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QM/MM METHODS FOR CRYSTALLINE DEFECTS. PART 1: LOCALITY OF THE TIGHT BINDING MODEL*

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Abstract. The tight binding model is a minimal electronic structure model for molecular modeling and simulation. We show that for a finite temperature model, the total energy in this model can be decomposed into site energies, that is, into contributions from each atomic site whose influence on their environment decays exponentially. This result lays the foundation for a rigorous analysis of QM/MM coupling schemes.

Key words. QM/MM coupling, crystalline defects, tight binding, strong locality

AMS subject classifications. 65N12, 65N25, 70C20, 81V45

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1. Introduction.

QM/MM coupling methods are a class of multiscale schemes in which a quantum mechanical (QM) simulation is "embedded" in a larger molecular mechanics (MM) simulation. Due to the high computational cost of QM models, schemes of this type have become an indispensable tool in many scientific disciplines [3, 22, 31, 38, 50, 58]. The present work is the first part in a series establishing the mathematical foundation of QM/MM schemes in the context of materials modeling.

It is pointed out in [21] that a minimal requirement for a QM model to be suitable for QM/MM coupling is the *strong locality* of forces,

$$\left|\frac{\partial f_n}{\partial y_m}\right| \to 0 \quad \text{"sufficiently rapidly" as } r_{nm} \to 0, \tag{1}$$

where $r_{nm} = |y_n - y_m|$ and f_n denotes the force acting on an atom at position y_n within a collection of nuclei at positions $\{y_\ell\} \subset \mathbb{R}^d$. The condition (1) is called *strong locality* to set it apart from the weaker condition of locality of the density matrix, which is already well understood (see, e.g., [2, 33] and section 1.2).

To study (1) we take a tight binding model at a finite electronic temperature (with an implicit screening assumption) as a model problem. We prove an even stronger condition than (1), *strong energy locality*: Given a finite collection of nuclei $y = \{y_\ell\}$, we decompose the total energy $E = E(y)$ into

$$E(y) = \sum_\ell E_\ell(y), \tag{2}$$

where the *site energies* $E_\ell(y)$ are *local* in the sense that

$$\left|\frac{\partial E_\ell(y)}{\partial y_n}\right| \lesssim e^{-\gamma r_{\ell n}}, \qquad \left|\frac{\partial^2 E_\ell(y)}{\partial y_n \partial y_m}\right| \lesssim e^{-\gamma(r_{\ell n} + r_{\ell m})} \tag{3}$$

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for some $\gamma > 0$, and analogous results for higher-order derivatives. While the specific form of the decomposition we employ (cf. section 2.3) is well known [28, 29], the locality result (3) is, to the best of our knowledge, new. We are aware of only one analogous result—for the Thomas–Fermi–von Weizsäcker (TFW) model [48].

This locality result has a range of consequences: (1) It provides a strong theoretical justification for the concept of an interatomic potential. (2) From a purely analytical point of view, there is little (if any) distinction between the tight binding model and interatomic potential models. This means that we can apply many of the analytical tools developed for interatomic potential models. For example, (3) we can rigorously formulate and analyze models of defects in infinite crystalline solids [27]. (4) We can extend the construction and analysis of atomistic/continuum multiscale schemes. In particular, the Cauchy–Born continuum limit analysis [51] can be directly applied without additional work.

(5) Our main motivation, however, is to formulate and analyze new QM/MM coupling schemes for crystal defects. In this endeavor we build on the successful theory of atomistic/continuum coupling [46], employing the tools and language of numerical analysis. The key idea is that, due to equations (2) and (3), the total energy can be approximated by

$$E(y) \approx \sum_{\ell \in \mathrm{QM}} E_\ell(y) + \sum_{\ell \in \mathrm{MM}} \tilde{E}_\ell(y),$$

where $\tilde{E}_\ell$ is *not an off-the-shelf site potential (Lennard-Jones, EAM, etc.)* as in previous works on QM/MM coupling, but instead is a *controlled approximation to* E_ℓ. We show in the companion paper [18] that this approach yields new QM/MM schemes (both energy-based and force-based) with rigorous rates of convergence in terms of the QM core region size.

1.1. Outline. In section 2 we focus on *finite systems*. We first present a thorough discussion of *real-space* tight binding models and then establish the results (2) and (3) in this context. In section 3 we then extend the definition of the site energy as well as the locality results to infinite systems (with an eye to crystal lattices) via a limiting procedure. In section 4 we briefly present two applications of the locality results in preparation for parts 2 and 3 of this series: We extend the crystal defect model and the convergence analysis for a truncation scheme from [27] to the tight binding model. Finally, in section 5, we present some preliminary numerical tests illustrating our analytical results.

1.2. Further remarks. Tight binding model. Tight binding models are minimalistic quantum mechanics type molecular models used to investigate and predict properties of molecules and materials in condensed phases. In terms of both accuracy and computational cost they are situated between accurate but computationally expensive ab initio methods and fast but limited empirical methods. While tight binding models are interesting in their own right, they also serve as a convenient toy model for more accurate electronic structure models such as (Kohn–Sham) density functional theory.

The study of defects in crystals is a field to which tight binding is well suited, as it is frequently the case that the deviations from ideal bonding are large enough that empirical potentials are not sufficiently accurate, but the system size required to isolate the defect (e.g., for dislocations or cracks) makes the use of ab initio calculations challenging. A number of studies have been carried out in which tight binding is applied to simulations of crystal defects; see, e.g., [40, 43, 49, 56].

Weak versus strong locality. By *weak locality* we mean that the electron density matrix has exponentially fast off-diagonal decay. In the context of tight binding, this means

$$\big[\Gamma(y)\big]_{mn} \lesssim e^{-\gamma r_{mn}} \tag{4}$$

(see (27) for the definition of the tight binding density matrix $\Gamma(y)$). In physics, this is often described by the term "nearsightedness" [39, 53], which states that the electron properties of insulators and metals at finite temperature do not depend on perturbations at distant regions. This property has, e.g., been exploited to create linear scaling electronic structure algorithms [1, 7, 33, 37]. Mathematical understanding of weak locality can be found in [2, 19].

However, the weak locality is not enough to validate a hybrid QM/MM approach [21]. We need the stronger locality condition (1) to guarantee that the QM region is not affected by the classical particles and moreover that the forces in the QM region can be computed to high accuracy by only considering a small QM neighborhood. The decay rate in (3) then gives a guide to how large the QM region needs to be (see also Theorem 17 and [18]).

Thermodynamic limit. Thermodynamic limit problems (infinite body limit), related to our analysis in section 3, have been studied at great length in the analysis literature. The monograph [15] gives an extensive account of the major contributions and also presents the thermodynamic limit problem for the Thomas–Fermi–von Weizsäcker (TFW) model for perfect crystals. The thermodynamic limit of the reduced Hartree–Fock (rHF) model is studied in [16] for perfect crystals. This literature also contains many results on the modeling of local defects in crystals in the framework of the TFW and rHF models; see, e.g., [6, 8, 9, 10, 11, 12, 42, 44].

These discussions are restricted to the case where the nuclei are fixed on a periodic lattice (or with a given local defect). Leaving the positions of the nuclei free is also a case of great physical and mathematical interest. Motivated by [27], we present such a model in section 4.1 but postpone a complete analysis to [17].

A related problem is the continuum limit of quantum models. The TFW and rHF models are studied in [5, 13], where it is shown that, in the continuum limit, the difference between the energies of the atomistic and continuum models obtained using the Cauchy–Born rule tends to zero. The tight binding and Kohn–Sham models are studied in a series of papers [23, 24, 25, 26] which establish the extension of the Cauchy–Born rule for smoothly deformed crystals. Our locality result yields an immediate extension of the analysis of the Cauchy–Born model in the MM case [51].

1.3. Notation. The symbol $\langle \cdot, \cdot \rangle$ denotes an abstract duality pairing between a Banach space and its dual. The symbol $|\cdot|$ normally denotes the Euclidean or Frobenius norm, while $\|\cdot\|$ denotes an operator norm. The constant C is a 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 system size, lattice position, or test functions. The dependencies of C will normally be clear from the context or stated explicitly.

1.4. List of assumptions. Our analysis requires a number of assumptions on the tight binding model or the underlying atomistic geometry. For the reader's convenience we list these with page references and brief summaries:

2. Tight binding model for finite systems. We begin by formulating a general non–self-consistent tight binding model for a finite system with N atoms. Let Λ_N be an index set with $\#\Lambda_N = N$. An atomic configuration is described by a map $y : \Lambda_N \to \mathbb{R}^d$ with $d \in \mathbb{N}$ denoting the space dimension. (We admit $d \neq 3$ mostly for the sake of mathematical generality; e.g., this allows us to formulate simplified in-plane or anti-plane models.)

We say that the map y is a *proper configuration* if the atoms do not accumulate:

L. $\exists\ \mathfrak{m} > 0$ such that $|y(\ell) - y(k)| \geq \mathfrak{m}\ \ \forall\ \ell, k \in \Lambda_N$ and $\ell \neq k$.

Let $\mathcal{V}_{\mathfrak{m}}^N \subset \left(\mathbb{R}^d\right)^{\Lambda_N}$ denote the subset of all $y \in (\mathbb{R}^d)^{\Lambda_N}$ satisfying **L**.

2.1. The Hamiltonian matrix. In the tight binding formalism one constructs a Hamiltonian matrix $\mathcal{H}$ in an "atomic-like basis set" $\{\phi_{\ell\alpha}(\mathbf{r} - y(\ell))\}_{\ell\in\Lambda_N,\alpha\in\Xi}$,

$$\Big(\mathcal{H}(y)\Big)_{\ell k}^{\alpha\beta} = \int_{\mathbb{R}^d} \phi_{\ell\alpha}(\mathbf{r} - y(\ell))\widehat{\mathcal{H}}(y)\phi_{k\beta}(\mathbf{r} - y(k))\ \mathrm{d}\mathbf{r}, \tag{5}$$

where Ξ is a small collection of the atomic orbitals per atom (with maximum size n_Ξ), and the integration on the right-hand side is usually replaced by an empirical function. The entries of the Hamiltonian matrix $\mathcal{H}$ depend on the atomic species, the atomic orbitals, and the configuration of nuclei. In practice, they are often described by empirical functions (*empirical tight binding*) which have been calibrated using experimental results or results from first principle calculations.

In either case, we can write the Hamiltonian matrix elements as

$$\Big(\mathcal{H}(y)\Big)_{\ell k}^{\alpha\beta} = h_{\ell k}^{\alpha\beta}(y), \tag{6}$$

where $h_{\ell k}^{\alpha\beta} : \mathcal{V}_{\mathfrak{m}}^N \to \mathbb{R}$ are functions depending on $\ell,\ k,\ \alpha$, and β.

The orbital indices α, β do not bring any additional insight into the problem we are studying, and they complicate the notation. Therefore, we ignore the indices α, β, which is equivalent to assuming that there is one atomic orbital for each atomic site (n_Ξ=1). The Hamiltonian matrix elements then simply become

$$\Big(\mathcal{H}(y)\Big)_{\ell k} = h_{\ell k}(y). \tag{7}$$

All our results can be generalized to cases with $n_\Xi > 1$ without difficulty. The only required modification is outlined in Appendix A.

We make the following standing assumptions on the functions $h_{\ell k}(y)$, which we justify below in Remark 1 and Examples 2, 3. Briefly, these assumptions are consistent with most tight binding models, with the only exception being that we assume that Coulomb interactions are screened.

H.tb. There exist positive constants $\bar{h}_0$ and γ_0 such that, for any $y \in \mathcal{V}_{\mathfrak{m}}^N$,

$$|h_{\ell k}(y)| \leq \bar{h}_0 e^{-\gamma_0|y(\ell)-y(k)|} \quad \forall\ \ell, k \in \Lambda_N. \tag{8}$$

H.loc. There exists $\mathfrak{n} \geq 4$ such that $h_{\ell k} \in C^{\mathfrak{n}}(\mathcal{V}_{\mathfrak{m}}^N)$. Moreover, there exist positive constants $\bar{h}_j$ and γ_j for $1 \leq j \leq \mathfrak{n}$ such that

$$\left| \frac{\partial^j h_{\ell k}(y)}{\partial [y(m_1)]_{i_1} \cdots \partial [y(m_j)]_{i_j}} \right| \leq \bar{h}_j e^{-\gamma_j \sum_{l=1}^{j} (|y(\ell) - y(m_l)| + |y(k) - y(m_l)|)} \quad \forall\, \ell, k \in \Lambda_N \tag{9}$$

with $m_1, \ldots, m_j \in \Lambda_N$ and $1 \leq i_1, \ldots, i_j \leq d$.

H.sym. **(i)** *(Isometry invariance)* If $y \in \mathcal{V}_{\mathfrak{m}}^N$ and $g : \mathbb{R}^d \to \mathbb{R}^d$ is an isometry, then

$$h_{\ell k}(y) = h_{\ell k}(g(y)) \quad \forall\, \ell, k \in \Lambda_N. \tag{10}$$

(ii) *(Permutation invariance)* If $y \in \mathcal{V}_{\mathfrak{m}}^N$ and $\mathcal{G} : \Lambda_N \to \Lambda_N$ is a permutation (relabeling) of Λ_N, then

$$h_{\ell k}(y) = h_{\mathcal{G}^{-1}(\ell)\mathcal{G}^{-1}(k)}(y \circ \mathcal{G}) \quad \forall\, \ell, k \in \Lambda_N. \tag{11}$$

Remark 1. (i) Condition (8) indicates that all the matrix elements are bounded by $\bar{h}_0$, which is independent of the system size. This is reasonable under the assumption **L** and that the number of atomic orbitals per atom in Ξ remains bounded as the number of atoms N increases.

(ii) The condition **H.tb** postulates exponential decay of the matrix elements with respect to the nuclei distance $|y(\ell) - y(k)|$. This is true in all tight binding models; as a matter of fact, most formulations employ a finite cut-off (zero matrix elements beyond a finite range of internuclear distance).

(iii) When $j = 1$ in **H.loc**, the condition (9) becomes

$$\left| \frac{\partial h_{\ell k}(y)}{\partial [y(m)]_i} \right| \leq \bar{h}_1 e^{-\gamma_1 (|y(\ell) - y(m)| + |y(k) - y(m)|)} \quad \forall\, \ell, k \in \Lambda_N \tag{12}$$

with $1 \leq i \leq d$. This states that there are no long-range interactions in the models, so that the dependence of the Hamiltonian matrix elements $h_{\ell k}(y)$ on site m decays exponentially fast to zero. This assumption is reasonable if one assumes that Coulomb interactions are screened.

(iv) In most tight binding models, the atomic orbitals are not orthogonal, which gives rise to an overlap matrix

$$\Big(\mathcal{M}(y)\Big)_{\ell\alpha k\beta} = \int_{\mathbb{R}^d} \phi_{\ell\alpha}(\mathbf{r} - y(\ell)) \phi_{k\beta}(\mathbf{r} - y(k)) d\mathbf{r}. \tag{13}$$

(In empirical tight binding models, $\mathcal{M}$ may again be given in functional form.)

On transforming the Hamiltonian matrix from a nonorthogonal to an orthogonal basis by taking the transformed Hamiltonian

$$\widetilde{\mathcal{H}} = \mathcal{M}^{-1/2} \mathcal{H} \mathcal{M}^{-1/2},$$

we obtain again the identity as an overlap matrix. Moreover, following the arguments in [2], it is easy to see that if $\mathcal{M}$ has an exponential decay property analogous to (8), then so does $\mathcal{M}^{-1/2}$. Thus, we see that the decay properties in **H.tb** and **H.loc** are not lost by this transformation, and we can, without loss of generality, ignore the overlap matrix.

(v) We have opted to work with an isolated system; however, it would be equally possible to employ periodic boundary conditions. In this case, tight binding models employ Bloch sums to take into account the periodic images; see, e.g., the Slater–Koster formalism [54]. Our entire analysis can be easily adapted to this case as well, and the resulting thermodynamic limit model would be identical to the one we obtain.

(vi) **H.sym (i)**, invariance of the Hamiltonian under isometries of deformed space, is true in the absence of an external (electric or magnetic) field; e.g., with $g(x) = x+c$, with some $c \in \mathbb{R}^d$, **(i)** implies translation invariance of the Hamiltonian. **H.sym (ii)** indicates that all atoms of the system belong to the same species so that the relabeling of the indices only gives rise to permutations of the rows and columns of the Hamiltonian.

The symmetry assumptions **H.sym** are natural and represent no restriction of generality. We require them to establish analogous symmetries in the site energies that we define in section 2.3. We remark, however, that **H.sym** must be modified for multiple atomic orbitals per site; see Appendix A.

Example 2. Many tight binding models use the "two-center approximation" [35], assuming that $h_{\ell k}(y)$ depends only on the vector between two atoms $y(\ell)$ and $y(k)$. If we only take into account the nearest neighbor interactions, then the Hamiltonian matrix elements of such models are given by

$$\Big(\mathcal{H}(y)\Big)_{\ell k} = \begin{cases} a_\ell & \text{if } \ell = k; \\ b_{\ell k}(y(\ell) - y(k)) & \text{if } y(\ell) \text{ is the nearest neighbor of } y(k); \\ 0 & \text{otherwise,} \end{cases} \tag{14}$$

where a_ℓ are constants and $b_{\ell k}$ are smooth functions. We observe that all our assumptions in **H.tb** and **H.loc** are trivially satisfied for this simple but common model.

Example 3. The Hamiltonian of an rHF model with the Yukawa potential [59] is

$$\widehat{\mathcal{H}}(y) = -\frac{1}{2}\Delta - \sum_{\ell \in \Lambda_N} Y_m(\cdot - y(\ell)) + \int_{\mathbb{R}^d} \rho(x) Y_m(\cdot - x) dx, \tag{15}$$

where ρ is assumed to be a fixed electron density, and Y_m is the Yukawa kernel with parameter $m > 0$:

$$Y_m(x) = \begin{cases} m^{-1} e^{-m|x|} & \text{if } d = 1; \\ \int_0^\infty e^{-m|x| \cosh t} dt & \text{if } d = 2; \\ |x|^{-1} e^{-m|x|} & \text{if } d = 3. \end{cases} \tag{16}$$

Note that both Y_m and its derivatives decay to 0 exponentially fast. If the basis functions $\{\phi_{\ell\alpha}\}_{\ell \in \Lambda_N, \alpha \in \Xi}$ are localized, i.e., the atomic orbitals for the ℓth atom have compact support around $y(\ell)$, or decay exponentially, then we have that the matrix elements generated by (5) satisfy the assumptions in **H.tb** and **H.loc**.

As a consequence of our assumptions, the following lemma states that the spectrum of the Hamiltonian is uniformly bounded with respect to the system size N.

LEMMA 4. *For any Λ_N satisfying* **L** *and* **H.tb**, *there exist constants $\underline{\sigma}$ and $\overline{\sigma}$ depending only on $\mathfrak{m}, \overline{h}_0, \gamma_0$, and d such that, for all $y \in \mathcal{V}_{\mathfrak{m}}^N$,*

$$\sigma(\mathcal{H}(y)) \subset [\underline{\sigma}, \overline{\sigma}]. \tag{17}$$

Proof. Let $\{\lambda_i\}_{1\le i\le N}$ be eigenvalues of $\mathcal{H}(y)$. Using (8) and the Geršgorin theorem [36], we have

$$|\lambda_i| \le \max_{\ell\in\Lambda_N}\left(|h_{\ell\ell}(y)| + \sum_{k\in\Lambda_N,\ k\neq\ell}|h_{\ell k}(y)|\right) \le \bar{h}_0 \max_{\ell\in\Lambda_N}\left(\sum_{k\in\Lambda_N} e^{-\gamma_0|y(\ell)-y(k)|}\right) \tag{18}$$

for any i. This together with the assumption **L** implies that

$$|\lambda_i| \le C\bar{h}_0\int_{\mathbb{R}^d} e^{-\gamma_0\mathfrak{m}|\mathbf{r}|}\,\mathrm{d}\mathbf{r} \le \frac{C_d\bar{h}_0}{(\mathfrak{m}\gamma_0)^d} \tag{19}$$

for any i, where C_d is a constant depending only on the dimension d. ∎

2.2. Band energy. The total energy of a configuration $y \in \mathcal{Y}^N_{\mathfrak{m}}$ is written as the sum of band energy and repulsive energy,

$$E^{\mathrm{tot}}(y) = E^{\mathrm{band}}(y) + E^{\mathrm{rep}}(y), \tag{20}$$

which we define as follows. For simplicity of notation, we will write $E = E^{\mathrm{band}}$ throughout this paper.

Given a deformation $y \in \mathcal{V}_{\mathfrak{m}}$, the associated Hamiltonian matrix $\mathcal{H}(y)$, and its eigenvalues ε_s and eigenvectors ψ_s, $s = 1,\dots,N$ (allowing for multiplicity, the dependence of ε_s and ψ_s on y is omitted for simplicity of notation),

$$\mathcal{H}(y)\psi_s = \varepsilon_s\psi_s, \quad s = 1,2,\dots,N, \tag{21}$$

the band energy of the system is defined by

$$E(y) = \sum_{s=1}^{N} f(\varepsilon_s)\varepsilon_s = \sum_{s=1}^{N} \mathfrak{f}(\varepsilon_s), \tag{22}$$

where f depends on the physical context. For example, at finite electronic temperature, f is the is Fermi–Dirac function

$$f(\varepsilon) = \left(1 + e^{(\varepsilon-\mu)/(k_{\mathrm{B}}T)}\right)^{-1}, \tag{23}$$

μ is a fixed chemical potential (more on that below), k_{B} is Boltzmann constant, and T is the temperature. In the zero-temperature limit, f becomes a step function. In practical simulation of conductors, f is often a smearing function (i.e., a numerical parameter) to ensure numerical stability (see, e.g., [30, 41, 47]).

In the present work, we shall not be too concerned about the origin of $\mathfrak{f}$ but simply accept it as a model parameter. Our analysis can be carried out whenever f is analytic (e.g., the Fermi–Dirac distribution) or, in insulators (systems with band gap at μ), also when f is a step function. For the sake of a unified presentation we shall present only the first case, but it will be immediately apparent how to treat insulators as well. Thus we shall assume the following for the remainder of the paper:

F. f is a configuration independent analytic function in an open neighborhood $D_f \subset \mathbb{C}$ of $[\underline{\sigma},\overline{\sigma}]$; cf. Lemma 4.

Remark 5. (i) The qualifier "configuration independent" in **F** essentially rephrases the assumption that the chemical potential μ is independent of the configuration y.

This is false in general but a reasonable assumption in our context since, in the next section, we shall consider limits of finite bodies in the form of lattices that are only locally distorted by defects. It is well known (though we are unaware of a rigorous proof) that the limiting potential μ is indeed configuration independent but is only a function of the far-field homogeneous lattice state.

(ii) We note, though, that there is a simple model in which the chemical potential is indeed independent of the configuration. Consider a single-species two-center approximation where $h_{\ell k}(y) = h(|y(\ell) - y(k)|)$ and $h_{\ell\ell}(y) \equiv a_0$. We define the chemical potential μ of this system such that $2\sum_{s=1}^{N} f(\varepsilon_s) = N$. Then it is easy to see that the spectrum is symmetric about a_0 and hence the chemical potential is always $\mu = a_0$.

(iii) In principle, one could perform a similar analysis for an insulating material. Here, an additional technical challenge arises in that one needs to ensure a uniform bound on the band gap with increasing system size. Thus, for the sake of simplicity, we focus on a finite temperature model instead.

The repulsive component of the energy is empirical and in most of the cases is simply described by a pair of potential interactions

$$E^{\rm rep}(y) = \frac{1}{2} \sum_{\ell,k\in\Lambda_N,\ \ell\neq k} U_{\ell k}\big(y(\ell) - y(k)\big), \tag{24}$$

where $U_{\ell k}$ is an empirical repulsive energy acting between atoms on $y(\ell)$ and $y(k)$. For future reference, we rewrite this in site energy form,

$$E^{\rm rep}(y) = \sum_{\ell\in\Lambda_N} E^{\rm rep}_\ell(y), \qquad E^{\rm rep}_\ell(y) = \frac{1}{2} \sum_{k\in\Lambda_N,\ k\neq\ell} U_{\ell k}\big(y(\ell) - y(k)\big), \tag{25}$$

and we shall assume the following throughout:

U. $U_{\ell k} \in C^{\mathfrak{n}}(\mathbb{R}^d \setminus B_{\mathfrak{m}})$, and there exist $c_U, \gamma_U > 0$ such that

$$|\nabla^j U_{\ell k}(\mathbf{r})| \le c_U \exp(-\gamma_U |\mathbf{r}|) \qquad \forall\ \ell, k \in \Lambda_N, \tag{26}$$

for $0 \le j \le \mathfrak{n}$.

In most of our analysis we shall only be concerned with the band energy E and have added $E^{\rm rep}$ mostly for the sake of completeness. The pair interaction in $E^{\rm rep}$ may be replaced with an arbitrary short-range interatomic potential.

2.2.1. Representation via contour integrals. Our analysis of the locality of interaction generated by the tight binding model builds on a representation of E in terms of contour integrals. The main issue is to represent the electronic density matrix as an operator-valued function of the Hamiltonian. This technique has been used in quantum chemistry in, for example, [24, 34] for tight binding and [14, 19, 25, 32, 45, 57] for density functional theory.

We begin by defining, for any proper configuration $y \in \mathcal{V}^N_{\mathfrak{m}}$, the electronic density matrix (or, simply, *density matrix*) of the system,

$$\Gamma(y) = \sum_s f(\varepsilon_s)|\psi_s\rangle\langle\psi_s| = f(\mathcal{H}(y)). \tag{27}$$

The band energy can then equivalently be written as

$$E(y) = \mathrm{Tr}\big(\mathcal{H}(y)\Gamma(y)\big) = \mathrm{Tr}\big(\mathcal{H}(y) f(\mathcal{H}(y))\big) = \mathrm{Tr}\big(\mathfrak{f}(\mathcal{H}(y))\big). \tag{28}$$

Lemma 4 and **F** imply that we can find a bounded contour $\mathscr{C} \subset D_f$, circling all the eigenvalues ε_s on the real axis (see Figure 1), and satisfying

$$\min\left\{\operatorname{dist}\big(\mathscr{C}, \sigma(\mathcal{H}(y))\big), \operatorname{dist}\big(\mathscr{C}, \mathfrak{s}(\mathfrak{f})\big)\right\} \geq \mathfrak{d}, \tag{29}$$

with nonanalytic region $\mathfrak{s}(\mathfrak{f})$ and a constant $\mathfrak{d} > 0$ that is independent of y or of N. Let

$$\mathscr{R}_z(y) := \big(\mathcal{H}(y) - zI\big)^{-1}$$

denote the resolvent of $\mathcal{H}(y)$; then

$$\mathfrak{f}(\mathcal{H}(y)) = -\frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \mathscr{R}_z(y)\, \mathrm{d}z, \tag{30}$$

which implies that

$$E(y) = -\frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \mathrm{Tr}\Big(\mathscr{R}_z(y)\Big)\, \mathrm{d}z. \tag{31}$$

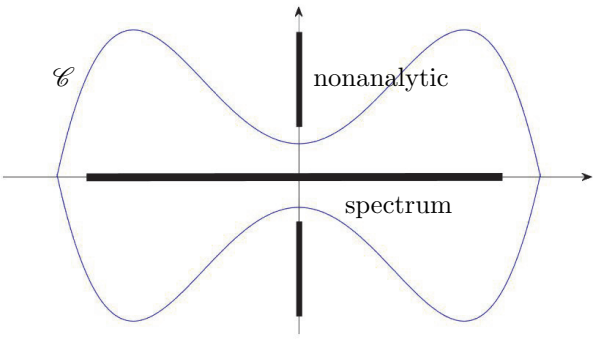

FIG. 1. *A schematic plot of the dumbbell-shaped Cauchy contour* $\mathscr{C}$.

It is already clear from (31) that the locality of the resolvents will play an important role in our analysis. Hence, we prove a decay estimate in the next lemma.

LEMMA 6. *Let* $\mathcal{H}(y), y \in \mathcal{V}_{\mathrm{m}}^N$, *be a tight binding Hamiltonian of the form* (7) *and* $\mathscr{C}$ *a contour satisfying* (29). *If* **L** *and* **H.tb** *are satisfied, then there exist constants* $\gamma_{\mathrm{r}} > 0$ *and* c_{r}, *independent of* y *or* N, *such that*

$$\Big(\mathscr{R}_z(y)\Big)_{\ell k} \leq c_{\mathrm{r}} e^{-\gamma_{\mathrm{r}}|y(\ell)-y(k)|} \quad \forall\ z \in \mathscr{C}. \tag{32}$$

Proof. This proof relies on the arguments provided by [24] and a Combes–Thomas type estimate [20]. For simplicity of notation, we will denote $\mathcal{H}(y)$ by $\mathcal{H}$ throughout this proof.

For k_0 and $\gamma_{\mathrm{r}} > 0$, let $B \in \mathbb{R}^{\Lambda_N \times \Lambda_N}$,

$$B_{\ell k} = \begin{cases} e^{\gamma_{\mathrm{r}}|y(\ell)-y(k_0)|} & \text{if } \ell = k; \\ 0 & \text{otherwise.} \end{cases} \tag{33}$$

From this definition, we have

$$\begin{aligned}\big[B\mathcal{H}B^{-1}-\mathcal{H}\big]_{\ell k} &= e^{\gamma_{\rm r}|y(\ell)-y(k_0)|}\mathcal{H}_{\ell k}e^{-\gamma_{\rm r}|y(k)-y(k_0)|}-\mathcal{H}_{\ell k}\\ &= \mathcal{H}_{\ell k}\big(e^{\gamma_{\rm r}(|y(\ell)-y(k_0)|-|y(k)-y(k_0)|)}-1\big).\end{aligned}$$

Assumptions **L** and **H.tb** yield

$$\begin{aligned}&\big\|B\mathcal{H}B^{-1}-\mathcal{H}\big\|_\infty \;\le\; \sup_{\ell\in\Lambda_N}\sum_{k\in\Lambda_N}|\mathcal{H}_{\ell k}|\Big(e^{\gamma_{\rm r}|y(\ell)-y(k)|}-1\Big)\\ &\le \bar{h}_0\sup_{\ell\in\Lambda_N}\left(\Big(\sum_{\substack{k\in\Lambda_N,\\ |y(\ell)-y(k)|>R}}e^{-(\gamma_0-\gamma_{\rm r})|y(\ell)-y(k)|}\Big)+\Big(\sum_{\substack{k\in\Lambda_N,\\ |y(\ell)-y(k)|\le R}}e^{-\gamma_0|y(\ell)-y(k)|}\Big)\big(e^{\gamma_{\rm r}R}-1\big)\right)\\ &\le C\Big(e^{-\frac{1}{2}(\gamma_0-\gamma_{\rm r})R}+e^{\gamma_{\rm r}R}-1\Big)\end{aligned}\tag{34}$$

for any $\gamma_{\rm r}<\gamma_0/2$ and $R>0$, where C is a constant depending only on $\bar{h}_0$, d, γ_0, $\gamma_{\rm r}$, and $\mathfrak{m}$. For any $\varepsilon>0$, we can choose R sufficiently large and then $\gamma_{\rm r}$ sufficiently small (depending on R) such that $\|B\mathcal{H}B^{-1}-\mathcal{H}\|_\infty<\varepsilon$. We note that the choice of R and $\gamma_{\rm r}$ does not depend on the system size N but only on ε and the constants $\bar{h}_0$, γ_0, $\mathfrak{m}$. Similarly, we have the same bound for $\|B\mathcal{H}B^{-1}-\mathcal{H}\|_1$. Using interpolation, we get the same bound for $\|B\mathcal{H}B^{-1}-\mathcal{H}\|_2$.

Note that

$$\begin{aligned}B(z-\mathcal{H})^{-1}B^{-1} &= (z-B\mathcal{H}B^{-1})^{-1}\\ &= (z-H)^{-1}(I-(B\mathcal{H}B^{-1}-\mathcal{H})(z-\mathcal{H})^{-1})^{-1}.\end{aligned}\tag{35}$$

Since (29) implies $\|(z-\mathcal{H})^{-1}\|_{\mathscr{L}(l^2)}\le 1/\mathfrak{d}$ for any $z\in\mathscr{C}$, we can choose R and $\gamma_{\rm r}$ such that $z-B\mathcal{H}B^{-1}$ is invertible and

$$\|B(z-\mathcal{H})^{-1}B^{-1}\|_{\mathscr{L}(l^2)}\le\frac{2}{\mathfrak{d}}.$$

Using $\big|[B(z-\mathcal{H})^{-1}B^{-1}]_{\ell k}\big|\le\|B(z-\mathcal{H})^{-1}B^{-1}\|_{\mathscr{L}(l^2)}\le 2/\mathfrak{d}$ and

$$\Big|\big[(z-\mathcal{H})^{-1}\big]_{\ell k}e^{\gamma_{\rm r}(|y(\ell)-y(k_0)|-|y(k)-y(k_0)|)}\Big|=\Big|\big[B(z-\mathcal{H})^{-1}B^{-1}\big]_{\ell k}\Big|\le\frac{2}{\mathfrak{d}},$$

consequently,

$$\big|\big[(z-\mathcal{H})^{-1}\big]_{\ell k}\big|\le\frac{2}{\mathfrak{d}}e^{-\gamma_{\rm r}(|y(\ell)-y(k_0)|-|y(k)-y(k_0)|)}.\tag{36}$$

Taking $k_0=k$, we obtain the stated exponential decay estimate. ∎

2.3. Site energy. Since the tight binding Hamiltonian (5) is given in terms of an atomic-like basis set, we can distribute the energy among atomic sites. This is a well-known idea which has been used for constructing interatomic potentials based on the bond-order concept (see, e.g., [28, 29, 55]).

Noting that $\|\psi_s\|_{\ell^2}=1$ for all s, we have

$$E(y)=\sum_{s=1}^N f(\varepsilon_s)\varepsilon_s=\sum_{s=1}^N f(\varepsilon_s)\varepsilon_s\sum_{\ell\in\Lambda_N}[\psi_s]_\ell^2=\sum_{\ell\in\Lambda_N}\sum_{s=1}^N f(\varepsilon_s)\varepsilon_s[\psi_s]_\ell^2.$$

That is, we have obtained the decomposition of the band energy

$$E(y) = \sum_{\ell \in \Lambda_N} E_\ell(y), \qquad \text{where} \tag{37}$$

$$E_\ell(y) = \sum_s f(\varepsilon_s)\varepsilon_s [\psi_s]_\ell^2 = \sum_s \mathfrak{f}(\varepsilon_s)[\psi_s]_\ell^2, \tag{38}$$

and we call $E_\ell(y)$ the site energy.

When the atomic orbitals are not orthogonal we slightly modify the definition of site energy for computational efficiency; see Appendix B for detailed discussions.

Such a decomposition is useful since, for example, classical interatomic potentials almost always decompose the total energy in such a way; hence the relation (37) can be used to establish a bridge between ab initio models and empirical interaction laws [28]. For our own purpose, the decomposition will (1) yield a relatively straightforward thermodynamic limit argument to define and analyze variational problems on the infinite lattice along the lines of [27], and (2) provide a starting point for the construction and analysis of concurrent multiscale scheme hybrid models, which we will pursue in the companion paper [18].

Our next aim is to establish locality of E_ℓ. We shall denote the partial derivatives of Hamiltonians by

$$\Big([\mathcal{H}_{,m}(y)]_i \Big)_{\ell k} = \frac{\partial h_{\ell k}(y)}{\partial [y(m)]_i} \quad \text{and} \quad \Big([\mathcal{H}_{,mn}(y)]_{ij} \Big)_{\ell k} = \frac{\partial^2 h_{\ell k}(y)}{\partial [y(m)]_i \partial [y(n)]_j}$$

with $1 \le i, j \le d$. From now on, for the sake of readability, we drop the argument (y) in $\mathscr{R}_z(y)$, $\mathcal{H}(y)$, $\mathcal{H}_{,m}(y)$, and $\mathcal{H}_{,mn}(y)$ whenever convenient and possible without confusion and in addition write $r_{mn} = |y(m) - y(n)|$. Let e_ℓ be the N dimensional canonical basis vector; then we obtain from (21) that

$$\begin{aligned} E_\ell(y) &= \sum_s \mathfrak{f}(\varepsilon_s) \, |[\psi_s]_\ell|^2 = \sum_s \mathfrak{f}(\varepsilon_s)(\psi_s, e_\ell)(\psi_s, e_\ell) = \sum_s \Big(\mathfrak{f}(\mathcal{H})\psi_s, e_\ell\Big)(\psi_s, e_\ell) \\ &= \sum_s (\psi_s, e_\ell)\Big(\psi_s, \mathfrak{f}(\mathcal{H})e_\ell\Big) = \Big(e_\ell, \mathfrak{f}(\mathcal{H})e_\ell\Big), \end{aligned}$$

and employing (30) we arrive at

$$E_\ell(y) = -\frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \big[\mathscr{R}_z\big]_{\ell\ell} \, \mathrm{d}z. \tag{39}$$

We can now calculate the first and second derivatives of $E_\ell(y)$ based on (39) and the regularity assumption in **H.loc**:

$$\frac{\partial E_\ell(y)}{\partial [y(m)]_i} = \frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \Big[\mathscr{R}_z \, [\mathcal{H}_{,m}]_i \, \mathscr{R}_z\Big]_{\ell\ell} \, \mathrm{d}z, \quad \text{and} \tag{40}$$

$$\begin{aligned} \frac{\partial^2 E_\ell(y)}{\partial [y(m)]_i \partial [y(n)]_j} = \frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \Big[& \mathscr{R}_z \big[\mathcal{H}_{,mn}\big]_{ij} \mathscr{R}_z - \mathscr{R}_z \, [\mathcal{H}_{,m}]_i \, \mathscr{R}_z \big[\mathcal{H}_{,n}\big]_j \mathscr{R}_z \\ & - \mathscr{R}_z \, [\mathcal{H}_{,n}]_j \, \mathscr{R}_z \big[\mathcal{H}_{,m}\big]_i \mathscr{R}_z \Big]_{\ell\ell} \, \mathrm{d}z. \end{aligned} \tag{41}$$

We also have higher-order derivatives of the site energy for $n \leq \mathfrak{n}$:

$$\frac{\partial^n E_\ell(y)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_n)]_{i_n}} = -\frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \Bigg[\sum_{l=1}^{n} \sum_{j_1+\cdots+j_l=n} \sum_{\mathcal{P}^{j_1,\cdots,j_l}_{m_1,\cdots,m_n}} (-1)^l \tag{42}$$

$$Q_z^{(l)}[y]\Big([\mathcal{H}_{,\mathcal{P}m_1\cdots\mathcal{P}m_{j_1}}(y)]_{\mathcal{P}i_1\cdots\mathcal{P}i_{j_1}}, \cdots, [\mathcal{H}_{,\mathcal{P}m_{n-j_l+1}\cdots\mathcal{P}m_n}(y)]_{\mathcal{P}i_{n-j_l+1}\cdots\mathcal{P}i_n} \Big) \Bigg]_{\ell\ell} \, \mathrm{d}z,$$

where $Q_z^{(n)} : \left(\mathbb{R}^{N\times N}\right)^n \mapsto \mathbb{R}^{N\times N}$:

$$Q_z^{(n)}[y](\Theta_1, \cdots, \Theta_n) = \mathscr{R}_z(y) \prod_{j=1}^{n} \Big(\Theta_j \mathscr{R}_z(y) \Big) \tag{43}$$

is a well-defined linear map for any z satisfying (29) and $\mathcal{P}^{j_1,\cdots,j_l}_{m_1,\cdots,m_n}$ is the multiset permutation of $m_1, \ldots, m_n$.

2.4. Properties of the site energy. In order for E_ℓ to be a "true" site energy it must satisfy certain properties: locality, permutation invariance, and isometry invariance. We establish these next.

First, we establish the locality of the site energy and its derivatives. We remark that in this result it is important that we are keeping μ fixed. Admitting y-dependent μ would introduce a small amount of nonlocality in the site energies, but it is reasonable to expect that this vanishes in the thermodynamic limit.

LEMMA 7 (locality). *If* **L**, **H.tb**, **H.loc**, *and* **F** *are satisfied, then, for* $1 \leq j \leq \mathfrak{n}$, *there exist positive constants* C_j *and* η_j *such that for any* $\ell \in \Lambda_N$,

$$\left| \frac{\partial^j E_\ell(y)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_j)]_{i_j}} \right| \leq C_j e^{-\eta_j \sum_{l=1}^{j} |y(\ell) - y(m_l)|}, \qquad 1 \leq i_1, \ldots, i_j \leq d. \tag{44}$$

Proof. We will only give the explicit proofs for $j = 1, 2$, the cases $j > 2$ being analogous (but tedious).

For $j = 1$, we have from Lemma 6 and the assumptions **L** and **H.loc** that

$$\begin{aligned}
\Big[\mathscr{R}_z \, [\mathcal{H}_{,m}]_i \, \mathscr{R}_z \Big]_{\ell\ell} &= \sum_{\ell_1,\ell_2 \in \Lambda_N} \big[\mathscr{R}_z\big]_{\ell\ell_1} \big([\mathcal{H}_{,m}]_i \big)_{\ell_1\ell_2} \big[\mathscr{R}_z\big]_{\ell_2\ell} \\
&\leq c_{\mathrm{r}}^2 \bar{h}_1 \sum_{\ell_1,\ell_2 \in \Lambda_N} e^{-\min\{\gamma_{\mathrm{r}},\gamma_1\}\left(r_{\ell\ell_1} + r_{\ell_1 m} + r_{m\ell_2} + r_{\ell_2\ell}\right)} \\
&= c_{\mathrm{r}}^2 \bar{h}_1 \Bigg(\sum_{\ell_1 \in \Lambda_N} e^{-\min\{\gamma_{\mathrm{r}},\gamma_1\}\left(r_{\ell\ell_1} + r_{\ell_1 m}\right)} \Bigg)^2 \\
&\leq C e^{-\min\{\gamma_{\mathrm{r}},\gamma_1\}|y(\ell)-y(m)|},
\end{aligned} \tag{45}$$

where C depends only on $\bar{h}_1, c_{\mathrm{r}}, \gamma_{\mathrm{r}}, \gamma_1, \mathfrak{m}$, and d. Together with (40) and **F**, this leads to

$$\frac{\partial E_\ell(y)}{\partial[y(m)]_i} \leq C_1 e^{-\eta_1 |y(\ell)-y(m)|} \quad \text{for } 1 \leq i \leq d. \tag{46}$$

For $j = 2$, we employ Lemma 6, **L**, and **H.loc** to estimate the three terms arising in the expression (41) of the site Hessian, using computations similar to those in (45):

$$\begin{aligned}
&\Big[\mathscr{R}_z\left[\mathcal{H}_{,m}\right]_i\mathscr{R}_z\left[\mathcal{H}_{,n}\right]_j\mathscr{R}_z\Big]_{\ell\ell}\\
&\qquad\le c_{\mathrm{r}}^3\bar{h}_1^2\sum_{\ell_1,\ell_2,\ell_3,\ell_4\in\Lambda_N} e^{-\min\{\gamma_{\mathrm{r}},\gamma_1\}\left(r_{\ell\ell_1}+r_{\ell_1 m}+r_{\ell_2 m}+r_{\ell_2\ell_3}+r_{\ell_3 n}+r_{\ell_4 n}+r_{\ell_4\ell}\right)}\\
&\qquad\le Ce^{-\frac{1}{2}\min\{\gamma_{\mathrm{r}},\gamma_1\}(|y(\ell)-y(m)|+|y(\ell)-y(n)|)};\\
&\Big[\mathscr{R}_z\left[\mathcal{H}_{,n}\right]_j\mathscr{R}_z\left[\mathcal{H}_{,m}\right]_i\mathscr{R}_z\Big]_{\ell\ell}\\
&\qquad\le Ce^{-\frac{1}{2}\min\{\gamma_{\mathrm{r}},\gamma_1\}(|y(\ell)-y(m)|+|y(\ell)-y(n)|)};\qquad\text{and}\\
&\Big[\mathscr{R}_z\left[\mathcal{H}_{,mn}\right]_{ij}\mathscr{R}_z\Big]_{\ell\ell}\\
&\qquad\le c_{\mathrm{r}}^2\bar{h}_2\sum_{\ell_1,\ell_2\in\Lambda_N} e^{-\min\{\gamma_{\mathrm{r}},\gamma_2\}(r_{\ell\ell_1}+r_{\ell_1 m}+r_{\ell_1 n}+r_{\ell_2 m}+r_{\ell_2 n}+r_{\ell_2\ell})}\\
&\qquad\le Ce^{-\frac{1}{2}\min\{\gamma_{\mathrm{r}},\gamma_2\}(|y(\ell)-y(m)|+|y(\ell)-y(n)|)}.
\end{aligned}$$

Inserting these three estimates into (41) together with **F** yields the desired result,

$$\frac{\partial^2 E_\ell(y)}{\partial[y(m)]_i\partial[y(n)]_j}\le C_2e^{-\eta_2\left(|y(\ell)-y(m)|+|y(\ell)-y(n)|\right)}\quad\text{for } 1\le i,j\le d.$$

∎

The next lemma summarizes the consequences of **H.sym**.

LEMMA 8 (symmetries). *Let $y\in\mathcal{V}_{\mathrm{m}}^N$. Assume that* **H.sym** *is satisfied.*

(i) (Isometry invariance) *If $g:\mathbb{R}^d\to\mathbb{R}^d$ is an isometry, then $E_\ell(y)=E_\ell(g(y))$.*

(ii) (Permutation invariance) *If $\mathcal{G}:\Lambda\to\Lambda$ is a permutation (relabeling) of Λ, then $E_\ell(y)=E_{\mathcal{G}^{-1}(\ell)}(y\circ\mathcal{G})$.*

Proof. (i) Let $y'=g(y)$. Since g is an isometry, we have that $y'\in\mathcal{V}_{\mathrm{m}}^N$. The assumption **H.sym (i)** implies $h_{mn}(y)=h_{mn}(y')$, which together with (39) yields

$$E_\ell(y)=-\frac{1}{2\pi i}\oint_{\mathscr{C}}\mathfrak{f}(z)\left[\mathscr{R}_z(y)\right]_{\ell\ell}\,\mathrm{d}z=-\frac{1}{2\pi i}\oint_{\mathscr{C}}\mathfrak{f}(z)\left[\mathscr{R}_z(y')\right]_{\ell\ell}\,\mathrm{d}z=E_\ell(y'). \tag{47}$$

(ii) Let $y'=y\circ\mathcal{G}$. The assumption **H.sym (ii)** implies $h_{mn}(y)=h_{\mathcal{G}^{-1}(m)\mathcal{G}^{-1}(n)}(y')$, which together with (39) leads to $E_\ell(y)=E_{\mathcal{G}^{-1}(\ell)}(y')$. ∎

3. Pointwise thermodynamic limit. Our aim in this section is to give a meaning to energy in the infinite body limit ("thermodynamic limit"). The notion of site energy makes this relatively straightforward: we will prove that fixing a site ℓ and "growing" the material around it to an infinite body yields a well-defined site energy functional E_ℓ for an infinite body. Total energy in an infinite body is of course ill defined, but using the site energies it then becomes straightforward to consider energy differences; cf. section 4.

We need the following additional assumption, connecting the Hamiltonians for growing index sets, in our analysis.

H.emb. Let $y^N:\Lambda_N\to\mathbb{R}^d$, $y:\Lambda_N\cup\{x'\}\to\mathbb{R}^d$ be two configurations satisfying **L**, and let $h_{\ell k}^N(y^N)$, $h_{\ell k}(y)$ be the corresponding Hamiltonian matrix elements of these two configurations satisfying **H.loc**. If $y^N(\ell)=y(\ell)$ for any $\ell\in\Lambda_N$, then for

$0 \le j \le \mathfrak{n} - 1$,

$$\frac{\partial^j h^N_{\ell k}(y^N)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_j)]_{i_j}} = \lim_{|y(x')|\to\infty} \frac{\partial^j h_{\ell k}(y)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_j)]_{i_j}} \quad \forall\ \ell, k \in \Lambda_N \tag{48}$$

with $m_1, \dots, m_j \in \Lambda_N$ and $1 \le i_1, \dots, i_j \le d$.

Remark 9. Intuitively, **H.emb** states that if one atom $y(x')$ in the system is moved to infinity, then the Hamiltonian matrix elements for the remaining subsystem $\{y(\ell) \mid \ell \in \Lambda_N\}$ no longer depend on $y(x')$.

At first glance, this appears to be a consequence of **H.tb** and **H.loc**. The reason we have to formulate it as a separate assumption is to make a connection between the Hamiltonians for Λ_N and $\Lambda_N \cup \{x'\}$. More generally, in Lemma 11, we obtain an analogous connection between the Hamiltonians for any two systems Λ_N, Λ_M with $\Lambda_N \subset \Lambda_M$.

Let Λ be a countable index set (or reference configuration); then we consider *deformed configurations* belonging to the class

$$\begin{aligned} \mathcal{V}_{\mathfrak{m}}(\Lambda) &:= \big\{ y : \Lambda \to \mathbb{R}^d,\ \ y|_{\Lambda_N} \subset \mathcal{V}^N_{\mathfrak{m}} \ \text{ for any finite } \Lambda_N \subset \Lambda \big\} \\ &= \big\{ y : \Lambda \to \mathbb{R}^d, |y(\ell) - y(k)| \ge \mathfrak{m}\ \forall\, \ell, k \in \Lambda \big\}. \end{aligned} \tag{49}$$

If $y \in \mathcal{V}_{\mathfrak{m}}(\Lambda)$, then **L** is satisfied for any finite subsystem $\Lambda_N \subset \Lambda$. In the following, whenever we assume **H.tb**, **H.loc**, and **H.emb** for infinite Λ, we mean that they are satisfied for the Hamiltonian matrices of any finite subsystem $\Lambda_N \subset \Lambda$.

For a bounded domain $\Omega \subset \mathbb{R}^d$, we shall denote the Hamiltonian, resolvent, and energy of the finite subsystem contained in Ω, respectively, by $\mathcal{H}^\Omega(y)$, $\mathscr{R}^\Omega_z(y)$, and $E^\Omega(y)$. For simplicity of notation, we drop the argument (y) whenever convenient.

THEOREM 10. *Let Λ be countable and $y \in \mathcal{V}_{\mathfrak{m}}(\Lambda)$ be a deformation. Suppose the assumptions* **F**, **H.tb**, **H.loc**, **H.emb**, *and* **H.sym** *are satisfied for all finite subsystems (with simultaneous choice of constants); then*

(i) (existence of the thermodynamic limits) *for any $\ell \in \Lambda$ and for any sequence of convex and bounded sets $\Omega_R \supset B_R(y(\ell))$, $R > 0$, the limit*

$$E_\ell(y) := \lim_{R\to\infty} E^{\Omega_R}_\ell(y) \tag{50}$$

exists and is independent of the choice of sets Ω_R;

(ii) (regularity and locality of the limits) *the limits $E_\ell(y)$ possess jth order partial derivatives with $1 \le j \le \mathfrak{n} - 1$, and it holds that*

$$\left| \frac{\partial^j E_\ell(y)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_j)]_{i_j}} \right| \le C_j e^{-\eta_j \sum_{l=1}^j |y(\ell) - y(m_l)|}, \tag{51}$$

$$1 \le i_1, \dots, i_j \le d,$$

where the constants C_j and η_j are the same as those in Lemma 7;

(iii) (isometry invariance) *if $g : \mathbb{R}^d \to \mathbb{R}^d$ is an isometry, then $E_\ell(y) = E_\ell(g(y))$;*

(iv) (permutation invariance) *if $\mathcal{G} : \Lambda \to \Lambda$ is a permutation (relabeling) of Λ, then $E_\ell(y) = E_{\mathcal{G}^{-1}(\ell)}(y \circ \mathcal{G})$.*

Before we prove Theorem 10 we establish an extension of **H.emb** which states that for two embedded systems, the difference between the two Hamiltonian matrix elements decays exponentially fast with respect to the distance to the interface.

LEMMA 11. *Let $\Lambda_M \supsetneq \Lambda_N$, $y^M : \Lambda_M \to \mathbb{R}^d$, and $y^N : \Lambda_N \to \mathbb{R}^d$ be two configurations satisfying* **L**. *Assume that there exists a convex set $\Omega \subset \mathbb{R}^d$ such that*

$$y^M(\ell) = y^N(\ell) \in \Omega \quad \forall\, \ell \in \Lambda_N \qquad \text{and} \qquad y^M(\ell) \in \Omega^{\rm c} \quad \forall\, \ell \in \Lambda_M \backslash \Lambda_N,$$

where $\Omega^{\rm c}$ is the complement of Ω in $\mathbb{R}^d$. If **F**, **H.loc, H.ext** *are satisfied, then, for $0 \le j \le \mathfrak{n} - 1$, there exist positive constants c_j, κ_j, which do not depend on M, N, and Ω, such that*

$$|h^M_{\ell k}(y^M) - h^N_{\ell k}(y^N)| \le c_0 \exp\Big(- \kappa_0 \Big(\operatorname{dist}\big(y^N(\ell), \Omega^{\rm c}\big) + \operatorname{dist}\big(y^N(k), \Omega^{\rm c}\big) \Big)\Big), \tag{52}$$

and

$$\begin{aligned} &\left| \frac{\partial^j h^M_{\ell k}(y^M)}{\partial [y(m_1)]_{i_1} \cdots \partial [y(m_j)]_{i_j}} - \frac{\partial^j h^N_{\ell k}(y^N)}{\partial [y(m_1)]_{i_1} \cdots \partial [y(m_j)]_{i_j}} \right| \\ &\qquad \le c_j \exp\Big(- \kappa_j \Big(\operatorname{dist}\big(y^N(\ell), \Omega^{\rm c}\big) + \operatorname{dist}\big(y^N(k), \Omega^{\rm c}\big) \\ &\qquad\qquad + \sum_{s=1}^{j} \big(|y^N(\ell) - y^N(m_s)| + |y^N(k) - y^N(m_s)| \big) \Big)\Big) \end{aligned} \tag{53}$$

for any $\ell, k, m_s \in \Lambda_N$ and $1 \le i_1, \ldots, i_j \le d$.

Proof. We first prove the case $j = 0$, i.e., (52). For each $\ell \in \Lambda_M \backslash \Lambda_N$, there exists a unique normalized vector ν_ℓ such that $y^M(\ell) - \nu_\ell \cdot \operatorname{dist}\big(y^M(\ell), \Omega\big) \in \overline{\Omega}$. Let $\{R^\mu_\ell\}_{\mu \in \mathbb{N}}$ be a sequence for each $\ell \in \Lambda_M \backslash \Lambda_N$, such that $R^\mu_\ell \to \infty$ as $\mu \to \infty$; then we define

$$\tilde{y}^\mu(\ell) := \begin{cases} y^N(\ell) & \text{if } \ell \in \Lambda_N; \\ y^M(\ell) + \nu_\ell \cdot R^\mu_\ell & \text{if } \ell \in \Lambda_M \backslash \Lambda_N. \end{cases}$$

Using **H.emb** with $j = 0$ and an elementary argument we can inductively choose R^μ_ℓ, such that $R^\mu := \min_{\ell \in \Lambda_M \backslash \Lambda_N} R^\mu_\ell \to \infty$ as $\mu \to \infty$ and

$$h^N_{\ell k}(y^N) = \lim_{\mu \to \infty} h^M_{\ell k}(\tilde{y}^\mu). \tag{54}$$

Let $n \in \Lambda_M \setminus \Lambda_N$, $\ell \in \Lambda_N$, and $c > 0$. Since Ω is convex, $(y^M(n) - y^M(\ell)) \cdot \nu_n \ge 0$, and therefore

$$|y^M(n) - y^M(\ell) + c\nu_n| \ge \Big(|y^M(n) - y^M(\ell)|^2 + c^2 \Big)^{1/2} \ge \frac{1}{\sqrt{2}} \big(|y^M(n) - y^M(\ell)| + c \big).$$

Using the assumptions **L** and **H.loc** with $j = 1$, we have that for $\ell, k \in \Lambda_N$

$$\begin{aligned} |h^M_{\ell k}(\tilde{y}^\mu) - h^M_{\ell k}(y^M)| \;&=\; \left| \int_0^1 \sum_{n \in \Lambda_M \backslash \Lambda_N} \frac{\partial h^M_{\ell k}}{\partial y(n)} \Big((1-t) y^M + t \tilde{y}^\mu \Big) \cdot \big(\tilde{y}^\mu(n) - y^M(n) \big) \, \mathrm{d}t \right| \\ &\le C \bar{h}_1 \int_0^1 \sum_{n \in \Lambda_M \backslash \Lambda_N} e^{-\gamma_1 \left(|y^M(\ell) - y^M(n) + t R^\mu \nu_n| + |y^M(k) - y^M(n) + t R^\mu \nu_n| \right)} \cdot R^\mu \, \mathrm{d}t \\ &\le C \bar{h}_1 \sum_{n \in \Lambda_M \backslash \Lambda_N} e^{-\frac{\gamma_1}{2} \left(|y^M(\ell) - y^M(n)| + |y^M(k) - y^M(n)| \right)} \cdot \int_0^1 e^{-\gamma_1 t R^\mu} R^\mu \, \mathrm{d}t \\ &\le c_0 e^{-\kappa_0 \left(\operatorname{dist}\left(y^N(\ell), \Omega^{\rm c}\right) + \operatorname{dist}\left(y^N(k), \Omega^{\rm c}\right) \right)} \cdot \big(1 - e^{-\gamma_1 R^\mu} \big), \end{aligned}$$

where $\kappa_0 = \gamma_1/2 - \varepsilon$ with any $\varepsilon \in (0, \gamma_1/2)$, and c_0 is a constant depending only on ε, $\bar{h}_1$, γ_1, $\mathfrak{m}$, and d. Note that neither κ_0 nor c_0 depends on the system sizes M, N, and Ω. Note that

$$\left|h^M_{\ell k}(y^M) - h^N_{\ell k}(y^N)\right| = \lim_{\mu\to\infty}\left|h^M_{\ell k}(y^M) - h^M_{\ell k}(\tilde{y}^\mu)\right| \le c_0 e^{-\kappa_0\left(\operatorname{dist}\left(y^N(\ell),\Omega^{\mathrm{c}}\right)+\operatorname{dist}\left(y^N(k),\Omega^{\mathrm{c}}\right)\right)},$$

which completes the proof of the case $j = 0$.

With the same arguments, we can prove (53) for $1 \le j \le \mathfrak{n} - 1$ by using the assumptions **H.loc** with index $j+1$ and **H.emb** with index j. ∎

Remark 12. The assumption that Ω is convex in Theorem 10 and Lemma 11 is only made for the sake of convenience. We use it to ensure that the integrand in the above proof satisfies assumption **L** on the paths along which we are integrating. One could generalize to a wider class of Ω by choosing the integral path more carefully.

Proof of Theorem 10. (i) Without loss of generality, we can assume that the upper bound of the spectrum $\overline{\sigma} < 0$ (one can always shift the eigenvalues if this is not satisfied) and the contour $\mathscr{C}$ is chosen such that it includes 0 and

$$\min\left\{\operatorname{dist}\left(\mathscr{C}, \sigma(\mathcal{H}(y))\right), \operatorname{dist}\left(\mathscr{C}, \mathfrak{s}(\mathfrak{f})\right), \operatorname{dist}\left(\mathscr{C}, \{0\}\right)\right\} \ge \mathfrak{d}. \tag{55}$$

Let $\ell \in \Lambda$ and $B_R(y(\ell)) \subset \Omega_R \subsetneq \Omega'$; then we define

$$\left[\widetilde{\mathcal{H}}^{\Omega_R}(y)\right]_{km} := \begin{cases} \left[\mathcal{H}^{\Omega_R}(y)\right]_{km} & \text{if } y(k), y(m) \in \Omega_R; \\ 0 & \text{otherwise for } y(k), y(m) \in \Omega'. \end{cases} \tag{56}$$

Note that (55) implies that the condition (29) is satisfied for the Hamiltonian $\widetilde{\mathcal{H}}^{\Omega_R}$ with the contour $\mathscr{C}$. Moreover, the resolvent $\widetilde{\mathscr{R}}^{\Omega_R}_z(y) = (\widetilde{\mathcal{H}}^{\Omega_R}(y) - zI)^{-1}$ is well defined for any $z \in \mathscr{C}$ and satisfies the estimate in (32). Under the assumption **F**, we can observe that the band energy and site energies of the Hamiltonian $\mathcal{H}^{\Omega_R}(y)$ and $\widetilde{\mathcal{H}}^{\Omega_R}(y)$ are the same.

We have from (39), (56), **L**, **H.tb**, and Lemmas 11 and 6 that

$$\begin{aligned} E^{\Omega'}_\ell(y) - E^{\Omega_R}_\ell(y) \;&=\; -\frac{1}{2\pi i}\oint_{\mathscr{C}} \mathfrak{f}(z)\left[\mathscr{R}^{\Omega'}_z - \widetilde{\mathscr{R}}^{\Omega_R}_z\right]_{\ell\ell}\mathrm{d}z \\ &\le C \sum_{y(\ell_1),y(\ell_2)\in\Omega'} \left[\mathscr{R}^{\Omega'}_z\right]_{\ell\ell_1}\left[\mathcal{H}^{\Omega'} - \widetilde{\mathcal{H}}^{\Omega_R}\right]_{\ell_1\ell_2}\left[\widetilde{\mathscr{R}}^{\Omega_R}_z\right]_{\ell_2\ell} \\ &\le C \sum_{y(\ell_1),y(\ell_2)\in\Omega'} e^{-\gamma_{\mathbf{r}} r_{\ell\ell_1}} e^{-\kappa_0\left(\operatorname{dist}\left(y(\ell_1),\Omega'\setminus\Omega_R\right)+\operatorname{dist}\left(y(\ell_2),\Omega'\setminus\Omega_R\right)\right)} e^{-\gamma_{\mathbf{r}} r_{\ell\ell_2}} \\ &\le C\left(\sum_{y(\ell_1)\in\Omega'} e^{-\gamma_{\mathbf{r}} r_{\ell\ell_1} - \kappa_0 \operatorname{dist}\left(y(\ell_1),\Omega'\setminus\Omega_R\right)}\right)^2 \;\le\; C e^{-\min\{\gamma_{\mathbf{r}},\kappa_0\}R}, \end{aligned} \tag{57}$$

where the last constant C depends only on $\bar{h}_0$, c_{r}, c_0, $\gamma_{\mathbf{r}}$, κ_0, $\mathfrak{m}$, and d but is independent of y or R. Since (57) holds for any $\Omega' \supsetneq B_R(y(\ell))$, it follows that $\{E^{\Omega_R}_\ell(y)\}_{R\in\mathbb{N}}$ is a Cauchy sequence. The uniqueness of the limit is also an immediate consequence of the fact that Ω' was arbitrary. This completes the proof of *(i)*.

(ii) *Case* $j = 1$. For $\ell, m \in \Lambda$, we take $R > 2|y(m) - y(\ell)|$ and then adopt the notation in the proof of *(i)*. With the expression of (40), we obtain by a direct

calculation that

$$\frac{\partial E_\ell^{\Omega'}(y)}{\partial [y(m)]_i} - \frac{\partial E_\ell^{\Omega_R}(y)}{\partial [y(m)]_i} = \frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \Bigg[\widetilde{\mathscr{R}}_z^{\Omega_R} \left(\widetilde{\mathcal{H}}^{\Omega_R} - \mathcal{H}^{\Omega'} \right) \mathscr{R}_z^{\Omega'} \left[\widetilde{\mathcal{H}}_{,m}^{\Omega_R} \right]_i \mathscr{R}_z^{\Omega'} + \widetilde{\mathscr{R}}_z^{\Omega_R} \left[\mathcal{H}_{,m}^{\Omega'} \right]_i \mathscr{R}_z^{\Omega'} \left(\widetilde{\mathcal{H}}^{\Omega_R} - \mathcal{H}^{\Omega'} \right) \widetilde{\mathscr{R}}_z^{\Omega_R} + \widetilde{\mathscr{R}}_z^{\Omega_R} \left(\left[\mathcal{H}_{,m}^{\Omega'} \right]_i - \left[\widetilde{\mathcal{H}}_{,m}^{\Omega_R} \right]_i \right) \widetilde{\mathscr{R}}_z^{\Omega_R} \Bigg]_{\ell\ell} \mathrm{d}z. \tag{58}$$

Using **L**, **H.tb**, and Lemmas 11 and 6, we can obtain from an argument similar to that in (57) that

$$\left| \frac{\partial E_\ell^{\Omega'}(y)}{\partial [y(m)]_i} - \frac{\partial E_\ell^{\Omega_R}(y)}{\partial [y(m)]_i} \right| \le C e^{-\min\{\gamma_{\mathbf{r}}, \kappa_0, \kappa_1\} \left(R + |y(\ell) - y(m)| \right)/2}, \tag{59}$$

where the constant C depends only on $\bar{h}_0, c_{\mathrm{r}}$, c_0, c_1, $\gamma_{\mathbf{r}}$, κ_0, κ_1, $\mathfrak{m}$, and d. Note that the estimate in (59) can be bounded by $Ce^{-\min\{\gamma_{\mathbf{r}}, \kappa_0, \kappa_1\} R/2}$, which does not depend on y. Therefore, we have that $\left\{ \partial E_\ell^R(y)/\partial [y(m)]_i \right\}_{R \in \mathbb{N}}$ converge uniformly to some limit, which together with *(i)* implies that $E_\ell(y)$ is differentiable with respect to $y(m)$ and the derivative is given by

$$\frac{\partial E_\ell(y)}{\partial [y(m)]_i} = \lim_{R \to \infty} \frac{\partial E_\ell^{B_R(y(\ell))}(y)}{\partial [y(m)]_i} \quad \text{for } 1 \le i \le d. \tag{60}$$

Case $j > 1$. For the second order derivatives, we can obtain from the expression (41) and a tedious calculation that

$$\begin{aligned} &\frac{\partial^2 E_\ell^{\Omega'}(y)}{\partial [y(m)]_i \partial [y(n)]_j} - \frac{\partial^2 E_\ell^{\Omega_R}(y)}{\partial [y(m)]_i \partial [y(n)]_j} \\ &= \frac{1}{2\pi i} \oint_{\mathscr{C}} \mathfrak{f}(z) \Bigg[\widetilde{\mathscr{R}}_z^{\Omega_R} \left(\mathcal{H}^{\Omega'} - \widetilde{\mathcal{H}}^{\Omega_R} \right) \mathscr{R}_z^{\Omega'} \left[\widetilde{\mathcal{H}}_{,m}^{\Omega_R} \right]_i \widetilde{\mathscr{R}}_z^{\Omega_R} \left[\mathcal{H}_{,n}^{\Omega'} \right]_j \widetilde{\mathscr{R}}_z^{\Omega_R} \\ &\quad + \mathscr{R}_z^{\Omega'} \left(\left[\widetilde{\mathcal{H}}_{,m}^{\Omega_R} \right]_i - \left[\mathcal{H}_{,m}^{\Omega'} \right]_i \right) \widetilde{\mathscr{R}}_z^{\Omega_R} \left[\widetilde{\mathcal{H}}_{,n}^{\Omega_R} \right]_j \mathscr{R}_z^{\Omega'} \\ &\quad + \widetilde{\mathscr{R}}_z^{\Omega_R} \left(\widetilde{\mathcal{H}}^{\Omega_R} - \mathcal{H}^{\Omega'} \right) \mathscr{R}_z^{\Omega'} \left[\widetilde{\mathcal{H}}_{,mn}^{\Omega_R} \right]_{ij} \mathscr{R}_z^{\Omega'} \\ &\quad + \widetilde{\mathscr{R}}_z^{\Omega_R} \left(\left[\mathcal{H}_{,mn}^{\Omega'} \right]_{ij} - \left[\widetilde{\mathcal{H}}_{,mn}^{\Omega_R} \right]_{ij} \right) \widetilde{\mathscr{R}}_z^{\Omega_R} + \cdots \Bigg]_{\ell\ell} \mathrm{d}z. \end{aligned}$$

For readability, we have omitted eight other terms in the square brackets, which have the same structure as the listed four terms. By estimating each term using the same arguments in (57), we can obtain

$$\left| \frac{\partial^2 E_\ell^{\Omega'}(y)}{\partial [y(m)]_i \partial [y(n)]_j} - \frac{\partial^2 E_\ell^{\Omega_R}(y)}{\partial [y(m)]_i \partial [y(n)]_j} \right| \le C e^{-\min\{\gamma_{\mathbf{r}}, \kappa_0, \kappa_1, \kappa_2\} \left(R + r_{\ell m} + r_{\ell n} \right)/4}, \tag{61}$$

which leads to the existence of $\partial^2 E_\ell(y)/\partial [y(m)]_i \partial [y(n)]_j$ and

$$\frac{\partial^2 E_\ell(y)}{\partial [y(m)]_i \partial [y(n)]_j} = \lim_{R \to \infty} \frac{\partial^2 E_\ell^{\Omega_R}(y)}{\partial [y(m)]_i \partial [y(n)]_j} \quad \text{for } 1 \le i, j \le d. \tag{62}$$

For $2 < j \leq \mathfrak{n} - 1$, we can obtain by similar arguments that

$$\frac{\partial^j E_\ell(y)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_j)]_{i_j}} = \lim_{R\to\infty} \frac{\partial^j E_\ell^{\Omega_R}(y)}{\partial[y(m_1)]_{i_1} \cdots \partial[y(m_j)]_{i_j}}, \quad 1 \leq i_1, \ldots, i_j \leq d, \tag{63}$$

for any sequence Ω_R satisfying the conditions of *(i)*.

The locality of E_ℓ in *(ii)* is now an immediate consequence of Lemma 7 and (60), (62), and (63).

(iii) Let $y' = g(y)$. Since g is an isometry, we have that $g\big(B_R(y(\ell))\big) = B_R(y'(\ell))$ for any $R > 0$. We can obtain from **H.sym (i)** and Lemma 8(i) that

$$E_\ell^{B_R(y(\ell))}(y) = E_\ell^{B_R(y'(\ell))}(y'). \tag{64}$$

Taking the limit $R \to \infty$ of (64) and *(i)* yield $E_\ell(y) = E_k(y')$.

(iv) This part of the proof is similar to the proof of (iii) and is a consequence of part (i) of the present result and Lemma 8(ii). ∎

Theorem 10 states the existence of the thermodynamic limits of the site energies, as well as the regularity, locality, and isometry/permutation invariance of the limits. In the following we shall always denote this limiting site energy by E_ℓ.

Remark 13. We have only considered the band energy of the system so far. The repulsive energy $E^{\rm rep}$ can be incorporated into our analysis without difficulty.

Using the expression (25) and the assumption **U**, it is easy to justify the thermodynamic limit of the repulsive site energy $E_\ell^{\rm rep}$, as well as its regularity and locality as those in Theorem 10. Moreover, the symmetry results in Theorem 10 are also clearly satisfied with the expression (25) for $E_\ell^{\rm rep}$. Therefore, all we have to do is to take the total site energy

$$E_\ell^{\rm tot} = E_\ell + E_\ell^{\rm rep}$$

and then use the existing results for E_ℓ. For convenience and readability, we still work with the site band energy E_ℓ and continue to ignore the repulsive component.

4. Applications.

4.1. Tight-binding model for point defects. As alluded to in the introduction, our primary aim in understanding the locality of the tight binding model is the construction and rigorous analysis of QM/MM hybrid schemes for crystalline defects, along the lines of [27]. The next step toward this end is a rigorous definition of a variational problem that is to be solved. Since we have shown in Theorem 10 that the total tight binding energy can be split into exponentially localized site energies, this is a relatively straightforward generalization of the analysis in [27], which considers MM site energies with bounded interaction radius.

Here, we only summarize the results, with an eye to the application we present in section 4.2. For simplicity we restrict ourselves to point defects only. Complete proofs and generalizations to general dislocation structures are given in [17].

We call an index set Λ a *point defect reference configuration* if

D. $\exists\ R_{\rm def} > 0, A \in {\rm SL}(d)$ such that $\Lambda \backslash B_{R_{\rm def}} = (A\mathbb{Z}^d) \backslash B_{R_{\rm def}}$ and $\Lambda \cap B_{R_{\rm def}}$ is finite.

While in previous sections we have worked with *deformations* y where $y(\ell)$ denotes the deformed position of an atom indexed by ℓ, it is now more convenient to work

with displacements $u : \Lambda \to \mathbb{R}^d$, $u(\ell) = y(\ell) - \ell$. For displacements u we define the *energy-difference functional*

$$\mathcal{E}(u) := \sum_{\ell \in \Lambda} \big[E_\ell(x+u) - E_\ell(x)\big], \tag{65}$$

where x denotes the identity map $x : \Lambda \to \mathbb{R}^d, x(\ell) = \ell$. Due to the exponential localization of E_ℓ, this series converges absolutely if u has compact support, i.e., for $u \in \dot{\mathscr{W}}^{\rm c}$ with

$$\dot{\mathscr{W}}^{\rm c} := \big\{u : \Lambda \to \mathbb{R}^d, \exists R > 0 \text{ s.t. } u = \text{const in } \Lambda \setminus B_R\big\};$$

cf. Theorem 14(i).

Next, still following [27], we extend the definition of $\mathcal{E}$ to a natural energy space. For $\ell \in \Lambda, \rho \in \Lambda - \ell := \{m - \ell, m \in \Lambda \setminus \{\ell\}\}$ we define $D_\rho u(\ell) := u(\ell + \rho) - u(\ell)$, and moreover,

$$Du(\ell) := \big(D_\rho u(\ell)\big)_{\rho \in \Lambda - \ell}.$$

We think of $Du(\ell) \in (\mathbb{R}^d)^{\Lambda - \ell}$ as an (infinite) finite-difference stencil. For any such stencil $Du(\ell)$ and $\gamma > 0$ we define the norm

$$\big|Du(\ell)\big|_\gamma := \Big(\sum_{\rho \in \Lambda - \ell} e^{-2\gamma|\rho|} \big|D_\rho u(\ell)\big|^2 \Big)^{1/2},$$

which gives rise to an associated seminorm on displacements,

$$\|Du\|_{\ell^2_\gamma} := \Big(\sum_{\ell \in \Lambda} |Du(\ell)|_\gamma^2 \Big)^{1/2}.$$

All (semi)norms $\|\cdot\|_{\ell^2_\gamma}, \gamma > 0$, are equivalent [17]. With these definitions we can now define the function space, which encodes the far-field boundary condition for displacements,

$$\dot{\mathscr{W}}^{1,2} := \big\{u : \Lambda \to \mathbb{R}^d, \|Du\|_{\ell^2_\gamma} < \infty\big\}.$$

We remark that $\dot{\mathscr{W}}^{\rm c}$ is dense in $\dot{\mathscr{W}}^{1,2}$ [17].

In addition to the far-field behavior imposed by the condition $u \in \dot{\mathscr{W}}^{1,2}$, we also require a variant of **L**, stating that atoms do not collide. Thus, our set of *admissible displacements* becomes

$$\mathrm{Adm}_{\mathfrak{m}} := \big\{u \in \dot{\mathscr{W}}^{1,2}, |\ell + u(\ell) - m - u(m)| > \mathfrak{m}|\ell - m| \ \forall\ \ell, m \in \Lambda\big\},$$

where $\mathfrak{m}$ is an arbitrary positive number. Again, we can observe that $\dot{\mathscr{W}}^{\rm c} \cap \mathrm{Adm}_{\mathfrak{m}}$ is dense in $\mathrm{Adm}_{\mathfrak{m}}$ [17]. We remark also that, due to the decay imposed by the condition $u \in \dot{\mathscr{W}}^{1,2}$, if $u \in \mathrm{Adm}_0$, then $u \in \mathrm{Adm}_{\mathfrak{m}}$ for some $\mathfrak{m} > 0$.

We can now state the main result concerning the energy-difference functional $\mathcal{E}$. The proof is an extension of [27, Lemma 2.1] and will be detailed in [17]. The main new ingredient in this extension, as well as in Theorem 15 below, is quantifying how rapidly the site energies approach those of a homogeneous crystal (without defect).

THEOREM 14. *Suppose that* **D** *is satisfied, as well as* **F**, **H.tb**, **H.loc**, **H.emb**, *and* **H.sym** *for all finite subsystems with simultaneous choice of constants.*

(i) $\mathcal{E} : \dot{\mathscr{W}}^{\rm c} \cap \mathrm{Adm}_0 \to \mathbb{R}$ *is well defined by* (65) *in the sense that the series converges absolutely.*

(ii) $\mathcal{E} : \dot{\mathscr{W}}^{\rm c} \cap \mathrm{Adm}_0 \to \mathbb{R}$ *is continuous with respect to the* $\|\cdot\|_{\ell^2_\gamma}$ *seminorm; hence, there exists a unique continuous extension to* Adm_0*, which we still denote by* $\mathcal{E}$*.*

(iii) $\mathcal{E} \in C^{\mathfrak{n}-1}(\mathrm{Adm}_0)$ *in the sense of Fréchet.*

In view of Theorem 14 the following variational problem is well defined:

$$\bar{u} \in \arg\min\big\{\mathcal{E}(u), u \in \mathrm{Adm}_0\big\}, \tag{66}$$

where "arg min" is understood in the sense of local minimality. We are not concerned with existence or uniqueness of minimizers but only their structure. This is discussed in the next result, which is an extension of [27, Theorem 2.3] (see [17] for the complete proof).

THEOREM 15. *Let* $\Upsilon > 0$*. Suppose that* **D** *is satisfied, as well as* **F**, **H.tb**, **H.loc**, **H.emb**, *and* **H.sym** *for all finite subsystems with simultaneous choice of constants. If* $\bar{u} \in \mathrm{Adm}_0$ *is a strongly stable solution to* (66)*, that is,*

$$\exists\, \bar{c} > 0 \text{ s.t. } \big\langle \delta^2\mathcal{E}(\bar{u})v, v\big\rangle \geq \bar{c}\|Dv\|^2_{\ell^2_\Upsilon} \qquad \forall v \in \dot{\mathscr{W}}^{\rm c}, \tag{67}$$

then there exists a constant $C > 0$ *such that* $\bar{u}$ *satisfies the decay*

$$|D\bar{u}(\ell)|_\Upsilon \leq C(1+|\ell|)^{-d} \qquad \forall \ell \in \Lambda. \tag{68}$$

Remark 16. (i) The constants $\bar{c}$ and C in Theorem 15 actually depend on the parameter Υ in the norm. Nevertheless, since all norms $\|\cdot\|_{\ell^2_\gamma}$ are equivalent, we hereafter ignore this dependence.

(ii) The condition (67) is stronger than actually required. Indeed, it suffices that $\bar{u}$ is a critical point and that strong stability is satisfied only in the far field; cf. [27, eq. (2.7)].

(iii) Higher-order decay estimates can be proven for higher-order gradients. For example, when $\mathfrak{n} \geq 5$, then $|D_{\rho_1}D_{\rho_2}\bar{u}(\ell)| \leq C|\ell|^{-d-1}$ for $|\ell|$ sufficiently large; see [27, 17] for more details. These estimates will be useful in our companion paper [18] for the construction of highly accurate MM potentials but are not required in the present work.

(iv) We emphasize that the rate of decay of the elastic field in (68) is generic and in particular independent of the decay of the interaction (in our case exponential).

4.2. Convergence of a numerical scheme. As a reference scheme to compare our QM/MM schemes against, and also as an elementary demonstration of the usefulness of the locality results and of the framework of section 4.1, we present an approximation error analysis for a basic truncation scheme.

To construct the scheme we first prescribe a radius $R > 0$ and restrict the set of admissible displacements to

$$\mathrm{Adm}_0(R) := \big\{u \in \mathrm{Adm}_0, u = 0 \text{ in } \Lambda \setminus B_R\big\}.$$

The pure Galerkin scheme $\bar{u}_R \in \arg\min\{\mathcal{E}(u), u \in \mathrm{Adm}_0(R)\}$ is analyzed in [27], and the convergence rate $\|D\bar{u} - D\bar{u}_R\|_{\ell^2_\gamma} \lesssim R^{-d/2}$ is proven.

In our case, the energy-difference $\mathcal{E}(u)$ is not computable for $u \in \mathrm{Adm}_0(R)$ due to the infinite interaction radius of the tight binding model. However, we can exploit the exponential localization to truncate it. To that end, we let $R^{\rm buf}$ be a buffer region

width (cf. Theorem 17 and Remark 18), $\Lambda_R := \Lambda \cap B_{R+R^{\rm buf}}$, and for any $v : \Lambda \to \mathbb{R}^d$ we define $v^R : \Lambda_R \to \mathbb{R}^d$ satisfying $v^R = v$ on Λ_R. Then, for $u \in {\rm Adm}_0$, we define the truncated energy-difference functional

$$\mathcal{E}_R(u) := E^{\Lambda_R}\big([x+u]^R\big) - E^{\Lambda_R}\big(x^R\big).$$

Clearly, $\mathcal{E}_R$ is well defined and $\mathcal{E}_R \in C^{\mathfrak{n}-1}({\rm Adm}_0)$ in the sense of Fréchet. To formulate the computational scheme, $\mathcal{E}_R$ need only be defined for $u \in {\rm Adm}_0(R)$, but for the analysis it will be convenient to define it for all $u \in {\rm Adm}_0$.

The computational scheme is now given by

$$\bar{u}_R \in \arg\min\big\{\mathcal{E}_R(u), u \in {\rm Adm}_0(R)\big\}. \tag{69}$$

THEOREM 17. *Let Υ be given in Theorem* 15*. Suppose that* **D** *is satisfied, as well as* **F**, **H.tb**, **H.loc**, **H.emb**, *and* **H.sym** *for all finite subsystems with simultaneous choice of constants.*

If $\bar{u}$ is a strongly stable solution to (66)*, then there are constants $C, R_0, c_{\rm buf}$ such that, for $R \ge R_0$ and $R^{\rm buf} \ge c_{\rm buf}\log(R)$, there exists a strongly stable solution $\bar{u}_R$ to* (69) *satisfying*

$$\big\|D\bar{u} - D\bar{u}_R\big\|_{\ell^2_\Upsilon} \le CR^{-d/2} \qquad \textit{and} \tag{70}$$

$$\big|\mathcal{E}(\bar{u}) - \mathcal{E}_R(\bar{u}_R)\big| \le CR^{-d}. \tag{71}$$

Proof. We closely follow the classical strategy of the analysis of finite element methods, which is detailed for a setting very close to ours in [27] in various approximation proofs.

1. *Quasi-best approximation.* Following [27, Lemma 7.3], we can construct $T_R\bar{u} \in {\rm Adm}_0(R)$ such that, for R sufficiently large,

$$\|DT_R\bar{u} - D\bar{u}\|_{\ell^2_\Upsilon} \le C\|D\bar{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R/2})} \le CR^{-d/2},$$

where Theorem 15 is used for the last inequality. We now fix some $r > 0$ such that $B_r(\bar{u}) \subset {\rm Adm}_{\mathfrak{m}}$ for some $\mathfrak{m} > 0$. Then, for R sufficiently large, we have that $T_R\bar{u} \in B_{r/2}(\bar{u})$ and hence $B_{r/2}(T_R\bar{u}) \subset {\rm Adm}_{\mathfrak{m}}$.

Since $\mathcal{E} \in C^3({\rm Adm}_0(R))$, $\delta\mathcal{E}$ and $\delta^2\mathcal{E}$ are Lipschitz continuous in $B_r(\bar{u}) \cap {\rm Adm}_0(R)$ with Lipschitz constants L_1 and L_2; that is,

$$\|\delta\mathcal{E}(\bar{u}) - \delta\mathcal{E}(T_R\bar{u})\| \le L_1\|D\bar{u} - DT_R(\bar{u})\|_{\ell^2_\Upsilon} \le CR^{-d/2} \qquad \text{and} \tag{72}$$

$$\|\delta^2\mathcal{E}(\bar{u}) - \delta^2\mathcal{E}(T_R\bar{u})\| \le L_2\|D\bar{u} - DT_R(\bar{u})\|_{\ell^2_\Upsilon} \le CR^{-d/2}. \tag{73}$$

2. *Stability.* Using (61) and the facts that $v = 0$ and $T_R\bar{u} = 0$ outside B_R, we have that there exists a constant $\gamma_{\rm s}$ such that

$$\big|\big\langle\big(\delta^2\mathcal{E}_R(T_R\bar{u}) - \delta^2\mathcal{E}(T_R\bar{u})\big)v, v\big\rangle\big| \le Ce^{-\gamma_{\rm s}R^{\rm buf}}R^d\|Dv\|^2_{\ell^2_\Upsilon}. \tag{74}$$

The proof of this identity is relatively straightforward but does require some details, which we present following the completion of the proof of the theorem. Together with (67) and (73) this leads to

$$\begin{aligned}
&\big\langle\delta^2\mathcal{E}_R(T_R\bar{u})v, v\big\rangle \\
&\quad = \big\langle\delta^2\mathcal{E}(\bar{u})v, v\big\rangle + \big\langle\big(\delta^2\mathcal{E}(T_R\bar{u}) - \delta^2\mathcal{E}(\bar{u})\big)v, v\big\rangle + \big\langle\big(\delta^2\mathcal{E}_R(T_R\bar{u}) - \delta^2\mathcal{E}(T_R\bar{u})\big)v, v\big\rangle \\
&\quad \ge \big(\bar{c} - C(R^{-d/2} + e^{-\gamma_{\rm s}R^{\rm buf}}R^d)\big)\|Dv\|^2_{\ell^2_\Upsilon} \ge \frac{\bar{c}}{2}\|Dv\|^2_{\ell^2_\Upsilon} \qquad \forall\, v \in {\rm Adm}_0(R),
\end{aligned} \tag{75}$$

for sufficiently large R and sufficiently large $c_{\rm buf}$.

3. *Consistency.* Similarly to (74), we can derive that there exists a constant $\gamma_{\rm c}$ such that

$$\big|\big\langle \delta\mathcal{E}_R(T_R\bar{u}) - \delta\mathcal{E}(T_R\bar{u}), v\big\rangle\big| \le Ce^{-\gamma_{\rm c}R^{\rm buf}} R^{d-1/2}\|Dv\|_{\ell^2_\Upsilon}. \tag{76}$$

We also present the detailed proof of (76) after the proof of this theorem.

In order to ensure the truncation of the electronic structure (the variational crime committed upon replacing $\mathcal{E}$ with $\mathcal{E}_R$) we must choose $R^{\rm buf}$ such that $e^{-\gamma_{\rm c}R^{\rm buf}} R^{d-1/2} \le CR^{-d/2}$, or equivalently, $e^{-\gamma_{\rm c}R^{\rm buf}} \le CR^{-(3d+1)/2}$. On taking logarithms, we observe that this is true provided that $R^{\rm buf} \ge c_{\rm buf}\log R$ for $c_{\rm buf}$ sufficiently large.

Next, employing (72), we obtain that

$$\begin{aligned}\big\langle \delta\mathcal{E}_R(T_R\bar{u}), v\big\rangle &= \big\langle \delta\mathcal{E}_R(T_R\bar{u}) - \delta\mathcal{E}(T_R\bar{u}), v\big\rangle + \big\langle \delta\mathcal{E}(T_R\bar{u}) - \delta\mathcal{E}(\bar{u}), v\big\rangle \\ &\le C\big(e^{-\gamma_{\rm c}R^{\rm buf}} R^{d-1} + R^{-d/2}\big)\|Dv\|_{\ell^2_\Upsilon} \le CR^{-d/2}\|Dv\|_{\ell^2_\Upsilon} \qquad \forall\, v \in \mathrm{Adm}_0(R),\end{aligned} \tag{77}$$

for sufficiently large R and appropriate $c_{\rm buf}$.

4. *Application of inverse function theorem.* With the stability (75) and consistency (77), the inverse function theorem [46, Lemma B.1] implies the existence of $\bar{u}_R$ and the estimate (70).

5. *Error in the energy.* For the estimate of the energy-difference functional, we have from $\mathcal{E} \in C^2(\mathrm{Adm}_0)$ that

$$\begin{aligned}\big|\mathcal{E}(\bar{u}_R) - \mathcal{E}(\bar{u})\big| &= \Big| \int_0^1 \big\langle \delta\mathcal{E}\big((1-s)\bar{u} + s\bar{u}_R\big), \bar{u}_R - \bar{u}\big\rangle \,\mathrm{d}s\Big| \\ &= \Big| \int_0^1 \big\langle \delta\mathcal{E}\big((1-s)\bar{u} + s\bar{u}_R\big) - \delta\mathcal{E}(\bar{u}), \bar{u}_R - \bar{u}\big\rangle \,\mathrm{d}s\Big| \le C\|D\bar{u}_R - D\bar{u}\|^2_{\ell^2_\Upsilon} \le CR^{-d}.\end{aligned} \tag{78}$$

Using (57) and $\bar{u}^R = 0$ in $\Lambda\backslash B_R$, there exists some constant $\gamma_{\rm e}$ such that

$$\begin{aligned}&|\mathcal{E}(\bar{u}_R) - \mathcal{E}_R(\bar{u}_R)| \\ &= \sum_{\ell\in\Lambda\cap B_{R+R^{\rm buf}/2}} \Big(E_\ell(x+\bar{u}^R) - E_\ell^{\Lambda_R}(x+\bar{u}^R) + E_\ell^{\Lambda_R}(x) - E_\ell(x)\Big) \\ &\quad + \sum_{\ell\in\Lambda\backslash B_{R+R^{\rm buf}/2}} \Big(E_\ell(x+\bar{u}^R) - E_\ell(x)\Big) + \sum_{\ell\in\Lambda_R\backslash B_{R+R^{\rm buf}/2}} \Big(E_\ell^{\Lambda_R}(x+\bar{u}^R) - E_\ell^{\Lambda_R}(x)\Big) \\ &\le C\left(\sum_{\ell\in\Lambda\cap B_{R+R^{\rm buf}/2}} e^{-\gamma_{\rm e}(R+R^{\rm buf}-|\ell|)} + \sum_{\ell\in\Lambda\backslash B_{R+R^{\rm buf}/2}} e^{-\gamma_{\rm e}(|\ell|-R)}\right)\end{aligned}$$

$$\le CR^{d-1}e^{-\gamma_{\rm e}R^{\rm buf}/2}. \tag{79}$$

Using (78) and (79) and possibly choosing a larger constant $c_{\rm buf}$, we obtain (71) for sufficiently large R. ∎

Proof of (74). Let $u := T_R\bar{u}$, $V_\ell^\Omega := V_\ell^\Omega(Du(\ell)) := E_\ell^\Omega(x+u) - E_\ell^\Omega(x)$, and

$V_\ell := V_\ell^\Lambda$. Using $u = 0$ in $\Lambda \setminus B_R$, we have

$$\begin{aligned}\big\langle \big(\delta^2\mathcal{E}_R(u) - \delta^2\mathcal{E}(u)\big)v, v\big\rangle \;&=\; \sum_{\ell\in\Lambda\cap B_R} \big\langle \big(\delta^2 V_\ell^{\Lambda_R} - \delta^2 V_\ell\big) Dv(\ell), Dv(\ell)\big\rangle \\ &\quad + \sum_{\ell\in\Lambda_R\setminus B_R} \big\langle \big(\delta^2 V_\ell^{\Lambda_R} - \delta^2 V_\ell\big) Dv(\ell), Dv(\ell)\big\rangle - \sum_{\ell\in\Lambda\setminus\Lambda_R} \big\langle (\delta^2 V_\ell) Dv(\ell), Dv(\ell)\big\rangle \\ &=: \mathrm{T}_1 + \mathrm{T}_2 + \mathrm{T}_3.\end{aligned}$$

It is obvious from (61) that, with $\gamma = \min\{\gamma_{\mathrm{r}}, \kappa_0, \kappa_1, \kappa_2\}/4$,

$$\begin{aligned}T_1 &\le C \sum_{\ell\in\Lambda\cap B_R} \sum_{\rho\in\Lambda-\ell} \sum_{\sigma\in\Lambda-\ell} e^{-\gamma(R+R^{\mathrm{buf}}-|\ell|+|\rho|+|\sigma|)} |D_\rho v(\ell)||D_\sigma v(\ell)| \\ &\le C e^{-\gamma R^{\mathrm{buf}}} \|Dv\|^2_{\ell^2_{\gamma/2}(\Lambda\cap B_R)} \le C_1 e^{-\gamma R^{\mathrm{buf}}} \|Dv\|^2_{\ell^2_\Upsilon(\Lambda\cap B_R)},\end{aligned}$$

where C_1 depends on C, γ, and Υ. Using $v = 0$ in $\Lambda \setminus B_R$, we have from (61) that

$$\begin{aligned}\mathrm{T}_2 &\le C \sum_{\ell\in\Lambda_R\setminus B_R} \sum_{\substack{\rho\in\Lambda-\ell \\ \ell+\rho\in B_R}} \sum_{\substack{\sigma\in\Lambda-\ell \\ \ell+\sigma\in B_R}} e^{-\gamma(R+R^{\mathrm{buf}}-|\ell|+|\rho|+|\sigma|)} |D_\rho v(\ell)||D_\sigma v(\ell)| \\ &\le C e^{-\gamma(R+R^{\mathrm{buf}})} \sum_{\ell\in\Lambda_R\setminus B_R} \left(\sum_{m\in\Lambda\cap B_R} \sum_{n\in\Lambda\cap B_R} e^{\gamma(2|\ell|-|\ell-m|-|\ell-n|)} \right)^{1/2} |Dv(\ell)|^2_{\gamma/2} \\ &\le C e^{-\gamma(R+R^{\mathrm{buf}})} \left(\sum_{m\in\Lambda\cap B_R} \sum_{n\in\Lambda\cap B_R} e^{\gamma(|m|+|n|)} \right)^{1/2} \|Dv\|^2_{\ell^2_{\gamma/2}(\ell\in\Lambda_R\setminus B_R)} \\ &\le C e^{-\gamma R^{\mathrm{buf}}} R^{d-1} \|Dv\|^2_{\ell^2_{\gamma/2}(\Lambda_R\setminus B_R)} \le C_1 e^{-\gamma R^{\mathrm{buf}}} R^{d-1} \|Dv\|^2_{\ell^2_\Upsilon(\Lambda_R\setminus B_R)}\end{aligned}$$

and from (51) that

$$\begin{aligned}\mathrm{T}_3 &\le C \sum_{\ell\in\Lambda\setminus\Lambda_R} \sum_{\substack{\rho\in\Lambda-\ell \\ \ell+\rho\in B_R}} \sum_{\substack{\sigma\in\Lambda-\ell \\ \ell+\sigma\in B_R}} e^{-\eta_2(|\rho|+|\sigma|)} |D_\rho v(\ell)||D_\sigma v(\ell)| \\ &\le C \sum_{\ell\in\Lambda\setminus\Lambda_R} \left(\sum_{m\in\Lambda\cap B_R} \sum_{n\in\Lambda\cap B_R} e^{-\eta_2(|\ell-m|+|\ell-n|)} \right)^{1/2} |Dv(\ell)|^2_{\eta_2/2} \\ &\le C \left(\sum_{m\in\Lambda\cap B_R} \sum_{n\in\Lambda\cap B_R} e^{-2\eta_2 R^{\mathrm{buf}}} \right)^{1/2} \|Dv\|^2_{\ell^2_{\eta_2/2}(\Lambda\setminus\Lambda_R)} \\ &\le C e^{-\eta_2 R^{\mathrm{buf}}} R^d \|Dv\|^2_{\ell^2_{\eta_2/2}(\Lambda\setminus\Lambda_R)} \le C_3 e^{-\eta_2 R^{\mathrm{buf}}} R^d \|Dv\|^2_{\ell^2_\Upsilon(\Lambda\setminus B_R)}.\end{aligned}$$

The estimates for T_1, T_2, and T_3 yield (74) with $\gamma_{\mathrm{s}} = \min\{\gamma, \eta_2\}$. ∎

Proof of (76). We continue to adopt the notation from the proof of (74). Using $u, v = 0$ in $\Lambda \setminus B_R$, we have

$$\begin{aligned}\big\langle \delta\mathcal{E}_R(u) - \delta\mathcal{E}(u), v\big\rangle &= \sum_{\ell\in\Lambda\cap B_R} \big\langle \delta V_\ell^{\Lambda_R} - \delta V_\ell, Dv(\ell)\big\rangle + \sum_{\ell\in\Lambda_R\setminus B_R} \big\langle \delta V_\ell^{\Lambda_R} - \delta V_\ell, Dv(\ell)\big\rangle \\ &\quad - \sum_{\ell\in\Lambda\setminus\Lambda_R} \big\langle \delta V_\ell, Dv(\ell)\big\rangle \\ &=: \mathrm{T}_1 + \mathrm{T}_2 + \mathrm{T}_3.\end{aligned}$$

From (59) it follows that, for $\ell \in \Lambda \cap B_R$, $|V^{\Lambda_R}_{\ell,\rho} - V_{\ell,\rho}| \le Ce^{-\gamma(R+R^{\mathrm{buf}}-|\ell|+|\rho|)}$ with $\gamma = \min\{\gamma_{\mathrm{r}}, \kappa_0, \kappa_1\}/2$, and hence,

$$\begin{aligned}
\mathrm{T}_1 &\le C \sum_{\ell\in\Lambda_R\setminus B_R} \sum_{\rho\in\Lambda-\ell} e^{-\gamma(R+R^{\mathrm{buf}}-|\ell|+|\rho|)}|D_\rho v(\ell)| \\
&\le C \sum_{\ell\in\Lambda\cap B_R} e^{-\gamma(R+R^{\mathrm{buf}}-|\ell|)}|Dv(\ell)|_{\gamma/2} \\
&\le C\Big(\sum_{\Lambda\cap B_R} e^{-2\gamma(R+R^{\mathrm{buf}}-|\ell|)}\Big)^{1/2} \|Dv\|_{\ell^2_{\gamma/2}(\ell\in\Lambda\cap B_R)} \\
&\le Ce^{-\gamma R^{\mathrm{buf}}} R^{(d-1)/2} \|Dv\|_{\ell^2_{\gamma/2}(\Lambda\cap B_R)}.
\end{aligned}$$

Similarly, using $v = 0$ in $\Lambda \setminus B_R$, we have from (59) that

$$\begin{aligned}
\mathrm{T}_2 &\le C \sum_{\ell\in\Lambda_R\setminus B_R} \sum_{\substack{\rho\in\Lambda-\ell \\ \ell+\rho\in B_R}} e^{-\gamma(R+R^{\mathrm{buf}}-|\ell|+|\rho|)}|D_\rho v(\ell)| \\
&\le Ce^{-\frac{\gamma}{2}(R+R^{\mathrm{buf}})}\Big(\sum_{\ell\in\Lambda_R\setminus B_R}\sum_{k\in B_R} e^{\gamma(|\ell|-|\ell-k|)}\Big)^{1/2}\Big(\sum_{\ell\in\Lambda_R\setminus B_R}\sum_{\substack{\rho\in\Lambda-\ell \\ \ell+\rho\in B_R}} e^{-\gamma|\rho|}|D_\rho v(\ell)|^2\Big)^{1/2} \\
&\le Ce^{-\frac{\gamma}{2}(R+R^{\mathrm{buf}})}\Big(\sum_{\ell\in\Lambda_R\setminus B_R}\sum_{k\in B_R} e^{\gamma|k|}\Big)^{1/2} \|Dv\|_{\ell^2_{\gamma/2}(\Lambda_R\setminus B_R)} \\
&\le Ce^{-\frac{\gamma}{2}R^{\mathrm{buf}}} R^{d-1}\big(R^{\mathrm{buf}}\big)^{1/2} \|Dv\|_{\ell^2_{\gamma/2}(\Lambda_R\setminus B_R)}.
\end{aligned}$$

Finally, from (51) we obtain

$$\begin{aligned}
\mathrm{T}_3 &\le C \sum_{\ell\in\Lambda\setminus\Lambda_R} \sum_{\substack{\rho\in\Lambda-\ell \\ \ell+\rho\in B_R}} e^{-\eta_1|\rho|}|D_\rho v(\ell)| \\
&\le C\Big(\sum_{\ell\in\Lambda\setminus\Lambda_R}\sum_{k\in B_R} e^{-\eta_1|\ell-k|}\Big)^{1/2}\Big(\sum_{\ell\in\Lambda\setminus\Lambda_R}\sum_{\substack{\rho\in\Lambda-\ell \\ \ell+\rho\in B_R}} e^{-\eta_1|\rho|}|D_\rho v(\ell)|^2\Big)^{1/2} \\
&\le C\Big(\sum_{k\in B_R}\sum_{\ell\in\Lambda\setminus\Lambda_R} e^{-\eta_1(|\ell|-R)}\Big)^{1/2} \|Dv\|_{\ell^2_{\eta_1/2}(\Lambda\setminus\Lambda_R)} \\
&\le Ce^{-\frac{\eta_1}{2}R^{\mathrm{buf}}} R^{d-1/2} \|Dv\|_{\ell^2_{\eta_1/2}(\Lambda\setminus\Lambda_R)}.
\end{aligned}$$

The estimates for T_1, T_2, and T_3 together yields (76) with $\gamma_{\mathrm{c}} = \min\{\gamma, \eta_1\}/2$. ∎

Remark 18. The choice of buffer width R^{buf} is the most interesting aspect of Theorem 17. As expected from the exponential localization results, we obtain that R^{buf} should be proportional to $\log(R)$. The fact that the constant of proportionality is important makes an implementation difficult. At least according to our proof, if we were to choose $R^{\mathrm{buf}} = c\log(R)$ with a small c, then we would obtain a reduced convergence rate.

Our numerical results in section 5.3 show no such dependence, which may indicate that our proof is in fact suboptimal; however, it is equally possible that this effect can only be observed for much larger system sizes than we are able to simulate.

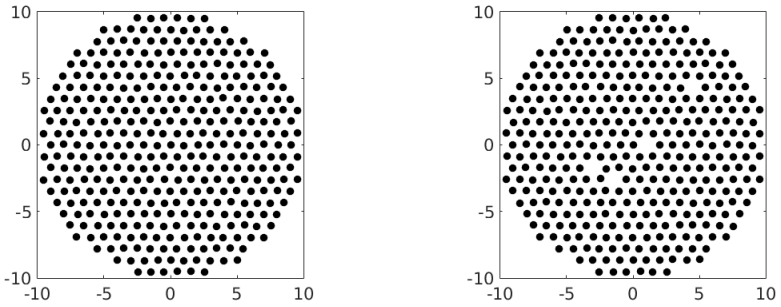

FIG. 2. *Two test configurations for the locality test in section* 5.2. *Left: Configuration* (1). *Right: Configuration* (2).

5. Numerical results. We present numerical experiments to illustrate the results of the paper: (1) the locality of the site energies and (2) the convergence of the truncation scheme described in section 4.2. Given that the present paper is primarily concerned with the analytical foundations, we will show only a limited set of results, employing a highly simplified toy model. We will present more comprehensive numerical results in the companion papers [18]. All numerical experiments were carried out in JULIA [4].

5.1. Toy model. The Hamiltonian matrix is given by

$$H_{\ell m}(y) = h(|y_\ell - y_m|) \quad \text{where} \quad h(r) = \big(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}\big) f_{\rm cut}(r),$$
$$\text{and} \quad f_{\rm cut}(r) = \begin{cases} \big(1 + e^{1/(r-r_{\rm cut})}\big)^{-1} & , r < r_{\rm cut}, \\ 0, & r \geq r_{\rm cut}, \end{cases}$$

with model parameters $\alpha = 2.0,\ r_0 = 1.0,\ r_{\rm cut} = 2.8$ and $k_{\rm B}T = 1.0,\ \mu = 0.0$. The pair potential term is set to be zero.

Numerical tests suggest that a triangular lattice $A_{\rm tri}\mathbb{Z}^d$ with

$$A_{\rm tri} = s \begin{pmatrix} 1 & 1/2 \\ 0 & \sqrt{3}/2 \end{pmatrix}$$

and s a scaling factor (close to 1.0) is a stable equilibrium in the sense of section 4.1.

We emphasize that this Hamiltonian does not describe any particular material. The two-dimensional setting and the single orbital per site simply make this a convenient setting for preliminary numerical tests.

5.2. Locality of the site energy. We construct two test configurations: (1) We "carve" a finite lattice domain $\Lambda_R = B_R \cap A_{\rm tri}\mathbb{Z}^d$ from the triangular lattice and perturb each position $y \in \Lambda_R$ by a vector with entries equidistributed in $[0, 0.1]$ to obtain y. (2) We obtain a second test configuration by removing some random lattice sites from Λ_R (vacancies) and perturb the remaining positions as in (1) to obtain y. We then compute the first and second site energy derivatives $E_{0,m}(y)$ and $E_{0,mn}(y)$ and plot them against, respectively, r_{0m} and $r_{0m} + r_{0n}$.

In the test shown in Figures 2 and 3, we chose $s = 1.0$ and $R = 10.0$, and the sites removed in (2) are $A_{\rm tri}(1, 0)$, $A_{\rm tri}(0, -3)$, $A_{\rm tri}(-2, 2)$, and $A_{\rm tri}(2, 5)$. We clearly observe the exponential decay predicted in Lemma 7.

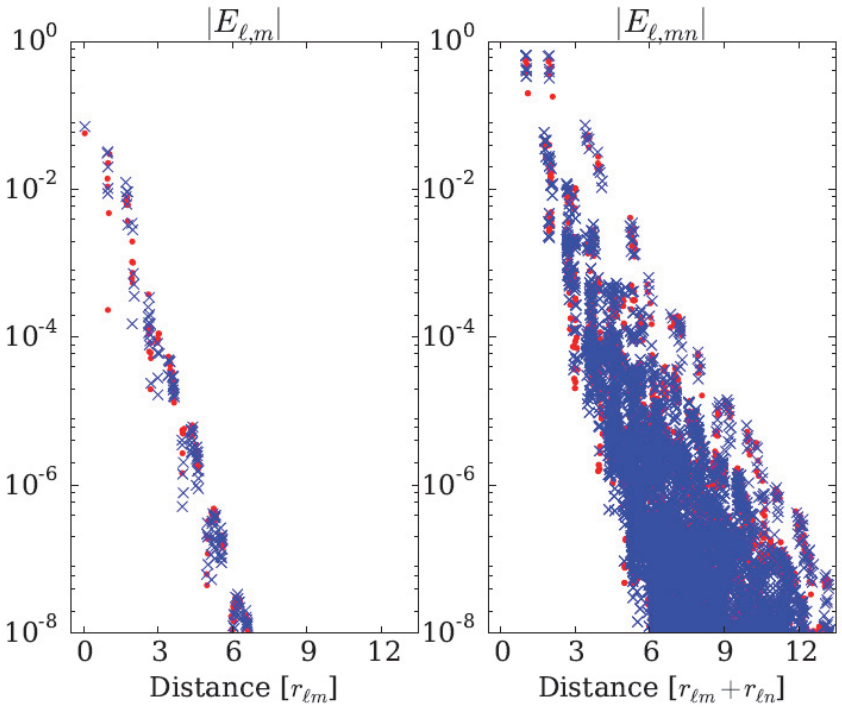

FIG. 3. *Locality of the site energy for the tight binding toy model described in section* 5.1. *Red dots denote configuration* (1)*, while blue crosses denote configuration* (2).

5.3. Convergence rate. In our second numerical experiment we confirm the prediction of Theorem 17. We adopt again the model from section 5.1. As reference configuration we choose a di-vacancy configuration,

$$\Lambda = A_{\rm tri}\mathbb{Z}^2 \setminus \big\{(0,0),(1,0)\big\}.$$

Then, for increasing radii R with associated buffer radii $R^{\rm buf}$,

(80)

	R	3	4	6	8	11
Set 1	$R^{\rm buf}$	2.1	2.4	2.8	3.0	3.4
Set 2	$R^{\rm buf}$	1.0	1.7	1.7	2.0	2.0
Set 3	$R^{\rm buf}$	1.0	1.0	1.7	1.7	2.0

we solve the problem (69). In Set 1 we have chosen $R^{\rm buf} = 1 + \log(R)$, while in Sets 2 and 3 we have chosen smaller buffer radii to investigate the effect of these choices on the error in the numerical solution.

The computed solutions $\bar{u}_R$ are compared against a high-accuracy solution with $R = 20, R^{\rm buf} = 11$, which yields the convergence graphs displayed in Figure 4, fully confirming the analytical prediction in Theorem 17. To measure errors, instead of $\|D\cdot\|_{\ell^2_\gamma}$, we employ the equivalent norm $\|D^{\rm nn}\cdot\|_{\ell^2}$ with $D^{\rm nn}u = (D_\rho u)_{\rho\in\pm A_{\rm tri}e_i, i=1,2}$.

We do not observe a pronounced buffer size effect. This could have a number of reasons, such as the fact that we are not far enough in the asymptotic regime or simply that the model we are employing is "too local" to observe this. We will present

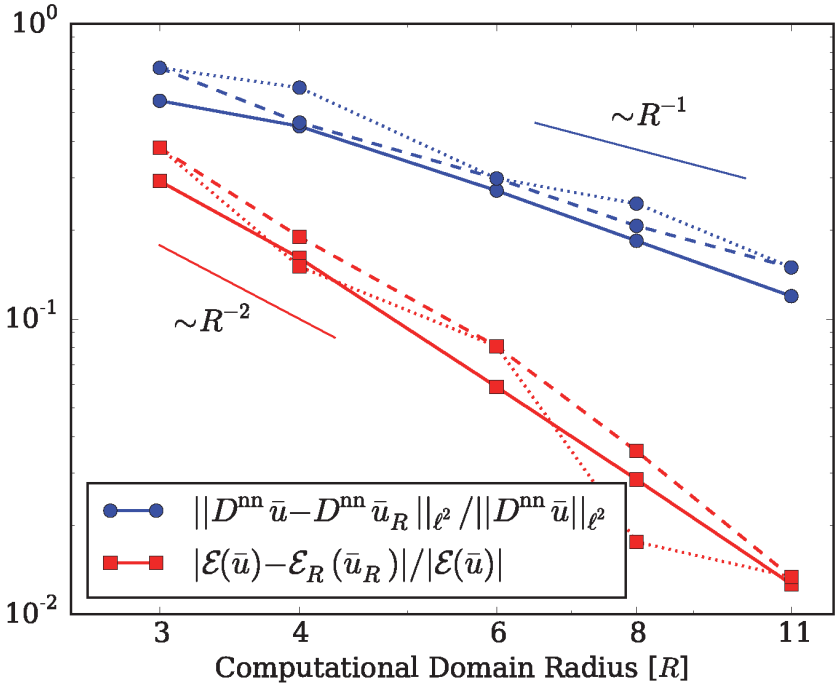

FIG. 4. *Convergence of* (69) *with increasing domain size* R*, as described in section* 5.3. *Set* 1: *Full lines. Set* 2: *Dashed lines. Set* 3: *Dotted lines.*

more extensive numerical results with a wider variety of tight binding models in Part 3 of this series.

6. Concluding remarks. The main purpose of this paper was to set the scene for a rigorous numerical analysis approach to QM/MM coupling. We have achieved this by developing a new class of locality results for the finite temperature tight binding model. Precisely, we have shown that the total band energy can be decomposed into contributions from individual sites in a meaningful, i.e., local, way.

This strong locality result is the basis for extending the theory of crystalline defects of [27], which we have hinted at in section 4.1, and carried out in detail in [17]. In a further forthcoming paper [18] we employ it to develop new QM/MM coupling schemes for crystalline defects as well as their rigorous analysis.

A key question that remains to be investigated is whether our locality results extend to more accurate electronic structure models such as Kohn–Sham density functional theory. Understanding this extension is critical to take the theory we are developing in the present paper and in [18] toward materials science applications. However, there are many technical issues arising from the nonlinearity, the continuous nature, and in particular the long-range Coulomb interaction.

Appendix A. Multiple orbitals per atom. We have assumed in section 2.1, and throughout this paper, that there is only one atomic orbital for each atom ($n_\Xi = 1$). In this case, the symmetry assumption **H.sym (i)** is natural. However, in practical calculations, there are multiple atomic-like orbitals $\phi_{\ell\alpha}$ associated with each atomic site ℓ. Here, α denotes both the orbital and angular quantum num-

bers of the atomic state. Many tight binding models employ one s-orbital $|s\rangle$, three p-orbitals $\{|x\rangle,\ |y\rangle,\ |z\rangle\}$, and five d-orbitals $\{|xy\rangle,\ |yz\rangle,\ |zx\rangle,\ |x^2-y^2\rangle,\ |3z^2-r^2\rangle\}$ per atom [29, 54]. Except for the s-orbital, all other orbitals have a spacial orientation, which means that the Hamiltonian matrix elements are *not* invariant under rotation/reflection. Therefore, **H.sym (i)** is invalid and must be reformulated.

We assume in the following that $n_\Xi > 1$ and $\{\phi_{\ell\alpha}\}_{1\le\alpha\le n_\Xi}$ is the set of atomic-like orbitals for the site ℓ. The Hamiltonian can be expressed by (5),

$$\Big(\mathcal{H}(y)\Big)_{\ell k}^{\alpha\beta} = \int_{\mathbb{R}^d} \phi_{\ell\alpha}(\mathbf{r}-y(\ell))\widehat{\mathcal{H}}(y)\phi_{k\beta}(\mathbf{r}-y(k))\ \mathrm{d}\mathbf{r}. \tag{81}$$

Applying an isometry g to y, we obtain

$$\Big(\mathcal{H}\big(g(y)\big)\Big)_{\ell k}^{\alpha\beta} = \int_{\mathbb{R}^d} \phi_{\ell\alpha}\big(\mathbf{r}-g(y(\ell))\big)\widehat{\mathcal{H}}\big(g(y)\big)\phi_{k\beta}\big(\mathbf{r}-g(y(k))\big)\ \mathrm{d}\mathbf{r}. \tag{82}$$

For simplicity of notation, we define

$$\psi_{\ell\alpha}(\mathbf{r}) = \phi_{\ell\alpha}\Big(g^{-1}(\mathbf{r})-y(\ell)\Big) \quad \text{and} \quad \varphi_{\ell\alpha}(\mathbf{r}) = \phi_{\ell\alpha}\Big(\mathbf{r}-g\big(y(\ell)\big)\Big).$$

We assume that the two sets of atomic orbitals $\{\psi_{\ell\alpha}\}_{1\le\alpha\le n_\Xi}$ and $\{\varphi_{\ell\alpha}\}_{1\le\alpha\le n_\Xi}$ span the same subspace. This is true for almost all tight binding models (see, e.g., [29, section 7.3.1]) since the set of the atomic orbitals always include all three p-orbitals (if the p-orbital is involved) and all five d-orbitals (if the d-orbital is involved). Then, there exists an orthogonal matrix $Q^\ell \in \mathbb{R}^{n_\Xi\times n_\Xi}$ such that $\varphi_{\ell\alpha} = \sum_{1\le\beta\le n_\Xi} Q^\ell_{\alpha\beta}\psi_{\ell\beta}$. We have from (82) that

$$\begin{aligned}\Big(\mathcal{H}\big(g(y)\big)\Big)_{\ell k}^{\alpha\beta} &= \int_{\mathbb{R}^d} \varphi_{\ell\alpha}(\mathbf{r})\widehat{\mathcal{H}}\big(g(y)\big)\varphi_{k\beta}(\mathbf{r})\ \mathrm{d}\mathbf{r}\\ &= \sum_{1\le\alpha',\beta'\le n_\Xi} Q^\ell_{\alpha\alpha'}Q^k_{\beta\beta'}\int_{\mathbb{R}^d} \psi_{\ell\alpha'}(\mathbf{r})\widehat{\mathcal{H}}\big(g(y)\big)\psi_{k\beta'}(\mathbf{r})\ \mathrm{d}\mathbf{r}.\end{aligned} \tag{83}$$

Since g is an isometry, it is natural to assume that

$$\Big(\mathcal{H}(y)\Big)_{\ell k}^{\alpha\beta} = \int_{\mathbb{R}^d} \psi_{\ell\alpha}(\mathbf{r})\widehat{\mathcal{H}}\big(g(y)\big)\psi_{k\beta}(\mathbf{r})\ \mathrm{d}\mathbf{r}. \tag{84}$$

Let $(\mathcal{H}(y))_{\ell k} := [(\mathcal{H}(y))_{\ell k}^{\alpha\beta}]_{1\le\alpha,\beta\le n_\Xi} \in \mathbb{R}^{n_\Xi\times n_\Xi}$ denote the local Hamiltonian; then we have from (83) and (84) that

$$\Big(\mathcal{H}\big(g(y)\big)\Big)_{\ell k} = Q^\ell\cdot\Big(\mathcal{H}(y)\Big)_{\ell k}\cdot\big(Q^k\big)^{\mathrm{T}}, \tag{85}$$

which yields

$$\mathcal{H}\big(g(y)\big) = Q\cdot\mathcal{H}(y)\cdot Q^{\mathrm{T}} \quad \text{with} \quad Q = \mathrm{diag}\left\{Q^1,\dots,Q^N\right\}, \tag{86}$$

where $\mathrm{diag}\{Q^1,\dots,Q^N\}$ denotes a block-diagonal matrix. Note that Q^ℓ are orthogonal matrices; hence Q is orthogonal as well. Therefore, the spectra of $\mathcal{H}(y)$ and $\mathcal{H}\big(g(y)\big)$ are equivalent:

$$\epsilon_s = \epsilon_s^g \qquad \text{for}\ \ 1\le s\le N\cdot n_\Xi. \tag{87}$$

Let

$$\Psi_s = \begin{pmatrix} \Psi_s^1 \\ \vdots \\ \Psi_s^N \end{pmatrix} \quad \text{with} \quad \Psi_s^\ell = \begin{pmatrix} \Psi_s^{\ell 1} \\ \vdots \\ \Psi_s^{\ell n_\Xi} \end{pmatrix} \qquad \text{for } \ 1 \le s \le N \cdot n_\Xi$$

be the eigenfunction of $\mathcal{H}(y)$ corresponding to the eigenvalue ϵ_s. Then the corresponding eigenfunction of $\mathcal{H}\big(g(y)\big)$ is

$$\Psi_s^g = Q\Psi_s = \begin{pmatrix} Q^1\Psi_s^1 \\ \vdots \\ Q^N\Psi_s^N \end{pmatrix}. \tag{88}$$

Next we note that, with multiple orbitals per atom, the expression (38) should be rewritten as

$$E_\ell(y) = \sum_s f(\varepsilon_s)\varepsilon_s \sum_\alpha \left(\Psi_s^{\ell\alpha}\right)^2 = \sum_s \mathfrak{f}(\varepsilon_s) \sum_\alpha \left(\Psi_s^{\ell\alpha}\right)^2. \tag{89}$$

Taking into account (87), (88), and (89), we obtain invariance of the site energy under isometries,

$$E_\ell(y) = E_\ell(g(y)). \tag{90}$$

To summarize, in the case of multiple orbitals, the assumption **H.sym (i)** should become

H.sym' (i). If $y \in \mathcal{V}_{\mathrm{m}}^N$ and $g : \mathbb{R}^d \to \mathbb{R}^d$ is an isometry on $\mathbb{R}^d$, then there exist orthogonal matrices $Q^\ell \in \mathbb{R}^{n_\Xi \times n_\Xi}$ for $\ell = 1, \dots, N$ such that (86) is satisfied. (This is equivalent to **H.sym (i)** when $n_\Xi = 1$.)

Remark 19. Slater and Koster worked out expressions such as (85) and (86) for all integrals between s-, p-, and d-orbitals and presented them in Table 1 of their paper [54]. This has been invaluable for practical calculations; see, e.g., [29, 52].

Remark 20. We stress again that all our assumptions and analysis in the present paper can be extended to the multiorbital case without any difficulty by taking the Hamiltonian as a block matrix with

$$h_{\ell k}(y) = \Big(\mathcal{H}(y)\Big)_{\ell k} \in \mathbb{R}^{n_\Xi \times n_\Xi} \tag{91}$$

and $|h_{\ell k}(y)|$ as the Frobenius norm of the submatrix.

Appendix B. Site energy with non-orthogonal orbitals. We consider the tight binding model with nonorthogonal atomic orbitals in this appendix. It has been shown in Remark 1 (iv) that the transformed Hamiltonian is

$$\widetilde{\mathcal{H}} = \mathcal{M}^{-1/2}\mathcal{H}\mathcal{M}^{-1/2}$$

when the overlap matrix is not an identity matrix. Then the transformed eigenvectors of $\mathcal{H}\psi_s = \varepsilon_s\psi_s$ become $\tilde{\psi}_s = \mathcal{M}^{1/2}\psi_s$, and following (37), the site energy is given by

$$E_\ell(y) = \sum_s f(\varepsilon_s)\varepsilon_s[\tilde{\psi}_s]_\ell^2 = \sum_s \mathfrak{f}(\varepsilon_s)[\mathcal{M}^{1/2}\psi_s]_\ell^2. \tag{92}$$

Since the square root of a matrix in (92) introduces additional computational cost for the site energy computations, we modify the definition of site energy in practice by

$$\widetilde{E}_\ell(y) = \sum_s \mathfrak{f}(\varepsilon_s)[\mathcal{M}\psi_s]_\ell[\psi_s]_\ell. \tag{93}$$

The following result states that the modified site energy (93) preserves the locality property.

LEMMA 21. *Assume that* **L**, **H.tb**, **H.loc**, *and* **F** *are satisfied, and moreover, the overlap matrix* $\mathcal{M}$ *satisfies the same conditions as those in* **H.tb**, **H.loc**.

Then, for $1 \le j \le \mathfrak{n}$, *there exist positive constants* $\tilde{C}_j$ *and* $\tilde{\eta}_j$ *such that for any* $\ell \in \Lambda_N$,

$$\left|\frac{\partial^j \widetilde{E}_\ell(y)}{\partial[y(m_1)]_{i_1}\cdots\partial[y(m_j)]_{i_j}}\right| \le \tilde{C}_j e^{-\tilde{\eta}_j \sum_{l=1}^j |y(\ell)-y(m_l)|}, \qquad 1 \le i_1,\dots,i_j \le d. \tag{94}$$

Proof. Let $\Xi = \mathfrak{f}(\widetilde{\mathcal{H}})$ (with $\Xi_{jk} = \sum_s \mathfrak{f}(\varepsilon_s)[\tilde{\psi}_s]_j[\tilde{\psi}_s]_k$). The assumptions on $\mathcal{H}$ and $\mathcal{M}$ imply that the transformed Hamiltonian $\widetilde{\mathcal{H}}$ also satisfies the conditions in **H.tb** and **H.loc**. Using Lemma 6 and arguments similar to those in the proof of Lemma 7, we have

$$|\Xi_{jk}| \le Ce^{-\gamma|y(j)-y(k)|} \quad \text{and} \quad \left|\frac{\partial \Xi_{jk}}{\partial[y(n)]_i}\right| \le Ce^{-\gamma(|y(n)-y(j)|+|y(n)-y(k)|)} \tag{95}$$

with some constants C and γ. Similarly, the assumptions on $\mathcal{M}$ also imply

$$\left|\mathcal{M}^{\pm 1/2}_{jk}\right| \le Ce^{-\gamma|y(j)-y(k)|} \quad \text{and} \quad \left|\frac{\partial \mathcal{M}^{\pm 1/2}_{jk}}{\partial[y(n)]_i}\right| \le Ce^{-\gamma(|y(n)-y(j)|+|y(n)-y(k)|)}. \tag{96}$$

We have from (92) and (93) that

$$\begin{aligned} E_\ell &= \sum_s \mathfrak{f}(\varepsilon_s) \sum_{jk} \mathcal{M}^{1/2}_{\ell j}\mathcal{M}^{1/2}_{\ell k}[\psi_s]_j[\psi_s]_k = \Xi_{\ell\ell}, \\ \widetilde{E}_\ell &= \sum_s \mathfrak{f}(\varepsilon_s) \sum_j \mathcal{M}_{\ell j}[\psi_s]_j[\psi_s]_\ell = [\mathcal{M}^{1/2}\Xi\mathcal{M}^{-1/2}]_{\ell\ell}. \end{aligned}$$

Therefore,

$$\frac{\partial \widetilde{E}_\ell}{\partial[y(n)]_i} = \sum_{jk}\left(\frac{\partial \mathcal{M}^{1/2}_{\ell j}}{\partial[y(n)]_i}\Xi_{jk}\mathcal{M}^{-1/2}_{k\ell} + \mathcal{M}^{1/2}_{\ell j}\frac{\partial \Xi_{jk}}{\partial[y(n)]_i}\mathcal{M}^{-1/2}_{k\ell} + \mathcal{M}^{1/2}_{\ell j}\Xi_{jk}\frac{\partial \mathcal{M}^{-1/2}_{k\ell}}{\partial[y(n)]_i}\right),$$

which together with (95), (96), and an argument similar to that in (45) completes the proof of (94) for $j = 1$.

The proofs for $2 \le j \le \mathfrak{n}$ are similar. ∎

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