates the movement of atoms in a crystal to the overall deformation of the bulk solid. For $F \in \mathbb{R}^{d \times d}$, the Cauchy-Born rule makes an approximation such that in a crystalline solid subject to a small strain, the positions of the atoms within the crystal lattice follow the overall strain of the medium. More precisely, the QM and MM site potentials are approximated by the Cauchy-Born elastic energy density functional $W^h_{cb}$, $W^{MM}_{cb} : \mathbb{R}^{d \times d} \rightarrow \mathbb{R}$ respectively, with

$$
W^h_{cb}(F) := V^h((F - I) \cdot \Lambda^h) \quad \text{and} \quad W^{MM}_{cb}(F) := V^{MM}((F - I) \cdot \Lambda^h).
$$

The derivative (virial stress) and even higher order derivatives with respect to the deformation $F$ can be obtained by direct calculations,

$$
\partial^2 F W^h_{cb}(F_0) := \partial^2 F W^h_{cb}(F)|_{F=F_0} = -\sum_{\rho=(\rho_1, \ldots, \rho_j) \in (\Lambda^h)^j} V^h_{\rho}(F_0 - I) \cdot \Lambda^h_\rho \bigotimes \rho_1 \bigotimes \cdots \bigotimes \rho_j =: \otimes \rho
$$

where $I \in \mathbb{R}^{d \times d}$ is the identity matrix and $\otimes$ denotes the standard kronecker product. We then introduce the following accuracy measure of the virial stress:

$$
\varepsilon^V_j := \left| \partial^{j+1} F W^h_{cb}(l) - \partial^{j+1} F W^{MM}_{cb}(l) \right|_{w_j^{1+1}} := \left( \sum_{\rho \in (\Lambda^h)^{j+1}} \left| (V^h_{\rho}(0) - V^{MM}_{\rho}(0)) \otimes \rho \right|^2 w_{j+1}(\rho) \right)^{1/2}
$$

for $j = 1, \ldots, n - 1$, where the weights $w_j$ is defined by (3.2).

### 3.2 Energy-mixing

The MM site potential $V^{MM} : (\mathbb{R}^d)_{\Lambda^h} \rightarrow \mathbb{R}$ is defined on the homogeneous reference configuration $\Lambda^h$, such that it can (i) be constructed uniformly and (ii) be compared with the QM site potential $V^h$ as shown in the previous subsection. We will therefore need an interpolation operator to map the displacements on the defective reference configuration $\Lambda$ to that on the corresponding homogeneous lattice $\Lambda^h$. It is shown in [8, Lemma D.1] that such an interpolation operator $P : \mathcal{W}^{1,2}(\Lambda) \rightarrow \mathcal{W}^{1,2}(\Lambda^h)$ exists such that, for some constant $C_* > 0$,

$$
\| DI^h u \|_{\mathcal{E}_{\Lambda}(\Lambda^h)} \leq C_* \| Du \|_{\mathcal{E}_{\Lambda}(\Lambda)} \quad \forall \ u \in \mathcal{W}^{1,2}(\Lambda).
$$
We emphasize that this interpolation is only introduced for the purpose of analysis, but does not affect the construction of the MM site potential or the coupling scheme, since the MM potential always has a cutoff and does not directly interact with the defect core region.

We now define the QM/MM hybrid energy difference functional by

\[ E^H(u) := \sum_{\ell \in \Lambda_{QM}} \left( V_{QM}^{\ell}(Du_0(\ell) + Du(\ell)) - V_{QM}^{\ell}(Du_0(\ell)) \right) + \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} \left( V_{MM}^{\ell}(Du_0(\ell) + DI_h u(\ell)) - V_{MM}^{\ell}(Du_0(\ell)) \right), \]  

(3.8)

with \( V_{QM}^{\ell}(g) := V_{\Lambda_{QM} \cup \Lambda_{BUF}}^{\ell}(g) \).

This energy difference functional was proposed in our previous paper [10] (the second part of this series), with a strict matching condition, which led to a convergent QM/MM scheme. However, in the present work we introduce “soft” matching conditions imposed via MLIPs and this will lead to a slight mismatch at the QM/MM interface (with error \( \varepsilon_1^E \) and \( \varepsilon_2^E \) respectively) that is difficult to converge to zero. This mismatch gives rise to the so-called “ghost-force” inconsistency; see Remark B.1 for the detailed mathematical reasoning. To reduce the effect of these “ghost forces” we employ ideas from the atomistic-to-continuum coupling literature [12, 28, 35, 32]. Specifically, we use a ghost-force correction [36]: to enforce the requirement that the homogeneous reference crystal is in equilibrium we make a dead load correction to the hybrid energy difference functional,

\[ E^{GFC}(u) := E^H(u) - \langle \delta E^H(0), \beta u \rangle, \]  

(3.9)

where \( \beta : \mathbb{R}^d \rightarrow \mathbb{R} \) is a characteristic function satisfying

\[ \beta(x) = \begin{cases} 0, & |x| < R_{QM}/2 \\ 1, & |x| \geq R_{QM}/2 \end{cases}. \]  

(3.10)

Note that \( \beta \) can also be chosen as a smooth cutoff function that transiting from 0 to 1 as going away from the defect core (see [29]). This is important in the atomistic/continuum coupling context but in the present work the step function is sufficient for our analysis and will be used throughout this paper.

The approximate equilibrium state of the defective system is then obtained by minimizing the energy difference functional with ghost force correction

\[ \tilde{u}^H \in \arg \min \{ E^{GFC}(u), u \in \mathcal{A}^H(\Lambda) \}, \]  

(3.11)

where the admissible set is given by

\[ \mathcal{A}^H(\Lambda) := \{ u \in \mathbb{R}^{1,2}(\Lambda) : y_0 + u \in \text{Adm}_0(\Lambda) \text{ and } u = 0 \text{ in } \Lambda_{FF} \}. \]  

(3.12)

The following result characterises precisely how the matching conditions \( \varepsilon_j^E \) affect the simulation error. The proofs are given in Appendix B.

**Theorem 3.1.** Suppose that either (P) or (D) is satisfied and that \( \tilde{u} \) is a strongly stable solution of (2.8) satisfying (S). If the assumption (RL) is satisfied, then for any \( K_E \in \mathbb{N}, 2 \leq K_E \leq n - 2, R_{QM} \) sufficiently large and \( \varepsilon_2^E \) sufficiently small, there exists an equilibrium \( \tilde{u}^H \) of (3.11)
such that
\[
\|D\bar{u} - D\bar{u}^H\|_{\beta_N} \leq C \left( \sum_{j=2}^{K_E} \varepsilon_j^E R_{QM}^{-\alpha_j} + R_{QM}^{-\alpha_{K_E}} + R_{MM}^{-d/2} \log^t R_{MM} + e^{-\kappa R_{BUF}} \right),
\]
where \(C\) is a constant independent of \(R_{QM}, R_{MM}, \varepsilon_E\), and \(\alpha_j\) and \(t\) are given by
\[
\alpha_j = \begin{cases} 
(2j - 3)d/2 & \text{if } (P) \\
(j - 2) & \text{if } (D) 
\end{cases}
\quad \text{and} \quad
\beta_{K_E} = \begin{cases} 
\alpha_{K_E} + d & \text{if } (P) \\
\alpha_{K_E} + 1 & \text{if } (D) 
\end{cases}
\quad \text{and} \quad
\quad t = \begin{cases} 
0 & \text{if } (P) \\
1 & \text{if } (D) 
\end{cases}.
\]

Our second result on energy mixing schemes demonstrates how adding soft matching conditions for the virials improves the rate in terms of the QM region size. As we will see below, this comes at essentially no additional computational cost.

**Theorem 3.2.** Under the conditions of Theorem 3.1, for any \(2 \leq K_E \leq n - 2\), we have
\[
\|D\bar{u} - D\bar{u}^H\|_{\beta_N} \leq C \left( \sum_{j=2}^{K_E} \varepsilon_j^E \varepsilon_{V_{K_E}} R_{QM}^{-\beta_{K_E}} + R_{QM}^{-\beta_{K_E}} + R_{MM}^{-d/2} \log^t R_{MM} + e^{-\kappa R_{BUF}} \right),
\]
with
\[
\alpha_j = \begin{cases} 
(2j - 3)d/2 & \text{if } (P) \\
(j - 2) & \text{if } (D) 
\end{cases}
\quad \beta_{K_E} = \begin{cases} 
\alpha_{K_E} + d & \text{if } (P) \\
\alpha_{K_E} + 1 & \text{if } (D) 
\end{cases}
\quad \text{and} \quad
\quad t = \begin{cases} 
0 & \text{if } (P) \\
1 & \text{if } (D) 
\end{cases}.
\]

The error estimates in the foregoing theorems identify how the error in the equilibrium geometry depends on the key approximation parameters, model accuracy, QM region size and MM region size. In [10, Theorem 4.1], it was assumed that \(\varepsilon_j^E = 0\) for \(j = 1, \ldots, K_E\) which then yields immediate rates of convergence in terms of QM and MM region size. For both theorems, one can then readily balance the \(R_{QM}\) and \(R_{MM}\) parameters to obtain a single rate. These optimal balanced are summarized in Table 1. Even with \(\varepsilon_j^E = 0\), Theorem 3.2 is a new result. Here, a key observation that will lead to particularly competitive QM/MM schemes is that the rate of convergence improves by a full power when \(\varepsilon_{V_{K_E}} = 0\).

In the present work, our focus is the dependence of the estimates on the \(\varepsilon_j^E\) parameters. By fitting MM potentials such that they are non-zero but “sufficiently small” we will obtain models where the rates from Table 1 appear in the pre-asymptotic regime. This will be clearly observed in the numerical tests of Section 4.

### 3.3. Force-mixing

To avoid the complications surrounding the ghost-forces correction, force-mixing schemes design the coupling in terms of QM and MM forces instead of energies. The approximate equilibrium state is then obtained by solving the following hybrid force balance equations: Find \(\bar{u}^H \in \mathcal{S}^H(\Lambda)\) such that
\[
\mathcal{F}_\ell^H(\bar{u}^H) = 0 \quad \forall \ \ell \in \Lambda^{QM} \cup \Lambda^{MM}
\]
where \(\mathcal{F}_\ell^H\) are the hybrid forces
\[
\mathcal{F}_\ell^H(u) = \begin{cases} 
\mathcal{F}_\ell^{QM}(u) & \ell \in \Lambda^{QM} \\
\mathcal{F}_\ell^{MM}(u) & \ell \in \Lambda^{MM} 
\end{cases},
\]
with $\mathcal{F}_{\ell}^{\text{MM}}(u) := \mathcal{F}_{\ell}^{\text{MM}}(u_0(\cdot - \ell) + I^\ell u(\cdot - \ell))$ and $I^h : \mathcal{V}^{1,2}(\Lambda) \to \mathcal{V}^{1,2}(\Lambda^h)$ the interpolation given in Section 3.2 and $\mathcal{F}_{\ell}^{\text{QM}}(u) := \mathcal{F}_{\ell}^{\text{QM}_{\Lambda}^{\text{BUF}}}(u)$. The error estimates for the QM/MM force-mixing scheme (3.15) are stated in the following theorems, whose proofs are again postponed to Appendix C.

**Theorem 3.3.** Suppose that either assumption (P) or (D) is satisfied and that $\bar{u}$ is a strongly stable solution of $$(2.11)$$ satisfying (S). If the assumptions (RL) is satisfied, for any $K_F \in \mathbb{N}$, $1 \leq K_F \leq n - 3$, $R_{QM}$ sufficiently large satisfying $\log \frac{R_{MM}}{R_{QM}} \leq C_{QM}^{MM}$, and $\varepsilon^i_{\alpha}$ sufficiently small, then there exists an equilibrium $\bar{u}^{H}$ of $(3.15)$ such that

$$
\|D\bar{u} - D\bar{u}^H\|_{\ell^2_N} \leq C \left( \sum_{j=1}^{K_F} \varepsilon_j R_{QM}^{-\alpha_j} + R_{QM}^{-\alpha_{K_F}+1} \right) \log R_{MM} + R_{MM}^{-d/2} \log t R_{MM} + e^{-\kappa_{\text{BUF}}},
$$

where $C$ is a constant independent of $R_{QM}$, $R_{MM}$, $\varepsilon^E$, and $\alpha_j$ and $t$ are given by

$$
\alpha_j = \begin{cases} (2j - 1)d/2 & \text{if (P)} \\ j - 1 & \text{if (D)} \end{cases} \quad \text{and} \quad t = \begin{cases} 0 & \text{if (P)} \\ 1 & \text{if (D)} \end{cases}.
$$

**Theorem 3.4.** Under the conditions of Theorem 3.3, for any $1 \leq K_F \leq n - 3$, we have

$$
\|D\bar{u} - D\bar{u}^H\|_{\ell^2_N} \leq C \left( \sum_{j=1}^{K_F} \varepsilon_j R_{QM}^{-\alpha_j} + R_{QM}^{-\beta_{K_F}+1} \right) \log R_{MM} + R_{MM}^{-d/2} \log t R_{MM} + e^{-\kappa_{\text{BUF}}},
$$

with

$$
\alpha_j = \begin{cases} (2j - 1)d/2 & \text{if (P)} \\ j - 1 & \text{if (D)} \end{cases}, \quad \beta_{K_F} = \begin{cases} \alpha_{K_F} + d & \text{if (P)} \\ \alpha_{K_F} + 1 & \text{if (D)} \end{cases} \quad \text{and} \quad t = \begin{cases} 0 & \text{if (P)} \\ 1 & \text{if (D)} \end{cases}.
$$

**Remark 3.1.** According to the assumption $\log \frac{R_{MM}}{R_{QM}} \leq C_{QM}^{MM}$, $R_{MM}$ is in fact bounded in terms of a polynomial of $R_{QM}$, and we could simply replace $\log R_{MM}$ with $\log R_{QM}$ in (3.17) and (3.18). However, we keep $\log R_{MM}$ to highlight the dependence of the error estimate on the growth of $R_{MM}$ relative to $R_{QM}$, and thus explain the necessity of carefully controlling the $R_{MM}$ parameter; see also [10] Remark 5.1.

The above estimates for the force-mixing scheme are consistent with our previous result in [10] Theorem 5.1. The optimal balance of $R_{QM}$ and $R_{MM}$ and resulting estimates for the force-mixing schemes are again summarized in Table 1 under the assumption that all matching parameters satisfy $\varepsilon^F_j = 0$. As in the energy-mixing schemes we observe that matching the $(K_F + 1)$-th derivative of the virial stress significantly improves the convergence rates of the coupling scheme. Moreover, we observe that the force-mixing schemes can be much cheaper than the energy-mixing schemes while achieving the same accuracy, since for force-mixing lower order derivatives need to be matched with the QM model.
Point defects in two dimension

| Case | no conditions on $\varepsilon_K^V$ | $\varepsilon_K^V \leq \epsilon$ ($K = K_E$ or $K_F + 1$) |
|------|----------------------------------|---------------------------------------------------|
| $K_E$ | 2 3 4 | 2 3 4 |
| $K_F$ | 1 2 3 | 1 2 3 |
| $R_{MM}$ | $R_{QM}^3$ $R_{QM}^5$ $R_{QM}^7$ | $R_{QM}^4$ $R_{QM}^6$ $R_{QM}^8$ |
| error | $R_{QM}^{-3}$ $R_{QM}^{-5}$ $R_{QM}^{-7}$ | $R_{QM}^{-4}$ $R_{QM}^{-6}$ $R_{QM}^{-8}$ |

Point defects in three dimension

| Case | no conditions on $\varepsilon_K^V$ | $\varepsilon_K^V \leq \epsilon$ ($K = K_E$ or $K_F + 1$) |
|------|----------------------------------|---------------------------------------------------|
| $K_E$ | 2 3 4 | 2 3 4 |
| $K_F$ | 1 2 3 | 1 2 3 |
| $R_{MM}$ | $R_{QM}^3$ $R_{QM}^5$ $R_{QM}^7$ | $R_{QM}^{11/3}$ $R_{QM}^{17/3}$ $R_{QM}^{23/3}$ |
| error | $R_{QM}^{-4.5}$ $R_{QM}^{-7.5}$ $R_{QM}^{-10.5}$ | $R_{QM}^{-5.5}$ $R_{QM}^{-8.5}$ $R_{QM}^{-11.5}$ |

Straight Dislocations

| Case | no conditions on $\varepsilon_K^V$ | $\varepsilon_K^V \leq \epsilon$ ($K = K_E$ or $K_F + 1$) |
|------|----------------------------------|---------------------------------------------------|
| $K_E$ | 2 3 4 | 2 3 4 |
| $K_F$ | 1 2 3 | 1 2 3 |
| $R_{MM}$ | $R_{QM}$ $R_{QM}^2$ $R_{QM}^3$ | $R_{QM}^2$ $R_{QM}^3$ $R_{QM}^4$ |
| error | $R_{QM}^{-1}$ $R_{QM}^{-2}$ $R_{QM}^{-3}$ | $R_{QM}^{-2}$ $R_{QM}^{-3}$ $R_{QM}^{-4}$ |

Table 1. The optimal choice of $R_{MM}$ and the error decay with respect to $R_{QM}$ for both point defects and dislocations, by using energy-mixing (varying $K_E$) and force-mixing (varying $K_F$) coupling schemes.

4. Numerical experiments

In this section, we present several numerical experiments to verify our theory. All results are given in atomic units (a.u.).
4.1. Constructions of the MLIPs. Following the instructions of our theory, we can construct MLIP for the QM/MM coupling scheme to achieve fast convergence of the equilibrium state approximations. The goal is to match the MLIP with the specific QM model used in the coupling, in the sense that approximations. The goal is to match the MLIP with the specific QM model used in the coupling scheme to achieve fast convergence of the equilibrium state approximations. The construction consists of two steps: (i) create the database from the QM model used in the coupling scheme; and (ii) use the database to train the MM model with some given machine-learning ansatz/format.

To create the database, we first need to specify the reference QM model. For tests of principles, an embedded atom model (EAM) [15] is used in our first example as the reference QM model (though it is actually an MM model). Then we use a practical tight binding model, the NRL model [13, 31, 37] (see a brief introduction in Appendix D), as the QM model in our second example.

If the energy-mixing scheme (3.11) is used, then the database contains the derivatives of QM site potential $\delta^j V^h(0)$ for $j = 1, 2, ..., K_E$ at the homogeneous lattice $\Lambda^h$, with a given $K_E \in \mathbb{N}$. Here, $K_E$ is determined by the required accuracy or convergence rates of the simulations, as instructed by Theorem 3.1. We can improve the accuracy according to Theorem 3.2. Similar to the energy-mixing scheme, the order $K_F$ is determined by the required accuracy of the simulations, and one can add the $(K_F + 1)$-th order derivatives of virial stress $\partial^{K_F+2} W^h_{cb}(l)$ to the database. If the force mixing scheme (3.15) is used, then the database contains the derivatives of QM force $\delta^j F^h(0)$ for $j = 1, 2, ..., K_F$ at the homogeneous lattice $\Lambda^h,$ with a given $K_F \in \mathbb{N}$. Similar to the energy-mixing scheme, the order $K_F$ is determined by the required accuracy of the simulations, and one can add the $(K_F + 1)$-th order derivatives of virial stress $\partial^{K_F+2} W^h_{cb}(l)$ to the database to improve the convergence rate. We mention that when creating the database from the QM tight binding models for both energy and force mixing schemes, the first order derivatives are calculated by the first order perturbation theory of eigenvalue problems [24], and the higher order derivatives are calculated by central finite difference approximations.

We then need to choose or construct an MLIP ansatz for the MM model, and used the above database to train the model so that the MM and QM models can match accurately enough in the coupling scheme. In our simulations, we use a recently developed atomic cluster expansion (ACE) [1, 12, 30] model as the MLIP (see a brief introduction in Appendix E).

Now that we have the database from the QM model (i.e. $V^h_{\rho}(0)$ for energy mixing and $F^h_{\ell}(0)$ for force mixing) and the MLIP ansatz (i.e. $V^{ACE}(:; c_B)$ for energy mixing and $F^{ACE}(:; c_B)$ for force mixing, see their detailed formulas in Appendix E), we can train the MLIP models by optimizing the parameters $\{c_B\}$ with the given data. More precisely, we obtain the parameters by minimizing the loss function

$$L_E(\{c_B\}) := \sum_{j=0}^{K_E} C_j^E (\varepsilon_j^E)^2 = \sum_{j=0}^{K_E} \left( \sum_{\rho=(\rho_1, \ldots, \rho_{j}) \in (\Lambda^h)^j} \left| V^h_{\rho}(0) - V^{ACE}_{\rho}(0; \{c_B\}) \right| w_j^{-1}(\rho) \right),$$

for energy-mixing scheme, where $w_j(\rho)$ is the weight function defined by (3.2) and $C_j^E$ are weights that may depend on the configurations and the observations (i.e. $V^h_{\rho}(0)$) for the energy-mixing scheme, similarly,

$$L_F(\{c_B\}) := \sum_{j=0}^{K_F} C_j^F (\varepsilon_j^F)^2 = \sum_{j=0}^{K_F} \left( \sum_{\ell=(\ell_1, \ldots, \ell_{j}) \in (\Lambda^h)^j} \left| F^h_{\ell}(0) - F^{ACE}_{\ell}(0; \{c_B\}) \right| w_j^{-1}(\ell) \right).$$
for the force-mixing scheme. If the (higher-order) derivatives of the virial stress are included in the database, then the loss functions are further improved by

\[
\mathcal{L}_V(\{c_B\}) := t\mathcal{L}_E(\{c_B\}) + (1-t)\mathcal{L}_F(\{c_B\}) + C_K^N(\varepsilon_Y^K)^2,
\]

where \( t = 1, K = K_E \) for energy-mixing scheme and \( t = 0, K = K_F + 1 \) for force-mixing scheme. The above least square problems are solved by a QR factorisation, or rank-revealing QR (rr-QR) factorisation if the \( L^2 \)-regularisation is used [42].

4.2. Numerical results for typical defected systems. We present some numerical simulations of two typical systems: (i) Tungsten (W) with EAM as the reference QM model; and (ii) Silicon (Si) with NRL tight binding model as the reference QM model. We consider systems with point defects and dislocations, and test the convergence of both energy mixing and force mixing to support our theory. We consider quasi two dimensional systems, in the sense that the truncations of the QM and MM domains are in the \( x \& y \) plane while periodic boundary condition is used in the \( z \) direction.

The simulations are implemented in the Julia packages SKTB.jl [21] (for the NRL tight binding model), ACE.jl [19] (for the ACE model) and QMMM2.jl [20] (for the QM/MM coupling scheme).

Example 1 (Tungsten). We first check numerically the patch test consistency in a homogeneous system. We minimize the energy functional (3.8) (without ghost force correction) by a QM/MM coupling scheme, and show a snapshot of the relaxation process in the left picture of Figure 4.2, where the red and blue points denote the atoms in QM and MM region respectively. We observe the effects of ghost forces around the interface, where the configuration is unstable during the energy minimisation.

We also consider the effects of ghost force in the QM/MM simulations of a defected system with a single vacancy at the origin. The MLIP is constructed by ACE, whose database contains the first and second derivatives of site potential such that \( \varepsilon_1^E \) and \( \varepsilon_2^E \) are trained to be sufficiently small (with relative errors less than \( 10^{-3} \)). We compute the forces \( f_{H}(0) \) for four different coupling methods at the reference configuration, and compare them with the pure QM forces \( f_{QM}^H(0) \) in the right picture of Figure 4.2. We observe that the spurious forces occur around the interface when the hybrid energy (3.8) is used directly, while the spurious forces vanish if the ghost force is corrected (with or without introducing the blended function in (3.9)) or a force-mixing scheme is used directly. Therefore, the hybrid energy functional (3.9) has no ghost forces, which makes the corresponding energy-mixing scheme a consistent coupling method.

We then run the QM/MM coupling simulations to obtain the approximate equilibrium state for both cases (P) and (D). In the Tungsten crystal, we consider a single vacancy at the centre for case (P), and a (001)[100] edge-dislocation for case (D). We choose sufficiently large \( R_{MM} \) and \( R_{BUF} \) in the simulations, such that the errors from the truncation of \( R_{QM} \) will dominate. The decay of approximate error \( \|D\tilde{u} - D\tilde{u}^H\|_{G_N} \) of the QM/MM coupling schemes are shown in Figure 4.3 and 4.4 for energy-mixing and force-mixing schemes respectively. We observe that the convergence rates perfectly match our theoretical predictions (compare also with the decay rates with respect to \( R_{QM} \) in Table 1).

Example 2 (Silicon). We now use a practical QM model, the NRL tight binding model, as the reference QM model in the coupling scheme. We consider a single vacancy at the centre for case (P) and a (110)[100] edge-dislocation for case (D) in the silicon crystal. For brevity of the...
presentations, we only show the convergence of the QM/MM approximations by force-mixing schemes, which have been shown to be more efficient than the energy-mixing scheme in both theory and previous example. The decay of the approximate error $\|D\bar{u} - D\bar{u}_H\|_{L^2}$ with respect to the size of QM regions are shown in Figure 4.5, which is again consistent with our theory (and Table 1).

5. Concluding remarks

In this paper, we analyze the QM/MM coupling algorithms for crystalline solids with embedded defects, where the MM models can be general interatomic potentials (or force fields) used in practice, including the “off-the-shell” models and MLIPs. We introduce some measurement on how well the atomistic models are coupling with the QM model, and provide a rigorous
Figure 4.4. (Example 1) Convergence rates of the force-mixing scheme for point defects (left) and dislocations (right).

Figure 4.5. (Example 2) Convergence rates of the force-mixing scheme for point defects (left) and dislocations (right).

numerical analysis on the convergence in terms of this measurement and the sizes of QM and MM regions. Our results not only explain why the QM/MM coupling methods could success or not, but also provide instructions on how to construct interatomic potential (or force fields) to couple the QM models, in particular, the data should be used to train the MLIPs.

Appendix Appendix A. Far-field boundary predictor for dislocations

We model dislocations by following the setting used in [18]. We consider a model for straight dislocations obtained by projecting a 3D crystal into 2D. Let $B \in \mathbb{R}^{3 \times 3}$ be a nonsingular matrix. Given a Bravais lattice $B\mathbb{Z}^3$ with dislocation direction parallel to $e_3$ and Burgers vector $b = (b_1, 0, b_3)$, we consider displacements $W : B\mathbb{Z}^3 \to \mathbb{R}^3$ that are periodic in the direction of the dislocation direction of $e_3$. Thus, we choose a projected reference lattice $\Lambda := A\mathbb{Z}^2 := \{(\ell_1, \ell_2) \mid \ell = (\ell_1, \ell_2, \ell_3) \in B\mathbb{Z}^3\}$. We also introduce the projection operator

$$P(\ell_1, \ell_2) = (\ell_1, \ell_2, \ell_3) \quad \text{for} \quad \ell \in B\mathbb{Z}^3.$$
It can be readily checked that this projection is again a Bravais lattice.

We prescribe the far-field predictor $u_0$ as follows according to [8, 18]. Let $\Lambda \subset \mathbb{R}^2$, $\hat{x} \in \mathbb{R}^2$ be the position of the dislocation core and $\Gamma := \{x \in \mathbb{R}^2 \mid x_2 = \hat{x}_2, \ x_1 \geq \hat{x}_1\}$ be the “branch cut”, with $\hat{x}$ chosen such that $\Gamma \cap \Lambda = \emptyset$. We define the far-field predictor $u_0$ by

$$u_0(x) := u^{\text{lin}}(\xi^{-1}(x)),$$

where $u^{\text{lin}} \in C^\infty(\mathbb{R}^2 \setminus \Gamma; \mathbb{R}^d)$ is the solution of continuum linear elasticity (CLE)

$$C^{ij}_{\alpha\beta} \frac{\partial^2 u^{\text{lin}}_{i\alpha}}{\partial x_\alpha \partial x_\beta} = 0 \quad \text{in} \ \mathbb{R}^2 \setminus \Gamma,$$

with $\arg(x)$ denoting the angle in $(0, 2\pi)$ between $x$ and $b_{12} = (b_1, b_2) = (b_0, 0)$, and $\eta \in C^\infty(\mathbb{R})$ with $\eta = 0$ in $(-\infty, 0]$ and $\eta = 1$ in $[1, \infty)$ which removes the singularity.

In order to model dislocations, the homogeneous site potential $V^h$ must be invariant under lattice slip. Following [18], we define the slip operator $S_0$ acting on the displacements $w : \Lambda \to \mathbb{R}^d$, by ($b_{12}$ represents the projection of the Burger’s vector to the $(x_1, x_2)$ plane)

$$S_0 w(x) := \begin{cases} w(x) & x_2 > \hat{x}_2, \\ w(x - b_{12}) - b & x_2 < \hat{x}_2. \end{cases}$$

We may then formulate the slip invariance condition by defining a mapping $S$, where $S$ is an $\ell^2$-orthogonal operator with dual $S^* = S^{-1}$ by

$$Su(\ell) := \begin{cases} u(\ell) & \ell_2 > \hat{x}_2, \\ u(\ell - b_{12}) & \ell_2 < \hat{x}_2. \end{cases} \quad S^* u(\ell) := \begin{cases} u(\ell) & \ell_2 > \hat{x}_2, \\ u(\ell + b_{12}) & \ell_2 < \hat{x}_2. \end{cases}$$

The slip invariance condition can now be expressed as

$$V^h(D(u_0 + u)(\ell)) = V^h(S^* DS_0(u_0 + u)(\ell)), \quad \forall \ \ell \in \Lambda, u \in \mathcal{W}^{1,2}(\Lambda),$$

where $u_0$ is defined by (A.2).

In our analysis we require that applying the slip operator to the predictor map $u_0$ yields a smooth function in the half-space $\Omega_\Gamma = \{x_1 \geq \hat{x}_1 + \hat{r} + b_1\}$. It is therefore natural to define (likewise to [18]) the elastic strains

$$e(\ell) := (e_{\rho}(\ell))_{\rho \in \Lambda - \ell}, \quad e_{\rho}(\ell) = \begin{cases} S^* D_{\rho} S_0 u_0(\ell) & \ell \in \Omega_\Gamma \\ D_{\rho} u_0(\ell) & \ell \notin \Omega_\Gamma, \end{cases}$$

and the analogous definition for corrector $u$

$$Du(\ell) := (D_{\rho} u(\ell))_{\rho \in \Lambda - \ell}, \quad D_{\rho} u(\ell) = \begin{cases} S^* D_{\rho} S u(\ell) & \ell \in \Omega_\Gamma \\ D_{\rho} u(\ell) & \ell \notin \Omega_\Gamma. \end{cases}$$
Using this notation, the slip invariance condition (A.5) may be written as, for $u \in \mathcal{U}^{1,2}(\Lambda)$,
\begin{equation}
    V^h(D(u_0 + u)(\ell)) = V^h(e(\ell) + Du(\ell)).
\end{equation}

The following lemma, proven in [8], is a straightforward extension of [18, Lemma 3.1].

**Lemma A.1.** If the predictor $u_0$ is defined by (A.2) and $e(\ell)$ is given by (A.6), then there exists a constant $C$ such that
\begin{equation}
    |e_\sigma(\ell)| \leq C|\sigma| \cdot |\ell|^{-1} \quad \text{and} \quad |D_\rho e_\sigma(\ell)| \leq C|\rho| \cdot |\sigma| \cdot |\ell|^{-1}.
\end{equation}

**Appendix B. Proofs for the energy-mixing scheme**

For $K \geq 2, g \in (\mathbb{R}^d)^A$, we define the $K$-th order Taylor’s expansion $T_KV^h$ at the homogeneous state by
\begin{equation}
    T_KV^h(g) := V^h(0) + \sum_{j=1}^K \frac{1}{j!} \delta^jV^h(0) [g \otimes j].
\end{equation}

In addition to the norm $\|D \cdot \|_{\ell^2}$ introduced in (2.2), one can construct a family of weighted norms that use weighted finite-difference stencils with infinite interaction range [8]. For a stencil $Du(\ell)$ and $\gamma > 0$, we can define the (semi-)norms
\begin{equation}
    |Du(\ell)|_{\ell^2,\gamma} := \left( \sum_{\rho \in \Lambda - \ell} w_\gamma(|\rho|) |D_\rho u(\ell)|^2 \right)^{1/2} \quad \text{and} \quad \|Du\|_{\ell^2,\gamma} := \left( \sum_{\ell \in \Lambda} |Du(\ell)|^2 \right)^{1/2}
\end{equation}
with $w_\gamma(|\rho|) := e^{-\gamma|\rho|}$. For convenience, we will use $w$ directly when there is no confusion in the context. We also have from [8, Appendix A] that for $\gamma > 0$, there exist constants $c, C > 0$ such that
\begin{equation}
    c\|Du\|_{\ell^2} \leq \|Du\|_{\ell^2,\gamma} \leq C\|Du\|_{\ell^2} \quad \forall u \in \mathcal{U}^{1,2}(\Lambda).
\end{equation}

We are ready to give the proofs of the main results (Theorem 3.1 and Theorem 3.2) for energy-mixing scheme and we essentially extend the proofs of [10, Theorem 4.1] to general cases. **Proof of Theorem 3.1.** Following the framework of the *a priori* error estimates in [10, 32, 35, 36], we divide the proof into three steps in order to apply the inverse function theorem [32, Lemma 2.2].

1. **Quasi-best approximation:** We first construct $T^H\tilde{u}(\ell) \in \mathcal{A}^H$ by
\begin{equation}
    T^H\tilde{u}(\ell) := \eta(\ell/R_{\text{MM}})(\tilde{u}(\ell) - a_{R_{\text{MM}}}),
\end{equation}
where $\eta \in C^1(\mathbb{R}^d)$ is a cutoff function satisfying $\eta(x) = 1$ for $|x| \leq 4/6$ and $\eta(x) = 0$ for $|x| \geq 5/6$ and $a_{R_{\text{MM}}} := \int_{B_{R_{\text{MM}}/6} \setminus \partial B_{R_{\text{MM}}/6}} I\tilde{u}(x) \, dx$ with $I\tilde{u}$ defined by the piecewise affine interpolant of $\tilde{u}$ with respect to the lattice [36, 33]. Then, for $R_{\text{MM}}$ sufficiently large, we have from the decay estimates (2.10) that
\begin{equation}
    \|D\tilde{u} - DT^H\tilde{u}\|_{\ell^2} \leq C\|D\tilde{u}\|_{\ell^2}(\mathcal{A} \setminus B_{R_{\text{MM}}/2}) \quad \text{and} \quad \|DT^H\tilde{u}(\ell)\|_w \leq C(1 + |\ell|)^{-d} \log^4(2 + |\ell|) \quad \forall \ell \in \Lambda.
\end{equation}
Using the norm equivalence (B.3), for $R_{\text{MM}}$ sufficiently large, we have
\begin{equation}
\|\delta\mathcal{E}(\bar{u}) - \delta\mathcal{E}(T^H\bar{u})\| \leq L_1\|D\bar{u} - DT^H\bar{u}\|_{\ell^2_N} \leq CL_1\|D\bar{u}\|_{\ell^2_N(\Lambda \setminus B_{R_{\text{MM}}/2})} \quad \text{and}
\end{equation}
\begin{equation}
\|\delta^2\mathcal{E}(\bar{u}) - \delta^2\mathcal{E}(T^H\bar{u})\| \leq L_2\|D\bar{u} - DT^H\bar{u}\|_{\ell^2_N} \leq CL_2\|D\bar{u}\|_{\ell^2_N(\Lambda \setminus B_{R_{\text{MM}}/2})},
\end{equation}
where $L_1$ and $L_2$ are uniform Lipschitz constants of $\delta\mathcal{E}$ and $\delta^2\mathcal{E}$ respectively since $\mathcal{E}$ is $(n-1)$-times continuously differentiable with respect to the $\|D\cdot\|_{\ell^2_N}$ norm.

2. Stability: We first observe that the ghost force correction term in (3.9) is a linear term with respect to $u$, hence its second variation with respect to $v \in \mathcal{A}^H$ vanishes, that is,
\begin{equation}
\langle \delta^2\mathcal{E}^{\text{GFC}}(T^H\bar{u})v, v \rangle = \langle \delta^2\mathcal{E}^{\text{H}}(T^H\bar{u})v, v \rangle \quad \forall \, v \in \mathcal{A}^H.
\end{equation}

Hence, for any $v \in \mathcal{A}^H$, we consider the stability of
\begin{equation}
\langle \delta^2\mathcal{E}^{\text{H}}(T^H\bar{u})v, v \rangle
\end{equation}
\begin{equation}
= \langle \delta^2\mathcal{E}^{\text{T}}(T^H\bar{u})v, v \rangle + \left( \langle \delta^2\mathcal{E}^{\text{H}}(T^H\bar{u})v, v \rangle - \langle \delta^2\mathcal{E}^{\text{T}}(T^H\bar{u})v, v \rangle \right)
\end{equation}
\begin{equation}
=: S_1 + S_2,
\end{equation}
where $\mathcal{E}^{\text{T}}$ is the hybrid energy functional
\begin{equation}
\mathcal{E}^{\text{T}}(u) := \sum_{\ell \in \Lambda^{\text{QM}}} \left( V^{\text{QM}}_{\ell}(Du_0(\ell) + Du(\ell)) - V^{\text{QM}}_{\ell}(Du_0(\ell)) \right)
\end{equation}
\begin{equation}
+ \sum_{\ell \in \Lambda^{\text{MMU}}_{\text{FF}}} \left( T_K V^{\text{BUF}}_#(Du_0(\ell) + Du(\ell)) - T_R V^{\text{BUF}}_#(Du_0(\ell)) \right),
\end{equation}
where $V^{\text{BUF}}_# : (\mathbb{R}^d)^{\mathcal{R}} \to \mathbb{R}$ with $\mathcal{R} = B_{R_{\text{BUF}}} \cap (\Lambda \setminus 0)$ satisfies $V^{\text{BUF}}_#(D_{\mathcal{R}}u(\ell)) = V^{\text{BUF}}_#(Du(\ell))$ and $T_K V^{\text{BUF}}_#$ is $K$-order Taylor's expansion of $V^{\text{BUF}}_#$. The term $S_1$ can be estimated by using the results of [10] Theorem 4.1
\begin{equation}
S_1 := \langle \delta^2\mathcal{E}^{\text{T}}(T^H\bar{u})v, v \rangle \geq c_E\|Dv\|_{\ell^2_N}^2
\end{equation}
with some constants $c_E > 0$ that are independent of model parameters.

To estimate $S_2$, for simplicity of notations, we denote $u_h(\ell) := u_0(\ell) + I^hT^H\bar{u}(\ell)$ and $v_h(\ell) := I^h v(\ell)$ for $v \in \mathcal{A}^H$ with $I^h$ defined by (3.7), we then split it into three parts
\begin{equation}
S_2 = \langle \delta^2\mathcal{E}^{\text{H}}(T^H\bar{u})v, v \rangle - \langle \delta^2\mathcal{E}^{\text{T}}(T^H\bar{u})v, v \rangle
\end{equation}
\begin{equation}
= \sum_{\ell \in \Lambda^{\text{MMU}}_{\text{FF}}} \left( \left( \delta^2 V^{\text{MM}}(Du_h(\ell)) - \delta^2 T_K V^{\text{MM}}(Du_0(\ell)) \right) Du_h(\ell), Du_h(\ell) \right)
\end{equation}
\begin{equation}
+ \sum_{\ell \in \Lambda^{\text{MMU}}_{\text{FF}}} \left( \left( \delta^2 T_K V^{\text{MM}}(Du_h(\ell)) - \delta^2 V^{h}(Du_0(\ell)) \right) Du_h(\ell), Du_h(\ell) \right)
\end{equation}
\begin{equation}
+ \sum_{\ell \in \Lambda^{\text{MMU}}_{\text{FF}}} \left( \left( \delta^2 T_K V^{h}(Du_0(\ell)) \right) Du_h(\ell), Du_h(\ell) \right)
\end{equation}
\begin{equation}
- \langle \delta^2 T_K V^{\text{BUF}}_#(Du_0(\ell) + DT^H\bar{u}(\ell))Dv(\ell), Dv(\ell) \rangle
\end{equation}
\begin{equation}
=: S_{21} + S_{22} + S_{23}.
\end{equation}
Using Taylor's expansion of $V^{MM}$ at the homogeneous state, we have

\[
|S_{21}| = \sum_{\ell \in \Lambda_{\text{MM} \cup \text{FF}}} \left\langle \left( \delta^2 V^{MM}(Du_h(\ell)) - \delta^2 T_K V^{MM}(Du_h(\ell)) \right) Du_h(\ell), Dv_h(\ell) \right\rangle \\
\leq C \sum_{\ell \in \Lambda_{\text{MM} \cup \text{FF}}} |Du_h(\ell)|_{\infty}^{K-1} |Dv_h(\ell)|_w^2 \leq C \|Du_h\|_{\mu_a}^{K-1} \|Dv\|_w^2.
\]

(B.14)

For $S_{22}$, we have

\[
|S_{22}| = \sum_{j=2}^{K} \sum_{\ell \in \Lambda_{\text{MM} \cup \text{FF}}} \left\langle \left( \delta^j V^{MM}(-0) - \delta^j V^h(0) \right) \left( Du_h(\ell) \right)^{j-2} Du_h(\ell), Dv_h(\ell) \right\rangle \\
\leq \frac{\varepsilon^E}{2} \sum_{\ell \in \Lambda_{\text{MM} \cup \text{FF}}} |Dv_h(\ell)|_w^2 + \sum_{j=3}^{K} \varepsilon^E \sum_{\ell \in \Lambda_{\text{MM} \cup \text{FF}}} |Du_h(\ell)|_{\infty}^{j-2} |Dv_h(\ell)|_w^2 \\
\leq \left( \frac{\varepsilon^E}{2} + \sum_{j=3}^{K} \varepsilon^E \|Du_h\|_{\mu_a}^{j-2} \right) \|Dv\|_w^2.
\]

(B.15)

Note that the locality assumption in (RL), for $S_{23}$, there exists a constant $\eta > 0$ such that

\[
|S_{23}| \leq Ce^{-\eta R_{BUF}} \|Dv\|_w^2.
\]

(B.16)

Combing from (B.9) to (B.16) and using the decay estimates (2.10) and the norm equivalence (B.3), we have that, for sufficiently large $R_{QM}$ and sufficiently small $\varepsilon^E_2$,

\[
\left\langle \delta^2 E^{GFC}(T^H \bar{u}) v, v \right\rangle \geq \frac{C_E}{2} \|Dv\|_w^2.
\]

(B.17)
3. Consistency: For any $v \in \mathcal{A}^H$, we have

$$\langle \delta \mathcal{E}^{\text{GFC}}(T^H \bar{u}), v \rangle$$

$$= \langle \delta \mathcal{E}^{\text{GFC}}(T^H \bar{u}) - \delta \mathcal{E}^H(T^H \bar{u}), v \rangle + \langle \delta \mathcal{E}^H(T^H \bar{u}) - \delta \mathcal{E}(\bar{u}), v \rangle$$

$$= \sum_{\ell \in \Lambda_{\text{QM}}} \langle \delta V^\text{QM}_\ell (Du_0(\ell) + DT^H \bar{u}(\ell)) - \delta V_{\ell}(Du_0(\ell) + DT^H \bar{u}(\ell)), Dv(\ell) \rangle$$

$$+ \sum_{\ell \in \Lambda_{\text{MM}} \cup \Lambda_{\text{FF}}} \left( \langle \delta V^h(Du_h(\ell)), Dv_h(\ell) \rangle - \langle \delta V_{\ell}(Du_0(\ell) + DT^H \bar{u}(\ell)), Dv(\ell) \rangle \right)$$

$$+ \sum_{\ell \in \Lambda_{\text{MM}} \cup \Lambda_{\text{FF}}} \langle \delta V^h(Du_h(\ell)) - \delta T_K V^\text{MM}(Du_h(\ell)), Dv_h(\ell) \rangle$$

$$+ \sum_{\ell \in \Lambda_{\text{MM}} \cup \Lambda_{\text{FF}}} \langle \delta T_K V^h(Du_h(\ell)) - \delta V^h(Du_h(\ell)), Dv_h(\ell) \rangle - \langle \delta \mathcal{E}^H(0), \beta v \rangle$$

(B.18) \(=\) \(T_1 + T_2 + T_3 + T_4\).

Following from the locality assumptions in (RL) and the definition of the interpolation operator \(I^h\) by (3.7), there exits a constant \(\kappa_1 > 0\) such that

\[|T_1| \leq Ce^{-\kappa_1 R_{\text{BUF}}} \|Dv\|_{\ell^2_w} \tag{B.19}\]

To estimate \(T_2\), we have from (B.1) and (3.7)

\[|T_2| = \sum_{\ell \in \Lambda_{\text{MM}} \cup \Lambda_{\text{FF}}} \langle \delta V^\text{MM}(Du_h(\ell)) - \delta T_K V^\text{MM}(Du_h(\ell)), Dv_h(\ell) \rangle\]

\[+ \sum_{\ell \in \Lambda_{\text{MM}} \cup \Lambda_{\text{FF}}} \langle \delta T_K V^h(Du_h(\ell)) - \delta V^h(Du_h(\ell)), Dv_h(\ell) \rangle\]

\[\leq C \sum_{\ell \in \Lambda_{\text{MM}} \cup \Lambda_{\text{FF}}} |Du_h(\ell)|_w^K |Dv_h(\ell)|_w \leq C \|Du_h\|_{\ell^2_{\text{BUF}}(\Lambda \cup \Lambda_{\text{MM}} \cup \Lambda_{\text{FF}})} \|Dv\|_{\ell^2_w} \tag{B.20}\]

For \(T_3\), after a direct calculation, we have from \(\text{[B.7]}\)

\[|T_3| \leq CL_1 \|D\bar{u}\|_{\ell^2_{\text{BUF}}(\Lambda \setminus B_{\Lambda_{\text{MM}}/2})} \|Dv\|_{\ell^2_w} \tag{B.21}\]
To estimate $T_4$, we first split it into two parts

$$T_4 = \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} \langle \delta T_{K} V^{MM}(D u_h(\ell)) - \delta T_{K} V^h(D u_h(\ell)), D u_h(\ell) \rangle - \langle \delta \mathcal{E}^h(0), \beta v \rangle$$

$$= \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} \langle \delta V^{MM}(0) - \delta V^h(0), D u_h(\ell) \rangle - \langle \delta \mathcal{E}^h(0), \beta v \rangle$$

$$+ \sum_{j=2}^{K} \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} \left( \langle \delta j V^{MM}(0) - \delta j V^h(0) \rangle (D u_h(\ell))^{j-1}, D u_h(\ell) \right)$$

(B.22) $=: T_{41} + T_{42}$.

To estimate $T_{41}$, for simplicity of notations, let $v_{\beta}(\ell) := v(\ell)\beta(\ell), \Omega_{QM}^{h,c} := \{ \ell \in \Lambda^h \mid |\ell| \leq c R_{QM} \}$ with the constant $0 \leq c \leq 1$. It is straightforward to write $\Omega_{QM}^{h,1/2} \subset \Omega_{QM}^{h,1}$, then we have

$$T_{41} = \sum_{\ell \in \Omega_{QM}^{h,1}} \mathcal{F}^{\ell}(0)v_h(\ell) - \sum_{\ell \in \Omega_{QM}^{h,1}} \mathcal{F}^{MM}(0)v_{\beta}(\ell)$$

$$+ \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} \sum_{\rho \in \Lambda^h_{\ell+\rho}} \left( V^{MM}(0)v(\ell + \rho) - V^h(0)v_h(\ell + \rho) \right)$$

$$+ \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} \sum_{\rho \in \Omega_{QM}^{h,1/2}} V^{MM}(0)v_h(\ell + \rho)$$

(B.23) $=: T_{41}^{(a)} + T_{41}^{(b)}$.

The term $T_{41}^{(a)}$ can be divided into two parts according to the blending function $\beta$, and noticing $\mathcal{F}^{\ell}_{MM}(0) = 0$ for every $\ell \in \Lambda^h$, after a direct calculation, then we have

$$T_{41}^{(a)} = \sum_{|\ell| \leq R_{QM}/2} \mathcal{F}^{\ell}_{MM}(0)v_h(\ell) + \sum_{R_{QM}/2 \leq |\ell| \leq R_{QM}} (\mathcal{F}^{\ell}_{MM}(0) - \mathcal{F}^{MM}(0))v(\ell)$$

(B.24) $\leq C e^{-\kappa_3 R_{BUF}} \|Dv\|_{E_0}$,

where the last inequality follows from the locality assumption in (RL). The term $T_{41}^{(b)}$ can be estimated similarly

(B.25) $|T_{41}^{(b)}| \leq C e^{-\kappa_3 R_{BUF}} \|Dv\|_{E_0}$.

We then estimate $T_{42}$ by

$$|T_{42}| = \sum_{j=2}^{K} \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} \left( \langle \delta j V^{MM}(0) - \delta j V^h(0) \rangle (D u_h(\ell))^{j-1}, D u_h(\ell) \right)$$

$$\leq \sum_{j=2}^{K} \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} |D u_h(\ell)|_{E_0}^{j-1} |D u_h(\ell)|_{E_0} \leq \left( \sum_{j=2}^{K} \|D u_h\|_{E_0}^{j-1} \right) \|Dv\|_{E_0} \cdot \sum_{j=2}^{K} \sum_{\ell \in \Lambda_{MM} \cup \Lambda_{FF}} |D u_h(\ell)|_{E_0}^{j-1}.$$
Taking into accounts from \((B.18)\) to \((B.25)\), and the norm equivalence \((B.3)\), let \(\kappa := \max\{\kappa_1, \kappa_2, \kappa_3\}\), we have
\[
\langle \delta \mathcal{E}^{\text{GFC}} (T^H \bar{u}), v \rangle \leq C \left( \sum_{j=2}^{K} \varepsilon_j^E \|D u_h\|_{\ell_2^h \cap B_{R_{\text{MM}}}/2}^{j-1} + \|D u_h\|_{\ell_2^h \cap B_{R_{\text{QF}}}/2}^j \right) \|D v\|_{\ell_2^E}.
\]
\[(B.26)\]
\[+ \|D \bar{u}\|_{\ell_2^E}(A \& B_{R_{\text{MM}}}/2) + e^{-\kappa R_{\text{BUF}}} \cdot \|D v\|_{\ell_2^E}.
\]

For case \((P)\), we obtain from \(u_0 = 0\) and \(|D \bar{u}(\ell)| \leq C(1 + |\ell|)^{-d}\)
\[
\langle \delta \mathcal{E}^{\text{GFC}} (T^H \bar{u}), v \rangle \leq C \left( \sum_{j=2}^{K} \varepsilon_j^E R_{\text{QF}}^{-2j-3d/2} + R_{\text{QF}}^{-2K-1d/2} + R_{\text{MM}}^{-d/2} + e^{-\kappa R_{\text{BUF}}} \right) \|D v\|_{\ell_2^E}.
\]
\[(B.27)\]

For case \((D)\), we obtain from \((A.9)\), \(|D u_0(\ell)| \leq C|\ell|^{-1}\) and \(|D \bar{u}(\ell)| \leq C(1 + |\ell|)^{-2}\log(2 + |\ell|)\)
\[
\langle \delta \mathcal{E}^{\text{GFC}} (T^H \bar{u}), v \rangle \leq C \left( \sum_{j=2}^{K} \varepsilon_j^E R_{\text{QF}}^{-j+2} + R_{\text{QF}}^{-K+1} + R_{\text{MM}}^{-d/2} \log R_{\text{MM}} + e^{-\kappa R_{\text{BUF}}} \right) \|D v\|_{\ell_2^E}.
\]
\[(B.28)\]

Combining the stability \((B.17)\) with consistency \((B.27)\) and \((B.28)\), we can apply the inverse function theorem \([32, \text{Lemma 2.2}]\) with \(K = K_F\) and use \((B.5)\) to obtain the stated results. \(\square\)

**Remark B.1.** If the ghost force correction \((3.9)\) is not applied, that is, \(\beta \equiv 0\), then the estimate of \(T_{41}\) in \((B.23)\) becomes to
\[
|T_{41}| \leq \varepsilon_1^E \sum_{\ell \in \Lambda_{\text{MM}, \text{AFF}}} \|D v_h(\ell)\|_{\ell_2^h} \leq C \varepsilon_1^E \cdot N_{\text{MM}}^{1/2} \cdot \|D v\|_{\ell_2^E},
\]
which is non-vanishing as \(\varepsilon_1^E\) is not exact zero (slight mismatch at the QM/MM interface). It gives rise to the so-called “ghost-force” inconsistency. Hence the ghost force correction term \(\langle \delta \mathcal{E}^H (0), \beta v \rangle\) is required to reduce the effect of “ghost-force”.

We then give the proof of Theorem 3.2 which is similar to that of Theorem 3.1. Due to adding the soft matching conditions for virials in Theorem 3.2 the only difference lies in the consistency part.

**Proof of Theorem 3.2.** The quasi-best approximation and the stability analysis are the same as that in the proof of Theorem 3.1. The main difference is the estimate of \(T_2\) in \((B.18)\). \(T_2\) can be further splitted into two parts
\[
T_2 = \sum_{\ell \in \Lambda_{\text{MM}, \text{AFF}}} \langle \delta V_{\text{MM}}(D u_h(\ell)) - \delta T_{K} V_{\text{MM}}(D u_h(\ell)), D v_h(\ell) \rangle
+ \sum_{\ell \in \Lambda_{\text{MM}, \text{AFF}}} \langle \delta T_{K} V^h(D u_h(\ell)) - \delta V^h(D u_h(\ell)), D v_h(\ell) \rangle
\]
\[(B.29)\]
\[= \sum_{\ell \in \Lambda_{\text{MM}, \text{AFF}}} \langle \mathcal{G}_1(D u_h(\ell)), D v_h(\ell) \rangle + \langle \mathcal{G}_2(D u_h(\ell)), D v_h(\ell) \rangle,
\]
where \(\mathcal{G}_1 := \delta V_{\text{MM}} - \delta T_{K+1} V_{\text{MM}} + \delta T_{K+1} V^h - \delta V^h\) and \(\mathcal{G}_2 := \delta T_{K+1} V_{\text{MM}} - \delta T_{K} V_{\text{MM}} + \delta T_{K} V^h - \delta T_{K+1} V^h\). The first term of \((B.29)\) can be similarly estimated by using the techniques in \((B.20)\)
\[
\sum_{\ell \in \Lambda_{\text{MM}, \text{AFF}}} \langle \mathcal{G}_1(D u_h(\ell)), D v_h(\ell) \rangle \leq C \|D u_h\|_{\ell_2^{K+2} \cap \Lambda_{\text{MM}, \text{AFF}}} \|D v\|_{\ell_2^E}.
\]
\[(B.30)\]
For the second term, let \( \Omega_{\text{MF}} := \{ x \in \mathbb{R}^d, |x| \geq R_{\text{QM}} \} \), and expanding the strain \( D_{\rho} u(\ell) \) at \( \ell \), then we have

\[
\left| \sum_{\ell \in \Lambda^{\text{AMM} \cup \text{FF}}} \langle \mathcal{G}_2(Du_{\ell}(\ell), Dv_{\ell}(\ell)) \rangle \right| \\
\leq \sum_{\ell \in \Lambda^{\text{AMM} \cup \text{FF}}} \sum_{\rho \in \Lambda^k} (V_{\rho}^h(0) - V_{\rho}^{\text{MM}}(0)) \left( \prod_{i=1}^{K} \nabla u_{\ell}(\ell) \cdot \rho_i \right) \left( \nabla v_{\ell}(\ell) \cdot \rho_{K+1} \right) \\
+ C \sum_{\ell \in \Lambda^{\text{AMM} \cup \text{FF}}} (\nabla u_{\ell}(\ell))^{K+1} (\nabla^2 u_{\ell}(\ell)) \nabla v_{\ell}(\ell)
\]

(B.31)

where the last inequality follows from the Cauchy-Schwarz inequality and the norm equivalence between \( \|Dv\|_{L_a^2(\Omega)} \) and \( \|\nabla v\|_{L^2(\Omega)} \).

Hence, substituting the estimate for \( T_2 \) in (B.18) with the new estimates (combining (B.29), (B.30) and (B.31)), we have the following consistency results

\[
\langle \delta \mathcal{E}^\text{GFC}(T^H \bar{u}), v \rangle \leq C \left( \sum_{j=2}^{K} \varepsilon_j^E \|Du_{\ell}\|_{L_{2j-2}(\Lambda^{\text{AMM} \cup \text{FF}})} + \varepsilon_K \|\nabla u_{\ell}\|_{L_{2K}(\Omega_{\text{MF}})} \right) + \|\nabla u_{\ell}\|_{L_{2K-2}(\Omega_{\text{MF}})} \|\nabla^2 u_{\ell}\|_{L^2(\Omega_{\text{MF}})} + \|D\bar{u}\|_{L_6(\Lambda \cup R_{\text{MM}}/2)} + e^{-\kappa R_{\text{MM}}} \) \cdot \|Dv\|_{L_a^2(\Omega)}
\]

(B.32)

Combining the decay estimates (2.10), the stability (B.17) and (B.5), we can obtain the stated results.

\[\square\]

APPENDIX Appendix C. PROOFS FOR THE FORCE-MIXING SCHEME

For \( v : \Lambda \rightarrow \mathbb{R} \), we will use the notation \( \langle \mathcal{F}^H(u), v \rangle := \sum_{\ell \in \Lambda^{\text{AMM} \cup \text{AMM}}} \mathcal{F}^H_{\ell}(u) \cdot v(\ell) \) in our analysis. For \( K \geq 1 \) and \( w : \Lambda \rightarrow \mathbb{R}^d \), we introduce the \( K \)-th order Taylor’s expansion \( T_K \mathcal{F}^h \) at the homogeneous state by

\[
T_K \mathcal{F}^h(w) := \sum_{j=1}^{K} \frac{1}{j!} \delta^j \mathcal{F}^h(0) \left[ w^\otimes j \right].
\]

(C.1)

The following two Lemmas are useful in our analysis in that they sometimes allow us to avoid stress-strain representations of residual forces that we need to estimate. We include them here for the sake of completeness and please refer to [10] for more details.

**Lemma C.1.** For any \( v \in \mathcal{A}^H \), there exists \( C > 0 \) such that

\[
\|v\|_{L_6} \leq C \|Dv\|_{L_a^2(1 + \log R_{\text{MM}})} \quad \text{if } d = 2 \quad \text{and}
\]

\[
\|v\|_{L_6} \leq C \|Dv\|_{L_a^2} \quad \text{if } d = 3.
\]

(C.2) (C.3)

**Lemma C.2.** Let \( 0 < L < R \) and \( u : \Lambda \rightarrow \mathbb{R} \) satisfy \( u(\ell) = 0 \quad \forall \ |\ell| \geq R \). If \( f : \Lambda \rightarrow \mathbb{R} \) satisfies \( |f(\ell)| \leq c|\ell|^{-p} \) with \( p \geq 3 \), then there exists a constant \( C \) such that

\[
\sum_{L \leq |\ell| \leq R} f(\ell) \cdot v(\ell) \leq C \left( 1 + \log \left( \frac{R}{L} \right) \right) \cdot L^{-p+1+d/2} \cdot \|Dv\|_{L_a^2} \quad \forall \ v \in \mathcal{A}^H.
\]

(C.4)
We are in positions to give the proofs of the main results (Theorem 3.3 and Theorem 3.4) for force-mixing scheme and most of the proofs essentially follow from [10] Proof of Theorem 5.1.

**Proof of Theorem 3.3.** Similar to the proofs for energy-mixing, we divide the proof into three steps in order to apply the inverse function theorem [32, Lemma 2.2].

1. **Quasi-best approximation:** We take the approximation $T^H \bar{u} \in \mathcal{A}^H$ constructed in Appendix B so that the properties from (B.5) to (B.8) are satisfied.

2. **Stability:** For any $v \in \mathcal{A}^H$, we have

   \[
   \langle \delta \mathcal{F}^H(T^H \bar{u}) v, v \rangle
   = \langle \delta \mathcal{F}^T(T^H \bar{u}) v, v \rangle + \langle (\delta \mathcal{F}^H(T^H \bar{u}) - \delta \mathcal{F}^T(T^H \bar{u})) v, v \rangle
   \]

   (C.5)

   where $\mathcal{F}^T$ is the QM/MM hybrid force

   \[
   \mathcal{F}^T_\ell(u) = \begin{cases} 
   \mathcal{F}^{\text{QM,}\ell\cup\text{BUF}}_\ell(u) & \ell \in \Lambda^{\text{QM}} \\
   T_K \mathcal{F}^{\text{BUF}}_\ell \left((u_0(\cdot - \ell) + u(\cdot - \ell))|_{B_{\text{BUF}}} \right) & \ell \in \Lambda^{\text{MM}} 
   \end{cases}
   \]

   where $\mathcal{F}^{\text{BUF}}_\ell : (\mathbb{R}^d)^R \to \mathbb{R}$ with $R = B_{\text{BUF}} \cap \Lambda^h$ satisfying

   \[
   \mathcal{F}^{\text{BUF}}_\ell (u_0(\cdot - \ell) + u(\cdot - \ell)|_{B_{\text{BUF}}}) = \mathcal{F}^{B_{\text{BUF}}(\ell)} (u).
   \]

   The term $G_1$ can be estimated by using [10] Theorem 5.1 directly

   \[
   G_1 := \langle \delta \mathcal{F}^T(T^H \bar{u}) v, v \rangle \geq c_F \|Dv\|^2_{l_2^h}
   \]

   with some constants $c_F > 0$ that are independent of model parameters.

   To estimate $G_2$, for simplicity of notations, let $u_h(\cdot - \ell) := u_0(\cdot - \ell) + I^hT^H \bar{u}(\cdot - \ell)$ with $I^h$ defined by (3.7), then we split it into three parts

   \[
   G_2 = \langle (\delta \mathcal{F}^H(T^H \bar{u}) - \delta \mathcal{F}^T(T^H \bar{u})) v, v \rangle
   \]

   \[
   = \sum_{\ell \in \Lambda^{\text{MM}}} \langle \delta \mathcal{F}^{\text{MM}}(u_h(\cdot - \ell)) - \delta T_K \mathcal{F}^{\text{MM}}(u_h(\cdot - \ell)), v \rangle v(\ell)
   + \sum_{\ell \in \Lambda^{\text{MM}}} \langle \delta T_K \mathcal{F}^{\text{h}}(u_h(\cdot - \ell)) - \delta \mathcal{F}^{\text{h}}(u_h(\cdot - \ell)), v \rangle v(\ell)
   + \sum_{\ell \in \Lambda^{\text{MM}}} \langle \delta T_K \mathcal{F}^{\text{MM}}(u_h(\cdot - \ell)) - \delta T_K \mathcal{F}^{\text{h}}(u_h(\cdot - \ell)), v \rangle v(\ell)
   + \sum_{\ell \in \Lambda^{\text{MM}}} \langle \delta \mathcal{F}^{\text{h}}(u_h(\cdot - \ell)) - \delta \mathcal{F}^T_\ell(T^H \bar{u}), v \rangle v(\ell)
   \]

   (C.8)

   $=: G_{21} + G_{22} + G_{23}$.

   The term $G_{21}$ can be bounded by using the techniques in [10] Appendix C

   \[
   |G_{21}| \leq C \log R_{\text{MM}} \cdot R_{\text{QM}}^{-K+1/2} \cdot \|Dv\|^2_{l_2^h}.
   \]

   (C.9)
To estimate $G_{22}$, we have

$$
G_{22} = \sum_{\ell \in \Lambda_{\text{MM}}} \langle \delta \mathcal{F}_{\text{MM}}(0) - \delta \mathcal{F}_{h}(0), v \rangle v(\ell) + \sum_{j=1}^{K} \sum_{\ell \in \Lambda_{\text{MM}}} \frac{1}{j!} \langle \delta^{j+1} \mathcal{F}_{\text{MM}}(0) - \delta^{j+1} \mathcal{F}_{h}(0)(u_{h}(\cdot - \ell))^{j}, v \rangle v(\ell)
$$

(C.10)

$$
=: G_{22}^{(a)} + G_{22}^{(b)}.
$$

We first estimate $G_{22}^{(a)}$ by

$$
|G_{22}^{(a)}| \leq C \varepsilon_{1}^{F} \cdot N_{\text{MM}}^{1/2} \log R_{\text{MM}} \cdot \| Dv \|_{2}^{2}.
$$

From the above estimate, matching the force constant (i.e. $\varepsilon_{1}^{F}$ sufficiently small) will lead to the stability of force-mixing schemes [4, 10]. For $G_{22}^{(b)}$, using Lemma C.2 and the decay estimates for the equilibrium state (2.10), after a direct calculation, we have

(C.11) $$
|G_{22}^{(b)}| \leq C \sum_{j=1}^{K} \varepsilon_{j+1}^{F} \cdot R_{\text{QM}}^{-j} \cdot \varepsilon_{1}^{F} \cdot N_{\text{MM}}^{1/2} \log R_{\text{MM}} \cdot \| Dv \|_{2}^{2}.
$$

which depends on the measurements $\varepsilon_{j}^{F}(j \geq 2)$ and $R_{\text{QM}}$.

The term $G_{23}$ can be similarly estimated by

(C.12) $$
|G_{23}| \leq C \log R_{\text{MM}} \cdot (e^{-\eta R_{\text{BUF}}} + R_{\text{QM}}^{-K+1/2}) \cdot \| Dv \|_{2}^{2}.
$$

Combing from (C.5) to (C.12), for sufficiently large $R_{\text{QM}}$ and sufficiently small $\varepsilon_{1}^{F}$, we have

(C.13) $$
\langle \delta \mathcal{F}(T^{H}\bar{u}), v \rangle \geq \frac{c_{F}}{2} \| Dv \|_{2}^{2}.
$$

3. Consistency: For any $v \in \mathcal{A}_{H}$, we have

$$
\langle \mathcal{F}(T^{H}\bar{u}), v \rangle = \langle \mathcal{F}^{T}(T^{H}\bar{u}), v \rangle + \langle \mathcal{F}(T^{H}\bar{u}) - \mathcal{F}^{T}(T^{H}\bar{u}), v \rangle
$$

(C.14)

$$
=: P_{1} + P_{2}.
$$

The term $P_{1}$ can be estimated by using the results of [10, Theorem 5.1]

(C.15) $$
|P_{1}| \leq C \| Dv \|_{2}^{2} \left\{ \begin{array}{ll}
R_{\text{QM}}^{-(2K+1)d/2} \log R_{\text{MM}} + R_{\text{MM}}^{-d/2} + e^{-\kappa_{1} R_{\text{BUF}}} & \text{if (P)} \\
R_{\text{QM}}^{-K} \log R_{\text{MM}} + R_{\text{MM}}^{-1} \log R_{\text{MM}} + e^{-\kappa_{1} R_{\text{BUF}}} & \text{if (D)}
\end{array} \right. .
$$
We then split $P_2$ into three parts

$$
P_2 = \langle \mathcal{F}^H(T^H \tilde{u}) - \mathcal{F}^T(T^H \tilde{u}), v \rangle = \sum_{\ell \in \Lambda_{MM}} \left( \mathcal{F}^H(u_h(\cdot - \ell)) - T_K \mathcal{F}^H(u_h(\cdot - \ell)) \right) v(\ell)$$

$$+ \sum_{\ell \in \Lambda_{MM}} \left( T_K \mathcal{F}^h(u_h(\cdot - \ell)) - \mathcal{F}^h(u_h(\cdot - \ell)) \right) v(\ell)$$

$$+ \sum_{\ell \in \Lambda_{MM}} \left( \mathcal{F}^h(u_h(\cdot - \ell)) - \mathcal{F}^T(\mathcal{F}^h(T^H \tilde{u})) \right) v(\ell)$$

$$+ \sum_{\ell \in \Lambda_{MM}} \left( T_K \mathcal{F}^h(u_h(\cdot - \ell)) - T_K \mathcal{F}^h(u_h(\cdot - \ell)) \right) v(\ell)$$

$$= P_{21} + P_{22} + P_{23}. \tag{C.16}$$

After a direct calculation, the term $P_{21}$ can be estimated by

$$|P_{21}| \leq C\|Dv\|_{L_2^w} \begin{cases} R_{QM}^{-(2K+1)d/2} \log R_{MM} & \text{if (P)} \\ R_{QM}^{-K} \log R_{MM} & \text{if (D)} \end{cases} \tag{C.17}$$

For $P_{22}$, there exists a constant $\kappa_2 > 0$ such that

$$|P_{22}| \leq Ce^{-\kappa_2 R_{BUF}} \cdot \|Dv\|_{L_2^w}. \tag{C.18}$$

To estimate $P_{23}$, we split into two parts

$$P_{23} = \sum_{\ell \in \Lambda_{MM}} \left( T_K \mathcal{F}^h(u_h(\cdot - \ell)) - T_K \mathcal{F}^h(u_h(\cdot - \ell)) \right) v(\ell)$$

$$= \sum_{\ell \in \Lambda_{MM}} (\mathcal{F}^h(0) - \mathcal{F}^h(0)) v_h(\ell) + \sum_{j=1}^k \frac{1}{j!} \left( \delta^j \mathcal{F}^h(0) - \delta^j \mathcal{F}^h(0) \right) v_h(\ell)$$

$$= P_{23}^{(a)} + P_{23}^{(b)}. \tag{C.19}$$

The term $P_{23}^{(a)}$ vanishes since $\mathcal{F}^{MM}(0) \equiv \mathcal{F}^h(0)$. To estimate the second term in \((C.19)\), we first rewrite it as $P_{23}^{(b)} = \sum_{j=1}^K \sum_{\ell \in \Lambda_{MM}} \mathcal{F}_j(\ell) v(\ell)$ with

$$|\mathcal{F}_j(\ell)| \leq \sum_{\xi \in \Lambda^h} \left| \frac{\mathcal{F}^{MM}(0) - \mathcal{F}^h(0)}{\prod_{i=1}^j \mathcal{F}(\xi) \cdot u_h(\ell + \xi)} \right| \cdot \prod_{i=1}^j \left( \mathcal{F}(\xi) \cdot u_h(\ell + \xi) \right)$$

$$\leq C \varepsilon \cdot \left( \sum_{\xi \in \Lambda^h} \mathcal{F}(\xi) u_h^2(\ell + \xi) \right)^{j/2} \leq C \varepsilon \cdot |\ell|^{-\alpha_j} \tag{C.20}$$
where $\alpha_j = (d - 1)j$ for (P) or $\alpha_j = j$ for (D), and the last inequality follows from the decay estimates for the equilibrium state. Hence, using Lemma C.2, the term $P_{23}$ can be bounded by

\[
|P_{23}| \leq C\|Dv\|_{\ell_6^2} \begin{cases} 
\sum_{j=1}^{K} \varepsilon_j R_{QM}^{-(2j-1)d/2} \cdot \log R_{MM} & \text{if (P)} \\
\sum_{j=1}^{K} \varepsilon_j R_{QM}^{-(j-1)} \cdot \log R_{MM} & \text{if (D)}
\end{cases}
\]

(C.21)

Combining from (C.14) to (C.21) and let $\kappa := \max\{\kappa_1, \kappa_2\}$, we have

\[
|\langle \mathcal{F}^H(T^H\bar{u}), v \rangle | \leq C\|Dv\|_{\ell_6^2} \begin{cases} 
\left( \sum_{j=1}^{K} \varepsilon_j R_{QM}^{-(2j-1)d/2} + R_{QM}^{-(2K+1)d/2} \right) \log R_{MM} + R_{MM}^{d/2} + e^{-\kappa R_{BUF}} & \text{if (P)} \\
\left( \sum_{j=1}^{K} \varepsilon_j R_{QM}^{-(j-1)} + R_{QM}^{-K} \right) \log R_{MM} + R_{MM}^{-1} \log R_{MM} + e^{-\kappa R_{BUF}} & \text{if (D)}
\end{cases}
\]

(C.22)

Taking into account stability (C.13) and consistency (C.22), we can apply the inverse function theorem [32, Lemma 2.2] with $K = K_F$ and use (B.5) to obtain the stated results.

We then give the proof of Theorem 3.4, which is similar to that of Theorem 3.3. Due to adding the soft matching conditions for virials in Theorem 3.4, the only difference lies in the consistency part.

\textbf{Proof of Theorem 3.4.} The difference is the estimate of $P_{21}$ in (C.16). The new estimate of $P_{21}$ now becomes to

\[
P_{21} = \sum_{\ell \in \Lambda_{MM}} \left( \mathcal{F}^H(u_h(\cdot - \ell)) - T_K \mathcal{F}^H(u_h(\cdot - \ell)) \right) v(\ell) + \sum_{\ell \in \Lambda_{MM}} \left( T_K \mathcal{F}^h(u_h(\cdot - \ell)) - \mathcal{F}^h(u_h(\cdot - \ell)) \right) v(\ell)
\]

(C.23)

\[
= \sum_{\ell \in \Lambda_{MM}} \left( \tilde{\mathcal{F}}_1(u_h(\cdot - \ell)) + \tilde{\mathcal{F}}_2(u_h(\cdot - \ell)) \right) \cdot v(\ell),
\]

where $\tilde{\mathcal{F}}_1 := \mathcal{F}^H - T_{K+1} \mathcal{F}^H + T_{K+1} \mathcal{F}^h - \mathcal{F}^h$ and $\tilde{\mathcal{F}}_2 := T_{K+1} \mathcal{F}^H - T_K \mathcal{F}^H + T_K \mathcal{F}^h - T_{K+1} \mathcal{F}^h$. The first term can be similarly estimated

\[
\left| \sum_{\ell \in \Lambda_{MM}} \tilde{\mathcal{F}}_1(u_h(\cdot - \ell)) \cdot v(\ell) \right| \leq C\|Dv\|_{\ell_6^2} \begin{cases} 
R_{QM}^{-(2K+3)d/2} \log R_{MM} & \text{if (P)} \\
R_{QM}^{-(K+1)} \log R_{MM} & \text{if (D)}
\end{cases}
\]

(C.24)
We expand $\mathcal{H}_2$ further by using the Taylor’s expansion of the strain
\[
\mathcal{H}_2(u_h) = \sum_{(\rho, \sigma) \in (\Lambda^h)^{K+2}} (V^h_{\rho\sigma}(0) - V^\text{QM}_{\rho\sigma}(0)) \left( \prod_{i=1}^{K+1} (\nabla_{\sigma_i} u_h(\ell) + \sum_{t=2}^{\infty} \frac{1}{t!} \nabla_{\sigma_i}^t u_h(\ell)) - \prod_{i=1}^{K+1} (\nabla_{\sigma_i} u(\ell - \rho) + \sum_{t=2}^{\infty} \frac{1}{t!} \nabla_{\sigma_i}^t u(\ell - \rho)) \right)
\]
\[
(C.25) = (\partial_F^{K+2} W^h_{cb}(l) - \partial_F^{K+2} W^h_{cb}(l)) : (\nabla u(\ell))^K \nabla^2 u(\ell) + O(\nabla^2 (\nabla u(\ell))^{K+1}).
\]
Hence, for the second term of \(C.23\), using the decay estimates for the equilibrium state \(2.10\) and Lemma \(C.2\), we have
\[
(C.26) \left| \sum_{\ell \in \Lambda^\text{MM}} \mathcal{H}_2(u_h(\cdot - \ell)) \cdot v(\ell) \right| \leq C \|Dv\|_{\ell^2} \left\{ \begin{array}{ll}
\left( \varepsilon_{K+1} V^{(2K+1)d/2} + R_{\text{QM}}^{(2K+1)d/2-1} \right) \log R_{\text{MM}} & \text{if (P)} \\
\left( \varepsilon_{K+1} R_{\text{QM}}^{-K} + R_{\text{QM}}^{-K-1} \right) \log R_{\text{MM}} & \text{if (D)}
\end{array} \right.
\]
Taking into account the above proofs and the proofs of Theorem 3.3, we can yield the stated results.

\[\square\]

**Appendix D. A semi-empirical QM model: The NRL tight binding**

In this paper, we use the tight binding model as the quantum mechanical model for simplicity of presentation. We note that our numerical scheme is in principle also suitable for general quantum mechanical models.

The NRL tight binding model is developed by Cohen, Mehl, and Papaconstantopoulos [13]. The energy levels are determined by the generalised eigenvalue problem
\[
(D.1) \quad \mathcal{H}(y) \psi_s = \lambda_s \mathcal{M}(y) \psi_s \quad \text{with} \quad \psi_s^T \mathcal{M}(y) \psi_s = 1,
\]
where $\mathcal{H}$ is the hamiltonian matrix and $\mathcal{M}(y)$ is the overlap matrix. The NRL hamiltonian and overlap matrices are construct both from hopping elements as well as on-site matrix elements as a function of the local environment. For carbon and silicon they are parameterised as follows (for other elements the parameterisation is similar):

To define the on-site terms, each atom $\ell$ is assigned a pseudo-atomic density
\[
\rho_{\ell} := \sum_k e^{-\lambda^2 r_{\ell k}} f_c(r_{\ell k}),
\]
where the sum is over all of the atoms $k$ within the cutoff $R_c$ of atom $\ell$, $\lambda$ is a fitting parameter, $f_c$ is a cutoff function
\[
f_c(r) = \frac{\theta(R_c - r)}{1 + \exp \left( (r - R_c)/l_c + L_c \right)},
\]
with $\theta$ the step function, and the parameters $l_c = 0.5$, $L_c = 5.0$ for most elements. Although, in principle, the on-site terms should have off-diagonal elements, the NRL model follows traditional practice and only include the diagonal terms. Then, the on-site terms for each atomic site $\ell$ are given by
\[
(D.2) \quad \mathcal{H}(y)_{\ell\ell}^{u u} := a_u + b_u \rho_{\ell}^{2/3} + c_u \rho_{\ell}^{4/3} + d_u \rho_{\ell}^2,
\]
where \( v = s, p, \text{ or } d \) is the index for angular-momentum-dependent atomic orbitals and \((a_v), (b_v), (c_v), (d_v)\) are fitting parameters. The on-site elements for the overlap matrix are simply taken to be the identity matrix.

The off-diagonal NRL Hamiltonian entries follow the formalism of Slater and Koster who showed in [41] that all two-centre (spd) hopping integrals can be constructed from ten independent “bond integral” parameters \( h_{vv'\mu} \), where

\[
(vv') = ss\sigma, sp\sigma, pp\sigma, pp\pi, sd\sigma, pd\sigma, pd\pi, dd\sigma, dd\pi, \text{ and } d\delta.
\]

The NRL bond integrals are given by

\[
h_{vv'\mu}(r) := (e_{vv'\mu} + f_{vv'\mu}r + g_{vv'\mu}r^2) e^{-h_{vv'\mu}r} f_c(r)
\]

with fitting parameters \( e_{vv'\mu}, f_{vv'\mu}, g_{vv'\mu}, h_{vv'\mu} \). The matrix elements \( H(y)_{\ell k} \) are constructed from the \( h_{vv'\mu}(r) \) by a standard procedure [41].

The analogous bond integral parameterisation of the overlap matrix is given by

\[
m_{vv'\mu}(r) := (\delta_{vv'\mu} + p_{vv'\mu}r + q_{vv'\mu}r^2 + r_{vv'\mu}r^3) e^{-s_{vv'\mu}r} f_c(r)
\]

with the fitting parameters \((p_{vv'\mu}), (q_{vv'\mu}), (r_{vv'\mu}), (s_{vv'\mu})\) and \( \delta_{vv'\mu} \) the Kronecker delta function.

The fitting parameters in the foregoing expressions are determined by fitting to some high-symmetry first-principle calculations: In the NRL method, a database of eigenvalues (band structures) and total energies were constructed for several crystal structures at several volumes. Then the parameters are chosen such that the eigenvalues and energies in the database are reproduced. For practical simulations, the parameters for different elements can be found in [37].

**Appendix Appendix E. The ACE interatomic potential model**

In this paper, we use the tight binding model as the quantum mechanical model for simplicity of presentation. We note that our numerical scheme is in principle also suitable for general quantum mechanical models.

Following [1], we briefly introduce the construction of ACE potential. Given \( N \in \mathbb{N} \), we first write the ACE site potential in the form of an atomic body-order expansion, \( V^{\text{ACE}}(\{g_j\}) = \sum_{N=0}^{N} \frac{1}{N!} \sum_{j_1 \neq \cdots \neq j_N} V_N(g_{j_1}, \cdots, g_{j_N}) \), where the \( N \)-body potential \( V_N : \mathbb{R}^{dN} \rightarrow \mathbb{R} \) can be approximated by using a tensor product basis [1] Proposition 1]

\[
\phi_{k\ell m}(\{g_j\}_{j=1}^N) := \prod_{j=1}^N \phi_{k_j \ell_j m_j}(g_j) \quad \text{with} \quad \phi_{k\ell m}(r) := P_k(r) Y_{\ell}^m(\hat{r}), \; r \in \mathbb{R}^d, \; r = |r|, \; \hat{r} = r / |r|,
\]

where \( P_k, \; k = 0, 1, 2, \cdots \) are the radial basis functions (for example, the Jacobi polynomials), and \( Y_{\ell}^m, \; \ell = 0, 1, 2, \cdots, \; m = -\ell, \cdots, \ell \) are the standard complex spherical harmonics. The basis functions are further symmetrised to a permutation invariance form

\[
\bar{\phi}_N = \sum_{(k, \ell, m) \text{ ordered}} \sum_{\sigma \in S_N} \phi_{k\ell m} \circ \sigma,
\]

where \( S_N \) is the collection of all permutations, and by \( \sum_{(k, \ell, m) \text{ ordered}} \) it means the sum is over all ordered triples of tuples \((k, \ell, m)\). The next step is to incorporate the invariance under point
reflections and rotations

\[ B_{k\ell i} = \sum_{m \in M_{\ell}} U_{m}^{k} \sum_{\sigma \in S_{N}} \phi_{k \ell m} \circ \sigma \quad \text{with} \quad M_{\ell} = \{ \mu \in \mathbb{Z}^{N} \mid -\ell_{\alpha} \leq \mu_{\alpha} \leq \ell_{\alpha} \}, \]

where the coefficients \( U_{m}^{k} \) are given in [1, Lemma 2 and Eq. (3.12)]. It was shown in [1] that the basis defined above is explicit but computational inefficient. The so-called “density trick” technique used in [2, 16, 39] can transform this basis into one that is computational efficient. The alternative basis is

\[ B_{k\ell i} = \sum_{m \in M_{\ell}} U_{m}^{k} A_{n\ell m} \quad \text{with the correlation} \quad A_{n\ell m} := \prod_{\alpha=1}^{N} \sum_{j=1}^{J} \phi_{n_{\alpha} l_{\alpha} m_{\alpha}}(g_{j}), \]

which avoids both the \( N! \) cost for symmetrising the basis as well as the \( C_{J}^{N} \) cost of summation over all order \( N \) clusters within an atomic neighbourhood. The resulting basis set is then defined by

(E.1) \[ B_{N} := \{ B_{k\ell i} \mid (k, \ell) \in \mathbb{N}^{2N} \text{ ordered}, \sum_{\alpha} \ell_{\alpha} \text{ even, } i = 1, \cdots, n_{k\ell} \}, \]

where \( n_{k\ell} \) is the rank of body-orders (see [1, Proposition 7 and Eq. (3.12)]).

Once the finite symmetric polynomial basis set \( B \subset \bigcup_{N=1}^{N} B_{N} \) is constructed, then the ACE site potential can be expressed by

(E.2) \[ V^{\text{ACE}}(g; \{ c_{B} \}_{B \in B}) = \sum_{B \in B} c_{B} B_{k\ell i}(g) \]

with the coefficients \( c_{B} \). The corresponding force of this potential is denoted by \( F^{\text{ACE}} \).

The family of potentials are systematically improvable (see [1, §6.2]): by increasing the body-order, cutoff radius and polynomial degree they are in principle capable of representing an arbitrary many-body potential energy surface to within arbitrary accuracy.

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