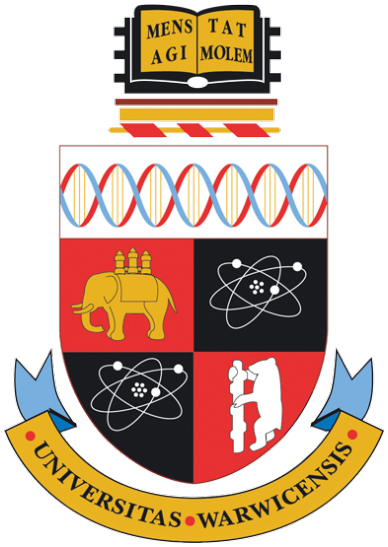
WARWICK
THE UNIVERSITY OF WARWICK



Analysis of an *ab initio* Potential Energy Landscape

by

Jack Thomas

Thesis

Submitted to the University of Warwick

for the degree of

Doctor of Philosophy

Mathematics Institute

September 2021

Contents

List of Figures

Acknowledgments

First and foremost, I would like to thank Christoph Ortner for his continued support, advice, and patience. His endless enthusiasm for Mathematics is contagious and his expert knowledge is inspiring. Each meeting left me motivated to work harder and learn more. I could not have hoped for a more supportive supervisor. I am also indebted to Huajie Chen for his hospitality when I visited Beijing. His generosity with his time and energy contributed to useful insights and led to a fruitful collaboration.

I have been extremely lucky to be a part of the MASDOC community and would like to thank the students and staff for providing a fantastic working environment for the past 4 years. Particular thanks must go "MASDOC house" (Chris, Dom, Hanson, Jacek, Jaro & Phil) for their lasting friendships.

I am grateful to Julian Braun, Andres Ross, Matthias Sachs, and Liwei Zhang for our regular discussions in group meetings over the past year or so. I must also thank various people that I met in the department and at events, conferences, and trips around the world. In particular, I would like to thank Eric Cancès, Gábor Csányi, Geneviève Dusson, Simon Etter, David Gontier, and Antoine Levitt.

Warwick,

September 2021

Declarations

Parts of this thesis have previously been published by the author in the following articles:

[98] Christoph Ortner, Jack Thomas, and Huajie Chen. Locality of interatomic forces in tight binding models for insulators. *ESAIM: Math. Model. Num. An., 54(6): 2295-2318 (2020).*

[95] Christoph Ortner and Jack Thomas. Point defects in tight binding models for insulators. *Math. Model. Methods Appl. Sci., 30(14): 2753-2797 (2020).*

[122] Jack Thomas. Locality of interatomic interactions in self-consistent tight binding models. *J. Nonlinear Sci., 30(6): 3293-3319 (2020).*

[123] Jack Thomas, Huajie Chen, and Christoph Ortner. Rigorous body-order approximations of an electronic structure potential energy landscape. [submitted] *arXiv e-prints, 2106.12572 (2021).*

I declare that to the best of my knowledge, the material contained in this thesis is original and my own work except where otherwise stated.

This thesis is submitted to the University of Warwick for the degree of Doctor of Philosophy and has not been submitted for a degree at any other university.

Abstract

A wide range of electronic, optical and magnetic properties of solids are determined by electronic structure. Computational methods, such as density functional theory, have been used successfully to model electronic structure and thus allowed the investigation and prediction of properties of materials. However, even now, the high computational cost of these *ab initio* methods severely limits their applicability in material modelling to thousands of atoms for static and hundreds of atoms for long-time dynamic simulations.

In modelling tasks involving only the mechanics of the atoms, one may bypass the electronic structure model entirely and replace it with a surrogate interatomic potential (IP), a functional form that may be fitted to theoretical data from a high fidelity *ab initio* model. The aim of this thesis is to provide a rigorous basis for IP models by justifying some of the underlying assumptions, in particular with an eye towards *physics-informed machine learning approaches*.

More specifically, we consider the tight binding model, a quantum mechanical model sharing many similarities with the more complex Kohn-Sham density functional theories, and prove that the potential energy landscape (PEL) can be decomposed into atom-centred site energy contributions depending only on atoms within a small cut-off radius of the central atom. Moreover, we obtain error estimates for body-ordered approximations, which allows one to reduce the dimensionality of the site energy contributions. In particular, we are able to decompose the PEL into low dimensional components which are easier to analyse, manipulate, and fit.

CHAPTER 1

Introduction

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

— P. Dirac, 1929 [37]

Many properties of materials observed at the macroscopic scale are ultimately driven by the quantum mechanical laws governing the behaviour of matter at the atomistic level. A drastic example of this phenomenon is the formation and evolution of defects in crystalline solids, a process involving the breaking and formation of chemical bonds and thus also on the quantum mechanical nature of the electrons, which has the potential to lead to catastrophic failure on a macroscopic scale, with serious consequences for engineering ap-

plications.

However, except in the very simplest of cases, the governing equations necessary for a complete description of these physical systems are far too computationally expensive to solve. Therefore, a hierarchy of approximate models must be considered where a reduction in computational complexity is obtained at the expense of accuracy and transferability. Depending on the application, one chooses an approximate model that is sufficiently rich to describe the physical phenomenon of interest, while remaining computationally tractable.

Figure 1.1 illustrates a ladder of approximations of the many-body problem, allowing for the simulation of larger system sizes and longer timescales but at the cost of accuracy. In the following sections, we describe the successive coarse-graining steps starting from Kohn–Sham density functional theory (DFT), which is itself already an approximation to the underlying quantum mechanical many-body problem, to interatomic potentials.

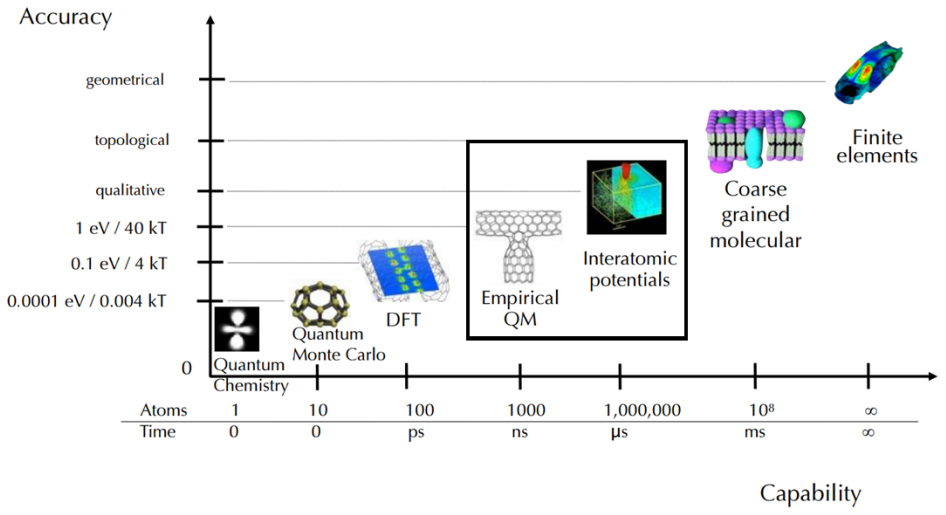


Figure 1.1: Schematic representation depicting coarse-graining of the underlying quantum mechanical many-body problem. The solid box indicates the main focus of this thesis. Image courtesy of Gábor Csányi.

1.1 Electronic Structure Models

A first and commonly made approximation to the fully quantum mechanical many-body problem is the *Born–Oppenheimer approximation* where the nuclear degrees of freedom are approximated by discrete points in space whereas the electrons are quantum mechanical particles. Indeed, this is a reasonable assumption in most situations because the mass of the electrons is much smaller than that of the nuclei and the electrons move with a higher velocity. Therefore, for a system of N nuclei with positions $\boldsymbol{r} \in (\mathbb{R}^3)^N$ and charges $Z \in \mathbb{R}^N$, the electronic degrees of freedom are governed by the high-dimensional wave function $\Psi\colon (\mathbb{R}^3)^N \to \mathbb{R}$ solving the time-independent Schrödinger equation $\widehat{\mathcal{H}}\Psi = E_0\Psi$ where E_0 is the smallest eigenvalue of $\widehat{\mathcal{H}}$, representing the ground state energy of the system.

The extremely high-dimensionality of the many-body wave function motivates the *mean field approximation* where the interactions between the electrons is replaced with a potential representing the mean potential generated by the electrons. This idea, together with the observation that ground state properties of the system can be written as functions of the electron density [72], leads to Kohn–Sham density functional theory [78]. In this context the single particle Schrödinger equations are known as the *Kohn–Sham equations*:

$$\Big(-\frac{1}{2}\Delta + V_{\text{eff}}[\rho](\boldsymbol{r})\Big)\psi_n(\boldsymbol{r}) = \varepsilon_n\psi_n(\boldsymbol{r}) \tag{1.1.1}$$

$$\rho(\boldsymbol{r}) = \sum_{n\ \text{occ}} |\psi_n(\boldsymbol{r})|^2 \tag{1.1.2}$$

where $V_{\text{eff}}[\rho] \coloneqq V_{\text{ext}} + V_{\text{H}}[\rho] + V_{\text{xc}}[\rho]$ is an effective potential (depending on the electron density ρ) describing the interaction between the nuclei and the electrons and between the electrons themselves. Here, $V_{\text{ext}}(\boldsymbol{r}) \coloneqq \sum_\ell \frac{-Z_\ell}{|\boldsymbol{r}-\boldsymbol{r}_\ell|}$ is the potential generated by the nuclei (where Z_ℓ are the atomic numbers), $V_{\text{H}}[\rho](\boldsymbol{r}) = \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}'$ is the Hartree potential representing the repulsion between the electrons at the mean-field level, and $V_{\text{xc}}[\rho]$ is the exchange-correlation potential, an (unknown) universal function of the electron density

which must be approximated. We may interpret ε_n as the energy of the electron occupying orbital ψ_n and the summation is over the occupied (lowest energy) orbitals. In particular, the Kohn–Sham equations must be solved self-consistently. That is, for a fixed input density ρ^{in}, the effective potential $V_{\text{eff}}[\rho^{\text{in}}]$ is constructed, the (linear) eigenvalue problem $(-\frac{1}{2}\Delta + V_{\text{eff}}[\rho^{\text{in}}])\psi_n = \varepsilon_n\psi_n$ is solved, and the output density $\rho^{\text{out}} = \sum_{n\,\text{occ}} |\psi_n|^2$ is defined. Then, a new input density is constructed from previous output densities and the procedure is repeated until self-consistency (*i.e.* until the input and output densities are equal to within a given tolerance).

The computational cost involved in solving the linear eigenvalue problem step scales cubically with respect to the system size N which limits the applicability of such calculations to systems consisting of tens to hundreds of atoms [86].

1.2 Tight Binding Models

Throughout this thesis we will consider a class of tight binding models which can either be seen as discrete approximations to density functional theory [53] or alternatively as electronic structure toy models sharing many similarities with the more complex Kohn–Sham DFT. Tight binding models therefore provide a mathematically convenient framework allowing one to study properties of the system without the need to deal with the additional technicalities related to the continuous setting and underlying system of partial differential equations.

We briefly introduce the construction of the tight binding Hamiltonian from the Kohn–Sham equations (1.1.1). To each atomic site ℓ, we assign N_{b} local "atomic orbitals" $\phi_{\ell a} \coloneqq \phi_{Z_\ell,a}(\,\cdot - \boldsymbol{r}_\ell)$ centred on $\boldsymbol{r}_\ell$ and only depending on ℓ via the atomic species Z_ℓ. Then, by projecting the Kohn–Sham equations (1.1.1) to this basis (that is, writing $\psi_n = \sum_{kb} C_{n,kb}\phi_{kb}$), we obtain an approximate discrete operator eigenvalue problem which is the basis for the tight binding

framework:

$$\mathcal{H}C_n = \varepsilon_n S C_n, \tag{1.2.1}$$

where the Hamiltonian is given by $\mathcal{H}_{\ell a,kb} \coloneqq \int \phi_{\ell a} \widehat{\mathcal{H}} \phi_{kb}$ and $S_{\ell a,kb} \coloneqq \int \phi_{\ell a}\phi_{kb}$ is known as the overlap matrix. Since the orbitals $\phi_{\ell a}$ are localised about atom ℓ, the discretised Hamiltonian $\mathcal{H}$ has off-diagonal decay. By applying the Löwdin transform, we can (with out loss of generality) assume that $\{\phi_{\ell a}\}$ is orthonormal (that is, $S = \mathrm{Id}$) [12, 29].

The specific form of the tight binding Hamiltonian discussed in this thesis (that is, the three-centre model described in §2.2) is obtained by approximating the effective potential with a sum of site contributions $V_{\mathrm{eff}} = \sum_\ell V_{\mathrm{eff},\ell} = \sum_\ell V_{\mathrm{eff},Z_\ell}(\,\cdot - \boldsymbol{r}_\ell)$ and noting that

$$\begin{aligned}
\mathcal{H}_{\ell a,kb} &= \frac{1}{2}\int \nabla\phi_{\ell a}\cdot\nabla\phi_{kb} + \int \phi_{\ell a}\big(V_{\mathrm{eff},\ell} + V_{\mathrm{eff},k}\big)\phi_{kb} + \sum_{m\notin\{\ell,k\}} \int \phi_{\ell a} V_{\mathrm{eff},m}\phi_{kb} \\
&= \frac{1}{2}\int \nabla\phi_{Z_\ell a}\cdot\nabla\phi_{Z_k b}(\,\cdot - \boldsymbol{r}_{\ell k}) \\
&\qquad + \int \phi_{Z_\ell a}\Big(V_{\mathrm{eff},Z_\ell} + V_{\mathrm{eff},Z_k}(\,\cdot - \boldsymbol{r}_{\ell k})\Big)\phi_{Z_k b}(\,\cdot - \boldsymbol{r}_{\ell k}) \\
&\qquad + \sum_{m\notin\{\ell,k\}} \int \phi_{Z_\ell a}(\,\cdot - \boldsymbol{r}_{\ell m}) V_{\mathrm{eff},Z_m}\phi_{Z_k b}(\,\cdot - \boldsymbol{r}_{km})
\end{aligned} \tag{1.2.2}$$

where $\boldsymbol{r}_{\ell k} \coloneqq \boldsymbol{r}_k - \boldsymbol{r}_\ell$. This defines the linear three-centre Hamiltonian used in this thesis.

1.2.1 Self-consistent Tight Binding

Of course, the effective potential should depend on the electron density $\rho(x) = \sum_n f_n|\psi_n(x)|^2$ (where f_n are the occupation numbers depending on ε_n from (1.1.1)) which in turn depends on the Hamiltonian itself. In particular, (1.1.1) or (1.2.1) must be solved self-consistently. For example, if we assume a local density approximation (LDA) for the exchange-correlation energy $E_{\mathrm{xc}} \coloneqq \int \rho(x)\varepsilon_{\mathrm{xc}}\big(\rho(x)\big)$, the effective potential V_{eff} may be approximated by the sum

of the following site contributions

$$\int \frac{\rho(y)}{|x-y|}\mathrm{d}y - \sum_\ell \frac{Z_\ell}{|x-\boldsymbol{r}_\ell|} + \varepsilon_{\mathrm{xc}}(\rho(x)) + \rho(x)\varepsilon'_{\mathrm{xc}}(\rho(x)) \tag{1.2.3}$$

$$\approx \sum_\ell \left[\frac{\rho_\ell - Z_\ell}{|x-\boldsymbol{r}_\ell|} + \Big(\varepsilon_{\mathrm{xc}}(\rho_\ell) + \rho_\ell\varepsilon'_{\mathrm{xc}}(\rho_\ell)\Big)\chi_{N_\ell}(x)\right] \tag{1.2.4}$$

where $N_\ell \coloneqq \boldsymbol{r}_\ell + N_{Z_\ell}$ is an atomic neighbourhood of $\boldsymbol{r}_\ell$ (possibly depending on the atomic species Z_ℓ) and $\rho_\ell = \sum_n f_n \sum_a |C_{n,\ell a}|^2$. Therefore, (1.2.2) should contain terms of the form

$$\sum_m \left[q_m \int \frac{\phi_{\ell a}\phi_{kb}}{|\,\cdot\, - \boldsymbol{r}_m|} + \Big(\varepsilon_{\mathrm{xc}}(\rho_m) + \rho_m\varepsilon'_{\mathrm{xc}}(\rho_m)\Big)\int_{N_m} \phi_{\ell a}\phi_{kb}\right] \tag{1.2.5}$$

$$\approx \delta_{\ell k}\left[\delta_{ab}\sum_{m\neq\ell}\frac{q_m}{r_{\ell m}} + v_0(\rho_\ell)_{ab}\right] =: \delta_{\ell k}[v_\ell]_{ab} \tag{1.2.6}$$

where $r_{\ell m} \coloneqq |\boldsymbol{r}_{\ell m}| = |\boldsymbol{r}_m - \boldsymbol{r}_\ell|$, $q_\ell \coloneqq \rho_\ell - Z_\ell$ are the partial charges, and v_0 is some function with values in $\mathbb{R}^{N_\mathrm{b}\times N_\mathrm{b}}$. Here, we have used the fact that $\{\phi_{\ell a}\}$ is a local basis to make the approximation $\int_{N_m}\phi_{\ell a}\phi_{kb} \approx 0$ unless $\ell = k = m$. Throughout this thesis, we suppose that v_ℓ is diagonal with constant diagonal, which simplifies the notation without affecting the results presented.

Therefore, the self-consistent tight binding Hamiltonian considered in this thesis takes the following form

$$\mathcal{H}[\rho]_{\ell a,kb} \coloneqq \mathcal{H}^{\mathrm{L}}_{\ell a,kb} + \delta_{\ell k}\delta_{ab}v(\rho)_\ell \tag{1.2.7a}$$

$$\rho_\ell = \sum_n f_n \sum_a |C_{n,\ell a}|^2 \tag{1.2.7b}$$

$$\text{where} \qquad \mathcal{H}[\rho]C_n = \varepsilon_n C_n \tag{1.2.7c}$$

and $\mathcal{H}^{\mathrm{L}}$ is the linear tight binding Hamiltonian of the form (1.2.2). Since the Hamiltonian depends on the electron density which in turn depends on the eigenpairs of the Hamiltonian, (1.2.7) is a system of nonlinear (self-consistent) equations. The formulation (1.2.7) naturally incorporates the density function tight binding (DFTB) method [49, 79, 106].

In Chapters 3 and 4, we consider the case where $\boldsymbol{r}$ and v are independent

inputs into the Hamiltonian and show that the site energies E_ℓ from (1.4.1) are local functions of $\{(\boldsymbol{r}_{\ell k}, v_k)\}$. In Chapter 5, we discuss self-consistent models and describe the extent to which the results can be extended to this setting. We briefly note here however that our analysis explicitly excludes full long-range Coulomb interactions and must instead consider the screened Yukawa potential $\sum_{m\neq\ell} \frac{q_m}{r_{\ell m}} e^{-\gamma_v r_{\ell m}}$ (for some $\gamma_v > 0$), for example. We briefly comment on the Coulomb case in §5.5.1.

1.2.2 Bond-order Potentials (BOP)

Due to the underlying eigenvalue problem, standard implementations of the tight binding model scale cubically with the number of particles in the system. However, to access key quantities of interest, only integrals with respect to certain spectral measures (the *local density of states* (LDOS)) are required rather than the whole eigen-decomposition of the Hamiltonian.

The main idea behind bond-order potentials (BOP) [39, 54, 74] is to bypass the eigenvalue problem by instead approximating the LDOS directly using only the information from finitely many *moments* $[\mathcal{H}^n]_{\ell\ell}$ where $\mathcal{H}$ is the tight binding Hamiltonian (1.2.2). Since $\mathcal{H}$ is sparse, BOP methods are linear scaling [57].

Related approaches, albeit in a slightly different setting, are the linear-scaling spectral Gauss quadrature (LSSGQ) [116] and spectral quadrature density functional theory (SQDFT) [117] methods where the LDOS is approximated by various quadrature rules.

We show that the quantities of interest in the BOP formalism converge exponentially to the corresponding tight binding quantities, thus rigorously justifying this linear-scaling approach. Moreover, we go some way to justify the LSSGQ and SQDFT methods.

1.3 Interatomic Potentials

The high computational cost of electronic structure models (e.g. naive implementations of tight binding models scale cubicly with the number of particles)

motivates the use of surrogate models for the simulation of materials, devised to remain computationally tractable but capture as much detail of the reference *ab initio* potential energy landscape (PEL) as possible.

Therefore, it may be advantageous to replace the electronic structure model with an interatomic potential (IP). Empirical IPs are purely phenomenological and aim to capture a minimal subset of desired properties of the reference *ab initio* PEL, severely limiting their transferability [36, 114].

Example 1.1 (Stillinger–Weber potential)**.** *A classical example of this approach is the Stillinger-Weber potential [114] for Si, which assigns to each atom* $\ell \in \Lambda$ *the site energy*

$$E_\ell^{\mathrm{sw}}(\boldsymbol{r}) \coloneqq \sum_{k \neq \ell} \left(A r_{\ell k}^{-p} + B r_{\ell k}^{-q}\right) f_{\mathrm{c}}(r_{\ell k}) + \sum_{\substack{k,m,n: \\ \ell \in \{k,m,n\}}} \lambda \big(\cos\theta_{kmn} + \tfrac{1}{3}\big)^2 f_{\mathrm{c}}(r_{mk})^\gamma f_{\mathrm{c}}(r_{mn})^\gamma \tag{1.3.1}$$

where $A, B, p, \lambda, \gamma > 0$ *are fixed parameters and* $f_c(r) \coloneqq e^{\frac{1}{r - r_0}} \chi_{[0,r_0)}(r)$ *for some cut-off radius* $r_0 > 0$*. The summation in the second term is over all* bond angles θ_{kmn} *between* $\boldsymbol{r}_{mk}$ *and* $\boldsymbol{r}_{mn}$ *involving atom* ℓ*. The angular part of this site energy favours systems with tetrahedral bond angles. Then, a "limited search" is carried out to choose parameters which capture certain desired properties. For example, the choice of parameters ensures that diamond structures are stable at low pressure.*

Empirical IPs, such as the Stillinger–Weber potential, are computationally inexpensive and can thus be used for large-scale, long-time dynamic simulations, for example. However, the simplicity of these parametric models limits their accuracy and transferability, and they are not systematically improvable.

1.3.1 Machine Learned Interatomic Potentials

The rapid growth in computational resources, increased both the desire and the possibility to match as much of an *ab inito* PEL as possible. A continuous

increase in the complexity of parameterisations [7, 8, 51] has over time led to a new generation of *machine-learned interatomic potentials* (MLIPs): for some functional form ε depending on parameters $\boldsymbol{\theta}$, one writes

$$E^{\mathrm{IP}}(\boldsymbol{r}) = \sum_{\ell} \varepsilon\big(\boldsymbol{\theta}; \{\boldsymbol{r}_k - \boldsymbol{r}_\ell\}_k\big) \tag{1.3.2}$$

and learns the parameters $\boldsymbol{\theta}$ by a fitting procedure with observations from the reference PEL. Examples include artificial neural networks [9–11], symmetric polynomials [16, 108], and kernel methods [6]. A striking case is the Gaussian approximation potential for Silicon [4], capturing the vast majority of the PEL of Silicon of interest for material applications.

In practice, there are two main parts in the construction of (1.3.2): *(i)* a set of *descriptors* (also known as *fingerprints*) that encodes information about the atomic environment, and *(ii)* a function of the descriptors (the *regression model*). If the set of descriptors satisfy the various physical symmetries (invariant under rotation, translation, reflection, and permutation of like-atoms), then the model respects the same physical symmetries. Moreover, if the system of descriptors is *complete* (that is, the descriptors uniquely determine the atomic environment), then the regression model is systematically improvable by increasing the number of descriptors [5].

For example, in the neural network potentials [9, 10], a set of Behler and Parrinello atom centred symmetry functions [11] are used as the descriptors, while the regression model is an artificial neural network. However, it is an open question as to whether these descriptors are complete.

More recent advances have been aimed at directly deriving a spanning set of functions invariant under rotations and permutations (of like-atoms). Examples include permutation invariant polynomials (PIPs) [16, 127], moment tensor potentials (MTPs) [108], and the atomic cluster expansion (ACE) [38]. For more details of the ACE construction and a review of PIPs and MTPs, see [2].

One of the main purposes of this thesis is to rigorously evaluate some of the

implicit or explicit assumptions underlying these machine-learned interatomic potential models, as well as more general models for atomic properties. The overarching principle in this work is to search for representations of properties of *ab initio* models in terms of *simple components* which are easier to analyse, manipulate analytically, and to fit than the PEL itself.

1.4 Summary of Results

1.4.1 Locality

For many materials (at least as long as Coulomb interaction does not play a role) the first step in the construction of an IP is to decompose the PEL into site energy contributions,

$$E(\boldsymbol{r}) = \sum_{\ell \in \Lambda} E_\ell(\boldsymbol{r}), \tag{1.4.1}$$

where one assumes that each E_ℓ is *local*, i.e., it depends only weakly on atoms far away. Partial justification for this assumption was given in [26, 29] for linear tight binding models at finite Fermi-temperature. In Chapter 3, we extend these results to insulators at zero Fermi-temperature and significantly improve the estimate for point defects.

In practice, one may therefore truncate the interaction by admitting only those atoms within a finite cut-off range. Typical cut-off radii range from 5Å to 8Å, which means that on the order 30 to 100 atoms still make important contributions. Thus the site energy is still an extremely high-dimensional object and short of identifying low-dimensional features it would be practically impossible to numerically approximate it, due to the curse of dimensionality.

Example 1.2 (Embedded Atom Model)**.** *A classical example that illustrates our search for such low-dimensional features is the embedded atom model (EAM) [36], which assigns to each atom $\ell \in \Lambda$ a site energy*

$$E_\ell^{\rm eam}(\boldsymbol{r}) = \sum_{k \neq \ell} \phi(r_{\ell k}) + F\big(\textstyle\sum_{k \neq \ell} \rho(r_{\ell k})\big).$$

While the site energy $E_\ell^{\rm eam}$ *remains* high-dimensional*, the representation is in terms of three* one-dimensional *functions* ϕ, ρ, F *which are easily represented, e.g. using splines or polynomials. Such a low-dimensional representation significantly simplifies parameter estimation, and vastly improves generalisation of the model outside a training set. Unfortunately, the EAM model and its immediate generalisations [7] have limited ability to capture a complex* ab initio *PEL. Still, this example inspires our search for representations of the PEL involving parameters that are both low-dimensional and short-ranged.*

1.4.2 Body-ordered Approximation

To control the dimensionality of the representation, a natural idea is to consider the following body-ordered expansion,

$$E_\ell(\boldsymbol{r}) \approx V_0 + \sum_{k\neq\ell} V_1(\boldsymbol{r}_{\ell k}) + \sum_{\substack{k_1,k_2\neq\ell \\ k_1<k_2}} V_2(\boldsymbol{r}_{\ell k_1}, \boldsymbol{r}_{\ell k_2}) + \cdots + \sum_{\substack{k_1,\ldots,k_N\neq\ell \\ k_1<\cdots<k_N}} V_N\big(\boldsymbol{r}_{\ell k_1}, \ldots, \boldsymbol{r}_{\ell k_N}\big), \qquad (1.4.2)$$

where $\boldsymbol{r}_{\ell k} \coloneqq \boldsymbol{r}_k - \boldsymbol{r}_\ell$ and $V_n(\boldsymbol{r}_{\ell k_1}, \ldots, \boldsymbol{r}_{\ell k_n})$ is an $(n+1)$*-body potential* modelling the interaction of a centre atom ℓ and n neighbouring atoms $\{k_1, \ldots, k_n\}$. This expansion was traditionally truncated at body-order *three* ($N = 2$) due to the exponential increase in computational cost with N. However, it was recently demonstrated by Shapeev's moment tensor potentials (MTPs) [108] and Drautz' atomic cluster expansion (ACE) [38] that a careful reformulation leads to models with at most linear N-dependence. Indeed, algorithms proposed in [2, 108] suggest that the computational cost may even be N-independent, but this has not been proven. Even more striking is the fact that the MTP and ACE models which are both *linear models* based on a body-ordered approximation, currently appear to outperform the most advanced nonlinear models in regression and generalisation tests [89, 134].

These recent successes are in stark contrast with the "folklore" that body-order expansions generally converge slowly, if at all [14, 38, 40, 64, 114]. The

fallacy in those observations is typically that they implicitly assume a vacuum cluster expansion. We demonstrate in Chapter 4 that a rapidly convergent body-order *approximation* can be constructed if one accounts for the chemical environment of the material. We will precisely characterise the convergence of such an approximation as $N \to \infty$, in terms of the Fermi-temperature and the band gap of the material. In the process, we also prove (asymptotic) error estimates for bond order potentials [74], as well as more general abstract approximation schemes.

1.4.3 Thermodynamic Limit

To study bulk properties of a material with local defects, it is convenient to consider an extended system of infinitely many nuclei where a naive definition of the total energy is of course ill-defined. However, as a result of the strong energy locality estimates described in §1.4.1, we are able to apply results of [27] to obtain a well-defined renormalised energy functional for infinite systems.

Of course to simulate such a system, we must consider finite computational domains and impose artificial boundary conditions. In Chapter 6, we consider a sequence of supercell models and extend [26] to the zero Fermi-temperature case by showing that, under a specific choice of electron numbers in the sequence of finite domain approximations, the thermodynamic limit is given by a grand canonical model with a defect-dependent chemical potential.

Moreover, in practice, a low but positive Fermi-temperature is chosen in order to approximate the sharp cut-off with a smooth Fermi-Dirac function, which ensures there is a unique Fermi-level, for example. We give detailed justification for this approach by identifying the limiting model as Fermi-temperature is sent to zero and obtain an exponential rate of convergence for the nuclei configuration.

CHAPTER 2

Mathematical Formulation of the Tight Binding Models

In this chapter, we briefly introduce the tight binding Hamiltonian and the main mathematical definitions which will be used throughout the thesis.

2.1 Atomic Configurations

For atomic index set Λ (for example $\Lambda = \{1, \dots, N_{\text{at}}\}$ or $\Lambda = \mathbb{N}$, or a multi-lattice as in Chapter 6), we denote by $\boldsymbol{r} = \{\boldsymbol{r}_\ell\}_{\ell\in\Lambda} \subseteq \mathbb{R}^d$ the set of atomic positions (for some spatial dimension $d \in \mathbb{N}$). We write $\boldsymbol{r}_{\ell k} \coloneqq \boldsymbol{r}_k - \boldsymbol{r}_\ell$ for the atomic positions relative to a central atom ℓ and $r_{\ell k} \coloneqq |\boldsymbol{r}_{\ell k}|$. Moreover, to each atomic site $\ell \in \Lambda$, we assign an *effective potential* (1.2.6) $v_\ell \in \mathbb{R}$ and the atomic species Z_ℓ. The *state of atom* ℓ will be denoted $\boldsymbol{X}_\ell \coloneqq (\boldsymbol{r}_\ell, v_\ell, Z_\ell)$ and, to simplify notation further, we write $\boldsymbol{X}_{\ell k} \coloneqq (\boldsymbol{r}_{\ell k}, v_\ell, v_k, Z_\ell, Z_k)$ for the *state of atom k relative to the central atom ℓ*. To denote the whole atomic configuration, we write $\boldsymbol{X} = (\boldsymbol{r}, v, Z) \coloneqq (\{\boldsymbol{r}_\ell\}_{\ell\in\Lambda}, \{v_\ell\}_{\ell\in\Lambda}, \{Z_\ell\}_{\ell\in\Lambda})$.

Throughout this chapter, we will assume that the configuration satisfies the following no-collision assumption:

(AC). *There exist positive constants* $\mathfrak{m} = \mathfrak{m}(\boldsymbol{X}), \mathfrak{c} = \mathfrak{c}(\boldsymbol{X}) > 0$ *such that* $r_{\ell k} \geqslant \mathfrak{m}$ *and* $|v_\ell| \leqslant \mathfrak{c}$ *for all* $\ell, k \in \Lambda$.

2.2 Tight Binding Hamiltonian

We consider $N_{\rm b}$ atomic orbitals per atom and denote the corresponding indices by $1 \leqslant a, b \leqslant N_{\rm b}$. Then, by arguing as in §1.2, the tight binding Hamiltonian $\mathcal{H} = \mathcal{H}(\boldsymbol{X})$ is given by the following block matrix:

(TB). *For* $\boldsymbol{X}$ *satisfying* **(AC)**, *and* $\ell, k \in \Lambda$, *we suppose that*

$$\mathcal{H}(\boldsymbol{X})_{\ell k} = h(\boldsymbol{X}_{\ell k}) + \sum_{m \notin \{\ell, k\}} t\big(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{k m}\big) + \delta_{\ell k} v_\ell \mathrm{Id}_{N_{\rm b}} \tag{2.2.1}$$

where h *and* t *have values in* $\mathbb{R}^{N_{\rm b} \times N_{\rm b}}$, *are independent of the effective potential* v, *and are* ν *times continuously differentiable with respect to the relative atomic positions for some* $\nu \geqslant 1$. *Moreover, we assume that there exist* $h_0, \gamma_0 > 0$ *such that*

$$\begin{aligned} \big|\nabla^j h(\boldsymbol{X}_{\ell k})\big| &\leqslant h_0 e^{-\gamma_0 r_{\ell k}}, \quad \text{and} \\ \big|\nabla^j t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{k m})\big| &\leqslant h_0 e^{-2\gamma_0 [r_{\ell m} + r_{m k}]}. \end{aligned} \tag{2.2.2}$$

for $0 \leqslant j \leqslant \nu$ *and all* $\ell, k, m \in \Lambda$.

Symmetries. *(i) We suppose that* $\mathcal{H}(\boldsymbol{X})$ *is symmetric (i.e.* $h(\boldsymbol{X}_{\ell k}) = h(\boldsymbol{X}_{k\ell})^{\rm T}$ *and* $t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{k m}) = t(\boldsymbol{X}_{k m}, \boldsymbol{X}_{\ell m})^{\rm T}$*). (ii) For orthogonal* $Q \in \mathbb{R}^{d \times d}$, *there exist orthogonal* $D^\ell(Q)$ *such that*

$$\mathcal{H}(Q\boldsymbol{X}) = D(Q) \mathcal{H}(\boldsymbol{X}) D(Q)^{\rm T}$$

where $D(Q) = \mathrm{diag}(\{D^\ell(Q)\}_{\ell \in \Lambda})$ *and* $Q\boldsymbol{X} \coloneqq (\{Q\boldsymbol{r}_\ell\}, v, Z)$. *The notation* $D(Q)$ *is inspired by the fact that they are most commonly block Wigner-D matrices.*

Remark 2.1. *(i) It is important to emphasise that the constants* $h_0, \gamma_0 > 0$ *in* (2.2.2) *are chosen to be independent of the atomic sites* $\ell, k, m \in \Lambda$.

(ii) The condition in (2.2.2) *with* $j = 0$ *is satisfied for most common linear tight binding models. In fact, in most tight binding models, a finite cut-off radius is used and so Hamiltonian entries are zero for atoms beyond a finite interaction range.*

(iii) The symmetry properties [112] are derived, e.g., in [29, Appendix A].

(iv) In practice, the number of atomic orbitals per atom depends on the atomic species. This notational complication can easily be avoided as outlined Appendix B.1.

We now briefly review elementary properties of the tight binding Hamiltonian:

Lemma 2.1. *There exists constants* $\gamma_j > 0$ *such that*

$$|\mathcal{H}(\boldsymbol{X})_{\ell k}| \leqslant Ce^{-\gamma_0 r_{\ell k}} \quad \textit{and} \quad \left|\frac{\partial^j \mathcal{H}(\boldsymbol{X})_{\ell k}}{\partial \boldsymbol{X}_{n_1} \dots \partial \boldsymbol{X}_{n_j}}\right| \leqslant Ce^{-\gamma_j \sum_{l=1}^{j} [r_{\ell n_l} + r_{n_l k}]} \quad (2.2.3)$$

for $1 \leqslant j \leqslant \nu$ *and* $n_1, \dots, n_j \in \Lambda$.

As a result of **(TB)**, $\mathcal{H}(\boldsymbol{X})$ is symmetric and so the spectrum is real. Moreover, as a direct result of Lemma 2.1, the spectrum is uniformly bounded [29, Lemma 4]:

Lemma 2.2. *There exists* $\underline{\sigma}, \overline{\sigma}$ *depending only on* $\boldsymbol{X}$ *through* $\mathfrak{m}(\boldsymbol{X})$ *and* $\mathfrak{c}(\boldsymbol{X})$ *from* **(AC)** *such that* $\sigma\big(\mathcal{H}(\boldsymbol{X})\big) \subseteq [\underline{\sigma}, \overline{\sigma}]$.

2.3 Metals, Insulators, and Defects

The structure of the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ will have a key role in the analysis. To illustrate the main ideas, we briefly describe typical spectra seen in metals and insulating systems.

In the case where $\boldsymbol{X}$ describes a multi-lattice in $\mathbb{R}^d$ formed by taking the union of finitely many shifted Bravais lattices, the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ is the union of finitely many continuous energy bands (see [77] or Appendix B.2). That is, there exist finitely many continuous functions, $\varepsilon^\alpha \colon \overline{\mathrm{BZ}} \to \mathbb{R}$, on the

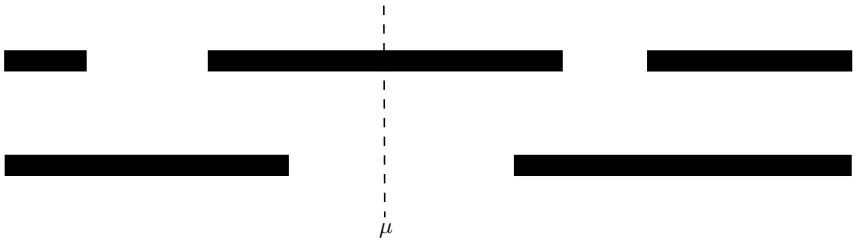


Figure 2.1: Schematic plots of the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ of a metal (top) and insulator (bottom).

Brillouin zone BZ, a compact connected subset of $\mathbb{R}^d$, such that

$$\sigma\big(\mathcal{H}(\boldsymbol{X})\big) = \bigcup_{\alpha} \varepsilon^{\alpha}(\mathrm{BZ}).$$

In particular, in this case, $\sigma\big(\mathcal{H}(\boldsymbol{X})\big) = \sigma_{\mathrm{ess}}\big(\mathcal{H}(\boldsymbol{X})\big)$ is the union of finitely many intervals on the real line. The *band structure* $\{\varepsilon^{\alpha}\}$ relative to the position of the chemical potential, μ, determines the electronic properties of the system [118]. In metals μ lies within a band, whereas for insulators, μ lies between two bands in a *spectral gap*. Schematic plots of these two situations are given in Figure 2.1.

We now consider perturbations of the reference configuration $\boldsymbol{X}$ consisting of a small global perturbation combined with a point defect:

($\mathbf{P}_\delta$). *Let $\delta \geqslant 0$. Suppose $\boldsymbol{X} = (\boldsymbol{r}, v, Z)$ satisfies* **(AC)** *and the* defect configuration $\boldsymbol{X}^{\mathrm{d}} = (\boldsymbol{r}^{\mathrm{d}}, v^{\mathrm{d}}, Z^{\mathrm{d}})$ *defined on some index set Λ^{d} satisfies* **(AC)** *and, for some $R_{\mathrm{d}} > 0$,*

- $\Lambda^{\mathrm{ff}} \coloneqq \{\ell \in \Lambda^{\mathrm{d}} \colon |\boldsymbol{r}^{\mathrm{d}}_{\ell}| > R_{\mathrm{d}}\} = \{\ell \in \Lambda \colon |\boldsymbol{r}_{\ell}| > R_{\mathrm{d}}\}$,
- $Z^{\mathrm{d}}_k = Z_k$ *for all $k \in \Lambda^{\mathrm{ff}}$, and*
- $\sup_{k \in \Lambda^{\mathrm{ff}}} \big[|\boldsymbol{r}^{\mathrm{d}}_k - \boldsymbol{r}_k| + |v^{\mathrm{d}}_k - v_k|\big] \leqslant \delta$.

For $(\boldsymbol{X}, \boldsymbol{X}^{\mathrm{d}})$ satisfying **($\mathbf{P}_\delta$)**, the Hamiltonians $\mathcal{H}(\boldsymbol{X})$ and $\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})$ may be defined on different spatial domains (e.g. when considering a vacancy or interstitial defect). Therefore, in order to directly compare these operators, we extend their definitions to the larger spatial domain $\Lambda \cup \Lambda^{\mathrm{d}}$ by inserting finitely many additional zero rows and columns. We denote the resulting operators by

$\widetilde{\mathcal{H}}(\boldsymbol{X})$ and $\widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}})$ (full details are presented in the proof of Proposition 2.3, below). We now see how the Hamiltonian is affected by considering point defect configurations:

Proposition 2.3 (Decomposition of the Hamiltonian)**.** *Fix $\varepsilon > 0$. Then, there exists $\delta > 0$ such that if $(\boldsymbol{X}, \boldsymbol{X}^{\mathrm{d}})$ satisfies $(\mathbf{P}_\delta)$, then there exists $R > 0$ and operators $P_\varepsilon, P_{\mathrm{FR}}$ such that*

$$\widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}}) = \widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}} + P_\varepsilon, \tag{2.3.1}$$

$[P_{\mathrm{FR}}]_{\ell k} = 0$ if $|\boldsymbol{r}_\ell| > R$ or $|\boldsymbol{r}_k| > R$, and $\|P_\varepsilon\|_{\ell^2 \to \ell^2} < \varepsilon$.

Moreover, $\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big) \setminus B_\varepsilon\big(\sigma\big(\mathcal{H}(\boldsymbol{X})\big)\big)$ is a finite set.

In particular, if $\boldsymbol{X}$ describes a multi-lattice, then, since local perturbations in the *defect core* are of finite rank, the essential spectrum is unchanged and we obtain finitely many eigenvalues bounded away from the spectral bands. Moreover, a small global perturbation can only result in a small change in the spectrum. A schematic plot of this situation is given in Figure 2.2.

To summarise this discussion, we make the following definitions:

Definition 2.2. *Fix $\varepsilon > 0$ and suppose $(\boldsymbol{X}, \boldsymbol{X}^{\mathrm{d}})$ satisfies $(\mathbf{P}_\delta)$ with $\delta = \delta(\varepsilon)$ coming from Proposition 2.3. Then, we define I_- and I_+ to be compact intervals and $\{\lambda_j\}$ to be a finite set such that*

$$B_\varepsilon\big(\sigma\big(\mathcal{H}(\boldsymbol{X})\big)\big) \subseteq I_- \cup I_+, \qquad \sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big) \subseteq I_- \cup \{\lambda_j\} \cup I_+, \tag{2.3.2}$$

and $\max I_- \leqslant \mu \leqslant \min I_+$. Moreover, we define

$$\mathsf{g} := \min I_+ - \max I_- \geqslant 0, \qquad \textit{and} \tag{2.3.3}$$

$$\mathsf{g}^{\mathrm{d}} := \min I_+ \cup \{\lambda_j : \lambda_j \geqslant \mu\} - \max I_- \cup \{\lambda_j : \lambda_j \leqslant \mu\}. \tag{2.3.4}$$

The parameters in Definition 2.2 are also displayed in Figure 2.2. The constant g is slightly arbitrary in the sense that as long as $B_\varepsilon\big(\sigma\big(\mathcal{H}(\boldsymbol{X})\big)\big) \subseteq I_- \cup I_+$, then there exists a finite set $\{\lambda_j\}$ as in (2.3.2). Choosing smaller g

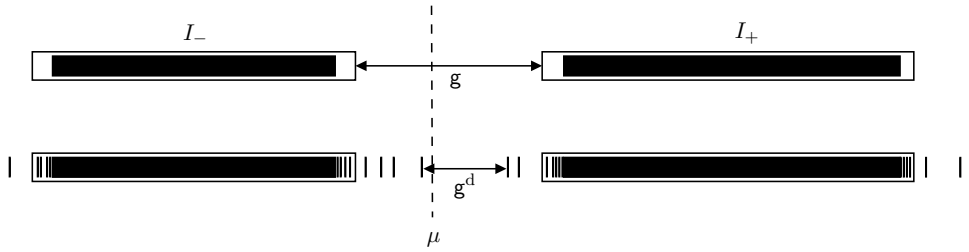


Figure 2.2: Top: Schematic plot of the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ for an insulating system, together with two compact intervals I_- and I_+ as in (2.3.2) and the constant g from (2.3.3). Bottom: The spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big)$ after considering perturbations satisfying **($\mathbf{P}_\delta$)**. While the edges of the spectrum may be accumulation points for a sequence of eigenvalues within the band gap, the number of such eigenvalues bounded away from the edges is finite.

reduces the size of the set $\{\lambda_j\}$.

2.4 Local Analytic Observables

Fix $\boldsymbol{X}$, $\boldsymbol{X}^{\mathrm{d}}$ satisfying Definition 2.2. We suppose that $O\colon U \to \mathbb{C}$ is analytic for some open subset $U \subseteq \mathbb{C}$ containing $I_- \cup I_+ \supseteq \sigma\big(\mathcal{H}(\boldsymbol{X})\big)$. Then, for $\ell \in \Lambda$, the corresponding local observables are defined as

$$O_\ell(\boldsymbol{X}) \coloneqq \operatorname{tr} O\big(\mathcal{H}(\boldsymbol{X})\big)_{\ell\ell} = \operatorname{tr}\bigg[\oint_{\mathscr{C}_O} O(z)\big(z - \mathcal{H}(\boldsymbol{X})\big)^{-1}\frac{\mathrm{d}z}{2\pi i}\bigg]_{\ell\ell} \tag{2.4.1}$$

where $\mathscr{C}_O \subseteq U$ is a simple closed positively oriented contour (or union of contours) encircling $I_- \cup I_+$. We use the notation $O(\boldsymbol{X}) \coloneqq \{O_\ell(\boldsymbol{X})\}_{\ell\in\Lambda}$. Similarly, if $\mathscr{C}_O$ encircles $I_- \cup \{\lambda_j\} \cup I_+$, we may use (2.4.1) to define $O_\ell(\boldsymbol{X}^{\mathrm{d}})$.

Remark 2.3 (Holomorphic Functional Calculus)**.** *In* (2.4.1)*, we have applied the holomorphic functional calculus to define the operator $O(\mathcal{H})$ for functions O analytic in some neighbourhood of $\sigma(\mathcal{H})$. This approach for the tight binding model has been widely used [26, 29, 45, 58].*

The distance between the contour $\mathscr{C}_O$ and the spectrum will be important for the analysis:

Definition 2.4. *For $\mathscr{C}_O$ as in* (2.4.1)*, we define*

$$\mathfrak{d}_O \coloneqq \inf_{z\in\mathscr{C}_O} \operatorname{dist}\big(z, I_- \cup I_+\big) \tag{2.4.2}$$

$$\mathfrak{d}_O^{\mathrm{d}} \coloneqq \inf_{z\in\mathscr{C}_O} \operatorname{dist}\big(z, I_- \cup \{\lambda_j\} \cup I_+\big). \tag{2.4.3}$$

If it is clear from the context, we write $\mathscr{C} = \mathscr{C}_O$, $\mathfrak{d} = \mathfrak{d}_O$, and $\mathfrak{d}^{\mathrm{d}} = \mathfrak{d}_O^{\mathrm{d}}$.

Although all of the results apply to general local observables, we will be primarily interested in the following two special cases.

Electron density. For fixed inverse Fermi-temperature $\beta \in (0,\infty]$ and chemical potential μ, the electron density is given by

$$\rho = F^\beta(\boldsymbol{X}) \qquad \text{where} \qquad F^\beta(z) \coloneqq \begin{cases} \big(1+e^{\beta(z-\mu)}\big)^{-1} & \text{if } \beta<\infty \\ \chi_{(-\infty,\mu)}(z) + \frac{1}{2}\chi_{\{\mu\}}(z) & \text{if } \beta=\infty. \end{cases} \tag{2.4.4}$$

When making the choice of chemical potential explicit in the notation, we will write $F^\beta(z;\mu)$ and $F^\beta(\boldsymbol{X};\mu)$. In Chapter 5, we consider the case where the effective potential, v_ℓ, itself depends on the electron density, introducing a nonlinearity into the system.

Grand potential. While nuclei are treated as classical particles, we assume that electrons are described by a grand canonical potential model. That is, the Fermi-temperature, volume and chemical potential are fixed model parameters and we consider the grand potential:

$$\begin{aligned} G_\ell^\beta(\boldsymbol{X}) &\coloneqq \operatorname{tr}\big[G^\beta\big(\mathcal{H}(\boldsymbol{X})\big)_{\ell\ell}\big] \qquad \text{where} \\ G^\beta(z) &\coloneqq \begin{cases} \frac{2}{\beta}\log\big(1-F^\beta(z)\big) & \text{if } \beta<\infty, \\ 2(z-\mu)\chi_{(-\infty,\mu)}(z) & \text{if } \beta=\infty. \end{cases} \end{aligned} \tag{2.4.5}$$

Again, we will also write $G_\ell^\beta(\boldsymbol{X};\mu)$ and $G^\beta(z;\mu)$ for (2.4.5).

Remark 2.5 (Zero Fermi-temperature Limit)**.** *We justify the zero Fermi-temperature definitions via a limiting argument, see Chapter 6 for the details.*

The next results summarise the main properties of these analytic functions:

Lemma 2.4. *For fixed $\beta \in (0, \infty]$, the functions $F^\beta(\,\cdot\,)$ and $G^\beta(\,\cdot\,)$ extend to analytic functions on $\mathcal{D}_\beta(\mu) \coloneqq \mathbb{C} \setminus \{\mu + ir \colon r \in \mathbb{R}, |r| \geqslant \frac{\pi}{\beta}\}$.*

Therefore, to define (2.4.1), for $O = F^\beta$ or G^β, we must choose $\mathscr{C}_\beta \subseteq \mathcal{D}_\beta(\mu)$. In particular, for zero Fermi-temperature ($\beta = \infty$), we require a spectral gap (that is, $\mu \notin \sigma(\mathcal{H})$) in order to define local observables (2.4.1) via the holomorphic functional calculus.

In order to describe the asymptotic behaviour in the zero Fermi-temperature limit, we require uniform bounds on F^β and G^β as $\beta \to \infty$:

Lemma 2.5. *Suppose $\mathscr{C}_\beta$ is a family of contours contained in a bounded set such that* (2.4.1) *holds for $O = F^\beta$ or G^β. Moreover, suppose there exists $\mathsf{b} \in (0, \pi)$ such that $\operatorname{dist}(z, \{\mu \pm i\pi\beta^{-1}\}) \geqslant \mathsf{b}\beta^{-1}$ for all $z \in \mathscr{C}_\beta$. Then, for $\beta_0 > 0$, we have*

$$\sup_{\beta \geqslant \beta_0} \sup_{z \in \mathscr{C}_\beta} |O^\beta(z)| < \infty$$

for both $O^\beta = F^\beta$ and G^β.

See Fig. 2.3 for a representative example of such a contour.

2.5 Proofs

2.5.1 Tight Binding Hamiltonian

For this section, we fix a configuration $\boldsymbol{X}$ and corresponding Hamiltonian $\mathcal{H} = \mathcal{H}(\boldsymbol{X})$ satisfying Definition 2.2 and **(TB)**, respectively.

We first show that the tight binding Hamiltonian is short ranged:

Proof of Lemma 2.1. In the $j = 0$ case, the result follows from the estimate $\sum_m e^{-2\gamma_0[r_{\ell m} + r_{mk}]} \leqslant \frac{C_{\mathfrak{m},d}}{\gamma_0^d} e^{-\gamma_0 r_{\ell k}}$ for some $C_{\mathfrak{m},d}$ depending on $\mathfrak{m}$ and d (see Appendix B.3).

Now suppose that $1 \leqslant j \leqslant \nu$. The result clearly holds if $\ell = k$ and so we assume $\ell \neq k$. Since h and t are independent of the effective potential all

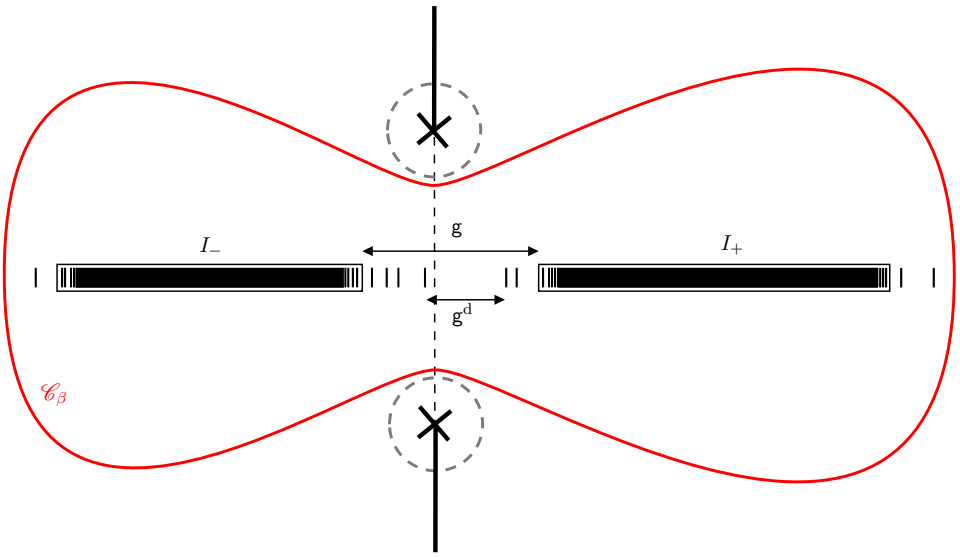


Figure 2.3: Schematic plot of an admissible integration contour $\mathscr{C}_\beta$ for F^β or G^β (see (2.4.1)).

mixed partial derivatives are zero. Moreover, we have

$$\frac{\partial \mathcal{H}(\boldsymbol{X})_{\ell k}}{\partial v_n} = \delta_{\ell k}\delta_{\ell n}\mathrm{Id}_{N_\mathrm{b}}. \tag{2.5.1}$$

and all higher order partial derivatives are zero.

A simple calculation reveals that

$$\frac{\partial^j h(\boldsymbol{X}_{\ell k})}{\partial \boldsymbol{r}_{n_1} \dots \partial \boldsymbol{r}_{n_j}} = \begin{cases} (-1)^{\sum_{l=1}^j \delta_{\ell n_l}} \nabla^j h(\boldsymbol{X}_{\ell k}) & \text{if } n_1, \dots, n_j \in \{\ell, k\}, \\ 0 & \text{otherwise.} \end{cases}$$

On the other hand, derivatives of the three centre term take the form

$$\begin{aligned} &\frac{\partial^j}{\partial \boldsymbol{r}_{n_1} \dots \partial \boldsymbol{r}_{n_j}} \sum_{m \notin \{\ell,k\}} t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km}) \\ &\qquad = \sum_{m \notin \{\ell,k\}} \left\langle \boldsymbol{\nabla}^{\otimes j} t \,;\, u_{n_1}^m, \dots, u_{n_j}^m \right\rangle (\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km}), \end{aligned} \tag{2.5.2}$$

where $u_n^m \coloneqq (\delta_{nm} - \delta_{n\ell}, \delta_{nm} - \delta_{nk})^{\mathrm{T}}$. (Here, we use the notation from (A.2.1)). In particular, if $n \in \{\ell, k\}$, then $u_n^m \neq 0$ and if $n \notin \{\ell, k\}$, then $u_n^m = (1,1)^{\mathrm{T}}\delta_{nm}$ and the summation over $m \notin \{\ell, k\}$ can be restricted to the single term $m = n$.

Therefore, in the case $n_1, \dots, n_j \in \{\ell, k\}$, the left hand side of (2.2.3) can be bounded above by

$$\left|\nabla^j h(\boldsymbol{X}_{\ell k})\right| + C_j \sum_{m \notin \{\ell,k\}} \left|\nabla^j t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km})\right| \leqslant C e^{-\gamma_j \sum_{l=1}^{j} [r_{\ell n_l} + r_{n_l k}]}, \quad (2.5.3)$$

where $\gamma_j \coloneqq \frac{1}{j}\gamma_0$.

On the other hand if $n_1, \dots, n_j \in \{\ell, k, n\}$ and $n_l = n \notin \{\ell, k\}$ for some $1 \leqslant l \leqslant j$, then the left hand side of (2.2.3) can be bounded above by

$$C_j \left|\nabla^j t(\boldsymbol{X}_{\ell n}, \boldsymbol{X}_{kn})\right| \leqslant C_j h_0 e^{-2\gamma_0 [r_{\ell n} + r_{nk}]} \leqslant C e^{-\gamma_j \sum_{l=1}^{j} [r_{\ell n_l} + r_{n_l k}]}. \quad (2.5.4)$$

In all other cases the left hand side of (2.2.3) is zero. □

As a direct corollary, $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ is bounded [29, Lemma 4]:

Proof of Lemma 2.2. The off-diagonal decay of the Hamiltonian allows us to conclude by applying the Gershgorin circle theorem [73]: for fixed $\ell \in \Lambda$, we have

$$\sum_{k \neq \ell} \left|\mathcal{H}(\boldsymbol{X})_{\ell k}\right| \leqslant C \sum_{k \neq \ell} e^{-\gamma_0 r_{\ell k}} \leqslant C_{\mathfrak{m}} \int e^{-\gamma_0 |\boldsymbol{r}|} \mathrm{d}\boldsymbol{r} = \frac{C_{\mathfrak{m},d}}{\gamma_0^d} \quad (2.5.5)$$

and so $|\lambda| \leqslant h_0 + \mathfrak{c} + C_{\mathfrak{m},d} \gamma_0^{-d}$ for all $\lambda \in \sigma\big(\mathcal{H}(\boldsymbol{X})\big)$. □

2.5.2 Perturbation of the Spectrum

In this section, we prove Proposition 2.3, a slightly stronger statement than Weyl's theorem [76] on the stability of the essential spectrum.

First, in order to compare $\mathcal{H}(\boldsymbol{X})$, an operator on $\ell^2(\Lambda; \mathbb{R}^{N_\mathrm{b}})$, and $\mathcal{H}(\boldsymbol{X}^\mathrm{d})$,

an operator on $\ell^2(\Lambda^{\mathrm{d}};\mathbb{R}^{N_{\mathrm{b}}})$, we first extend the definitions to $\Lambda\cup\Lambda^{\mathrm{d}}$ by defining

$$\begin{aligned}\widetilde{\mathcal{H}}(\boldsymbol{X})_{\ell k} &\coloneqq \begin{cases}\mathcal{H}(\boldsymbol{X})_{\ell k} & \text{if } \ell,k\in\Lambda,\\ 0 & \text{otherwise}\end{cases} \qquad \text{and}\\ \widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}})_{\ell k} &\coloneqq \begin{cases}\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})_{\ell k} & \text{if } \ell,k\in\Lambda^{\mathrm{d}},\\ 0 & \text{otherwise.}\end{cases}\end{aligned} \tag{2.5.6}$$

Since this only introduces at most finitely many additional zero rows and columns corresponding to additional atoms within the defect core, the spectra only change by the addition of finitely many zero eigenvalues. Shifting the spectrum away from $\{0\}$, we are able to replace $\mathcal{H}(\boldsymbol{X})$ and $\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})$ with $\widetilde{\mathcal{H}}(\boldsymbol{X})$ and $\widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}})$, respectively.

That is, for an appropriate contour $\mathscr{C}$, we choose $z_0\in\mathbb{C}$ such that the contour $\mathscr{C}+z_0$ does not encircle $\{0\}$, and note that for $O(\,\cdot\,;\mu)=F^\beta$ or G^β with chemical potential μ, we have

$$\begin{aligned}O_\ell(\boldsymbol{X}) &= \oint_{\mathscr{C}} O(z;\mu)\big(z-\mathcal{H}(\boldsymbol{X})\big)^{-1}_{\ell\ell}\,\frac{\mathrm{d}z}{2\pi i}\\ &= \oint_{\mathscr{C}+z_0} O(z-z_0;\mu)\big(z-z_0-\mathcal{H}(\boldsymbol{X})\big)^{-1}_{\ell\ell}\,\frac{\mathrm{d}z}{2\pi i}\\ &= \oint_{\mathscr{C}+z_0} O(z;\mu+z_0)\big(z-(\widetilde{\mathcal{H}}(\boldsymbol{X})+z_0)\big)^{-1}_{\ell\ell}\,\frac{\mathrm{d}z}{2\pi i}.\end{aligned}$$

The exact same argument also applies to $\widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}})$. In the following we assume that the spectra $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ and $\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big)$ are bounded away from zero.

Now that the Hamiltonians are directly comparable, we obtain the following decomposition:

Proof of Proposition 2.3. For fixed $R_0>0$, we let P_ε be the operator (depending on R_0) with matrix entries

$$[P_\varepsilon]_{\ell k} \coloneqq \begin{cases}\big[\widetilde{\mathcal{H}}(\boldsymbol{X})-\widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}})\big]_{\ell k} & \text{if } \ell,k\in\Lambda^{\mathrm{ff}} \text{ or } r_{\ell k}>R_0,\\ 0 & \text{otherwise}\end{cases}$$

and suppose that P_{FR} is defined such that (2.3.1) is satisfied. In particular, $[P_{\mathrm{FR}}]_{\ell k} = 0$ if $|\boldsymbol{r}_\ell|, |\boldsymbol{r}_k| > R_{\mathrm{d}}$ (i.e. if $\ell, k \in \Lambda^{\mathrm{ff}}$), or if $|\boldsymbol{r}_\ell| \leqslant R_{\mathrm{d}}$ and $|\boldsymbol{r}_k| > R \coloneqq R_{\mathrm{d}} + R_0$ (or *vice versa*). It remains to show that $\|P_\varepsilon\|_{\ell^2 \to \ell^2} < \varepsilon$ for sufficiently small δ and sufficiently large R_0.

We first consider the case $\ell, k \in \Lambda^{\mathrm{ff}}$. Along the diagonal ($\ell = k$), we have the bound $|[\mathcal{H}(\boldsymbol{X}) - \mathcal{H}(\boldsymbol{X}^{\mathrm{d}})]_{\ell k}| \leqslant |v_\ell - v_\ell^{\mathrm{d}}| \leqslant \delta$. Moreover, supposing δ is sufficiently small such that $|\theta \boldsymbol{r}_{\ell k} + (1-\theta)\boldsymbol{r}_{\ell k}^{\mathrm{d}}| \geqslant \frac{1}{2} r_{\ell k}$ for all $\ell, k \in \Lambda$ and $\theta \in [0,1]$, we have

$$\big|h(\boldsymbol{X}_{\ell k}) - h(\boldsymbol{X}_{\ell k}^{\mathrm{d}})\big| = \big|\nabla h\big((\xi_{\ell k}, Z_\ell, Z_k)\big) \cdot \big(\boldsymbol{r}_{\ell k} - \boldsymbol{r}_{\ell k}^{\mathrm{d}}\big)\big| \leqslant C\delta e^{-\frac{1}{2}\gamma_0 r_{\ell k}} \tag{2.5.7}$$

for some $\xi_{\ell k} \in [\boldsymbol{r}_{\ell k}, \boldsymbol{r}_{\ell k}^{\mathrm{d}}]$. Similarly, we have

$$\sum_m \big|t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km}) - t(\boldsymbol{X}_{\ell m}^{\mathrm{d}}, \boldsymbol{X}_{km}^{\mathrm{d}})\big| \leqslant C\delta e^{-\frac{1}{2}\gamma_0 r_{\ell k}}. \tag{2.5.8}$$

In particular, using the off-diagonal decay of the Hamiltonian (Lemma 2.1), we have: for $\psi \in \ell^2$ with $\|\psi\|_{\ell^2} = 1$,

$$\|P_\varepsilon \psi\|_{\ell^2}^2 \leqslant C\Big[\delta^2 \sum_{\ell k} e^{-\gamma_0 r_{\ell k}} |\psi_k|^2 + \sum_{\substack{\ell \notin \Lambda^{\mathrm{ff}}, k \in \Lambda \cup \Lambda^{\mathrm{d}}: \\ r_{\ell k} > R_0}} e^{-\gamma_0 r_{\ell k}}\Big] \tag{2.5.9}$$

$$\leqslant C\Big[\delta^2 + \int_{|x| > R_0} e^{-\gamma_0 |x|} \mathrm{d}x\Big]. \tag{2.5.10}$$

Therefore, we may choose δ sufficiently small and R_0 sufficiently large so that $\|P_\varepsilon\|_{\ell^2 \to \ell^2} < \varepsilon$.

Using the operator norm perturbation result [76, p. 291], we have

$$\operatorname{dist}\Big(\sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}})\big), \sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big)\Big) \leqslant \|P_\varepsilon\|_{\ell^2 \to \ell^2} < \varepsilon$$

and so $\sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}^{\mathrm{d}})\big) \subseteq B_\varepsilon\big(\sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big)\big)$. Therefore, we have

$$\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big) \setminus B_\varepsilon\big[\sigma\big(\mathcal{H}(\boldsymbol{X})\big)\big] \subseteq B_\varepsilon\big[\sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big) \setminus \sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X})\big)\big].$$

We conclude by showing that $\sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big) \setminus \sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X})\big)$ is finite. Since P_{FR} is finite rank, we may directly apply Weyl's theorem [76] on the stability of the essential spectrum (i.e. $\sigma_{\mathrm{ess}}\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big) = \sigma_{\mathrm{ess}}\big(\widetilde{\mathcal{H}}(\boldsymbol{X})\big)$) and conclude

$$\begin{aligned}\sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big) \setminus \sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X})\big) &\subseteq \sigma\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big) \setminus \sigma_{\mathrm{ess}}\big(\widetilde{\mathcal{H}}(\boldsymbol{X})\big) \\ &= \sigma_{\mathrm{disc}}\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big) \setminus \sigma_{\mathrm{ess}}\big(\widetilde{\mathcal{H}}(\boldsymbol{X}) + P_{\mathrm{FR}}\big)\end{aligned}$$

is both compact and discrete and therefore finite. □

2.5.3 Fermi-Dirac Distribution and Grand Potential

Proof of Lemma 2.4. Firstly, we note that $F^\beta(\,\cdot\,)$ is analytic away from the simple poles at $\{z \in \mathbb{C}\colon 1 + e^{\beta(z-\mu)} = 0\} = \mu + i(2\mathbb{Z}+1)\pi\beta^{-1}$.

Moreover, extending $G^\beta(\,\cdot\,)$ into the complex plane amounts to choosing a branch cut of the complex logarithm. Therefore, for each $n \in \mathbb{Z}$, we define,

$$G_n^\beta(z) \coloneqq \frac{2}{\beta}\Big[\log\big|1 - F^\beta(z)\big| + i\mathrm{Arg}_n(1 - F^\beta(z))\Big] \quad \text{where} \tag{2.5.11}$$

$$\mathrm{Arg}_n(z) = \mathrm{Arg}(z) \pmod{2\pi} \quad \text{and} \quad \mathrm{Arg}_n(z) \in ((n-1)\pi, (n+1)\pi].$$

Choosing the principal branch of the complex logarithm, we get G_0^β which agrees with G^β on the real axis.

Now, $G_n^\beta(\,\cdot\,)$ is analytic on the set that avoids the branch cut of the complex logarithm and the non-analyticity of $1 - F^\beta$. That is, $G_n^\beta(\,\cdot\,)$ is analytic on

$$\begin{cases} \{z \in \mathbb{C}\colon 1 - F^\beta(z) \notin (-\infty, 0]\} \setminus \left\{\mu + \frac{(2k+1)\pi i}{\beta}\right\}_{k\in\mathbb{Z}} & \text{for } n \text{ even}, \\ \{z \in \mathbb{C}\colon 1 - F^\beta(z) \notin [0, \infty)\} \setminus \left\{\mu + \frac{(2k+1)\pi i}{\beta}\right\}_{k\in\mathbb{Z}} & \text{for } n \text{ odd}. \end{cases}$$

Rewriting $1 - F^\beta$ we obtain,

$$1 - F^\beta(z) = \frac{e^{\beta(z-\mu)}\big(1 + e^{\beta(\overline{z}-\mu)}\big)}{|1 + e^{\beta(z-\mu)}|^2} = \frac{e^{\beta(\mathrm{Re}(z)-\mu)}}{|1 + e^{\beta(z-\mu)}|^2}\Big(e^{i\beta\,\mathrm{Im}(z)} + e^{\beta(\mathrm{Re}(z)-\mu)}\Big). \tag{2.5.12}$$

The factor, $e^{\beta(\mathrm{Re}(z)-\mu)}|1 + e^{\beta(z-\mu)}|^{-2}$, is real and positive and so $1 - F^\beta(z)$

avoids the branch cut if and only if $h(z) \coloneqq e^{i\beta \operatorname{Im}(z)} + e^{\beta(\operatorname{Re}(z)-\mu)}$ does. Now, $h(z) \in (-\infty, 0]$ if and only if $\operatorname{Re}(z) \leqslant \mu$ and $\beta \operatorname{Im}(z) \in \pi(2\mathbb{Z}+1)$. On the other hand $h(z) \in [0, \infty)$ if and only if $\beta \operatorname{Im}(z) \in 2\pi\mathbb{Z}$.

In particular, we may conclude that G_0^β is analytic on

$$A_\beta^0 \coloneqq \Big\{ z \in \mathbb{C} \colon \operatorname{Re}(z) > \mu \Big\} \cup \Big\{ z \in \mathbb{C} \colon \beta \operatorname{Im}(z) \in (-\pi, \pi) \Big\}$$

and G_n^β (for $n \neq 0$) is analytic on the set

$$A_\beta^n \coloneqq \Big\{ z \in \mathbb{C} \colon \operatorname{Re}(z) < \mu,\, \beta \operatorname{Im}(z) \in ((n-1)\pi, (n+1)\pi) \Big\}.$$

Since $A_\beta^n \cap A_\beta^{n+1} = \{ z \in \mathbb{C} \colon \operatorname{Re}(z) < \mu,\, \beta \operatorname{Im}(z) \in (n\pi, (n+1)\pi) \}$, and by (2.5.12), we have that

$$\operatorname{Arg}_n(1 - F^\beta(z)) = \operatorname{Arg}_{n+1}(1 - F^\beta(z)) \in (n\pi, (n+1)\pi]$$

for all $z \in A_\beta^n \cap A_\beta^{n+1}$. That is, $G_n^\beta = G_{n+1}^\beta$ on $A_\beta^n \cap A_\beta^{n+1}$.

We may therefore consider the analytic continuation of G_n^β to $A_\beta^n \cup A_\beta^{n+1}$. We do this for each $n \in \mathbb{Z}$ and since $\bigcup_{n\in\mathbb{Z}} A_\beta^n = \mathcal{D}_\beta(\mu)$ this concludes the proof. □

We now denote by $z \mapsto G^\beta(z)$ the analytic continuation of (2.4.5) to $D_\beta(\mu)$.

Proof of Lemma 2.5. Since $\mathscr{C}_\beta$ are contained in a bounded set S, we can find a strip of width $r > 0$ about the real axis containing all $\mathscr{C}_\beta$. This means that for fixed $\beta > 0$, the number branches of the complex logarithm that we must consider, as in (2.5.11), in order to have extended G^β to the whole of S is at most a constant multiple of $\frac{r\beta}{\pi}$. This means that

$$\big|\operatorname{Arg}_n(1 - F^\beta(z))\big| \leqslant (n+1)\pi \leqslant Cr\beta$$

for all n such that $S \cap \{\beta \operatorname{Im}(z) \in ((n-1)\pi, (n+1)\pi)\} \neq \emptyset$ and $z \in A_\beta^n$. Therefore, for $z \in S$ and $\beta > 0$, we have that $\operatorname{Im}\big(G^\beta(z)\big)$ is bounded on S

independently of β.

Fix $\beta > \beta_0$. Now we show that, away from the singularities, $\operatorname{Re}\big(G^\beta(z)\big)$ is uniformly bounded. Since $\operatorname{Re}\big(G^\beta(z;\mu)\big) = 2\operatorname{Re}(z-\mu) - \frac{2}{\beta}\log\big|1+e^{\beta(z-\mu)}\big|$ and $2(z-\mu)$ is uniformly bounded on S, we conclude by showing

$$\tfrac{2}{\beta}\log\Big|1+e^{\beta(z-\mu)}\Big| \leqslant \tfrac{2}{\beta}\log\bigg(1+\exp\Big(\beta\sup_{z\in S}|\operatorname{Re}(z)-\mu|\Big)\bigg) \leqslant C$$

for some $C > 0$ depending only on S and β_0. Therefore, all that is left to show is that $|1+e^{\beta(z-\mu)}|$ is uniformly bounded below by a positive constant. If $\operatorname{Re}(z-\mu) < -c\beta^{-1}$ for some $c > 0$ then $|1+e^{\beta(z-\mu)}| \geqslant 1-e^{-c} > 0$ and if $\operatorname{Re}(z-\mu) > c\beta^{-1}$ then $|1+e^{\beta(z-\mu)}| \geqslant e^c - 1 > 0$. Moreover, if $|\beta\operatorname{Im}(z) - r| \geqslant \theta$ for all $r \in \mathbb{R}$ such that $|r| \geqslant \pi$, then $|1+e^{\beta(z-\mu)}| \geqslant \tan(\theta) > 0$. □

CHAPTER 3

Locality of Interatomic Interactions

in Linear Tight Binding Models

This chapter is based on the article [98] "Locality of interatomic forces in tight binding models for insulators" published in ESAIM: Mathematical Modelling and Numerical Analysis, 54(6): 2295-2318 (2020). This paper is co-authored by Huajie Chen, who ran the numerical simulations, and Christoph Ortner.

3.1 Introduction

A starting assumption in most interatomic potential (IP) models for materials is that the potential energy landscape (PEL) can be decomposed into site energies, i.e. contributions from individual atoms that depend only on a small neighbourhood.

Partial justification for this assumption was given in [26, 29] for linear tight binding models at finite Fermi-temperature. In particular, it was shown that the grand potential has the site energy decomposition $\sum_\ell G_\ell^\beta(\boldsymbol{X})$ where the

site contributions G_ℓ^β, defined in (2.4.5), are *local*:

$$\left| \frac{\partial G_\ell^\beta(\boldsymbol{X})}{\partial \boldsymbol{r}_k} \right| \lesssim e^{-\eta\, r_{\ell k}} \tag{3.1.1}$$

for some $\eta > 0$. Similar estimates hold for higher derivatives.

However, one expects (and this is made precise in this chapter) that the exponent η in (3.1.1), which measures the interatomic interaction range, in general satisfies $\eta \sim \beta^{-1}$. This means that, for moderate to low temperature regimes (e.g. room temperature), the practical value of (3.1.1) is limited. The main purpose of this chapter is to demonstrate that, for insulators, the presence of a spectral gap significantly improves the estimate. Specifically, we consider a linear tight-binding model at either zero or finite Fermi-temperature, with electrons in a grand-canonical ensemble. In this setting we prove that (3.1.1) holds with η independent of β but instead η is linear in the spectral gap.

Moreover, we demonstrate that "pollution" of the spectral gap by a point spectrum caused by local defects in the crystal, affects only the pre-factors, but not the exponent η in (3.1.1). We therefore significantly strengthen the estimates of [26, 29] to the case of insulating multi-lattice materials in the presence of point defects as well as extending the results to zero Fermi-temperature models.

3.2 General Locality Estimates

With the notation of Chapter 2, we have the following locality estimates for general systems at finite Fermi-temperature or insulators at zero Fermi-temperature. Recall from Appendix A that $\|O\|_{\mathscr{C}} := \frac{\mathrm{len}(\mathscr{C})}{2\pi} \sup_{z\in\mathscr{C}} |O(z)|$ denotes the contour norm.

Theorem 3.1. *Suppose that $\boldsymbol{X}$ and O satisfy Definitions 2.2 and 2.4, respectively. Then, for $1 \leqslant j \leqslant \nu$, there exist positive constants C_j and η_j such*

that

$$\left|\frac{\partial^j O_\ell(\boldsymbol{X})}{\partial \boldsymbol{X}_{m_1}\dots\partial \boldsymbol{X}_{m_j}}\right| \leqslant C_j\|O\|_{\mathscr{C}} e^{-\eta_j \sum_{l=1}^{j} r_{\ell m_l}} \tag{3.2.1}$$

for any $\ell, m_1, \dots, m_j \in \Lambda$. *Moreover,* $C_j \sim \mathfrak{d}^{-(j+1)}$ *and* $\eta_j \sim \mathfrak{d}$ *as* $\mathfrak{d} \to 0$ *where* $\mathfrak{d}$ *is the constant from* (2.4.2) *applied to* O.

Remark 3.1. *In the case* $O = F^\beta$ *or* G^β, *we may choose* $\mathscr{C}$ *(depending on* β*) so that* $\|O\|_{\mathscr{C}}$ *is independent of* β *(Lemma 2.5) and* $\mathfrak{d} \geqslant c\big(\beta^{-1} + \operatorname{dist}(\mu, I_- \cup I_+)\big)$ *for some fixed constant* $c > 0$. *In particular, we have* (3.2.1) *with* $\eta_j \sim \beta^{-1} + \mathsf{g}$ *as* $\beta^{-1} + \mathsf{g} \to 0$ *as long as the* $\mathsf{g} \to 0$ *limit is approached symmetrically about* μ.

Sketch of the Proof. The estimate (3.2.1) for some $C_j, \eta_j > 0$ was previously known [29, Theorem 10] for functions O analytic in a neighbourhood of $[\underline{\sigma}, \overline{\sigma}]$ (in particular, for $O = F^\beta$ or G^β at finite Fermi-temperature). Here, we carefully track the $\mathfrak{d}$ dependence in the estimates and, in particular, extend the results to the zero Fermi-temperature case (i.e. $O = F^\infty$ or G^∞ for insulators).

The exponents in these estimates depend on the distance between the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ and the integration contour $\mathscr{C}$ as in (2.4.1), see Figure 2.3 for a schematic plot of such a contour. Therefore, the asymptotic behaviour of these constants comes from the analyticity of O (see Lemma 2.4) and the spectral gap (see Definition 2.2). We give a full proof in §3.6.1 below. □

3.3 Locality Estimates for Point Defects

In this section, we consider a reference configuration $\boldsymbol{X}$ and corresponding *point defect reference configurations* $\boldsymbol{X}^{\mathrm{d}}$ arising as in $(\mathbf{P}_\delta)$. Moreover, we use the notation from Definition 2.2.

Proposition 2.3 allows us to approximate $\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})$ as a finite rank update of the reference Hamiltonian $\mathcal{H}(\boldsymbol{X})$. This means we can apply the existing locality estimates of Theorem 3.1 on the reference spectrum. The approximation does not affect the exponent in the estimates and only increases the constant pre-factor. We show that the pre-factor may be chosen to depend on the atomic

sites and this converges to the corresponding pre-factor in the defect-free case, as we send the atomic sites away from the defect core. That is, away from the defect, the locality estimates resemble the corresponding estimates for the reference configuration.

Theorem 3.2. *Fix $(\boldsymbol{X}, \boldsymbol{X}^{\rm d})$ and O satisfying Definitions 2.2 and 2.4, respectively, and the constants (C_j, η_j) from Theorem 3.1 when applied to $O(\boldsymbol{X})$. Then, for $1 \leqslant j \leqslant \nu$, $\ell \in \Lambda^{\rm d}$, and $\boldsymbol{m} = (m_1, \dots, m_j) \in (\Lambda^{\rm d})^j$, there exist positive constants $C_j^{\rm d} = C_j^{\rm d}(\ell, \boldsymbol{m})$ such that*

$$\left| \frac{\partial^j O_\ell(\boldsymbol{X}^{\rm d})}{\partial \boldsymbol{X}^{\rm d}_{m_1} \dots \partial \boldsymbol{X}^{\rm d}_{m_j}} \right| \leqslant C_j^{\rm d} \|O\|_{\mathscr{C}} e^{-\eta_j \sum_{l=1}^j r_{\ell m_l}} \tag{3.3.1}$$

Moreover, $C_j^{\rm d}(\ell, \boldsymbol{m})$ is uniformly bounded independently of $(\ell, \boldsymbol{m})$ and, if $\ell, m_1, \dots, m_j \in B_R(\xi)$ for some $R > 0$, then $C_j^{\rm d}(\ell, \boldsymbol{m}) \to C_j$ as $|\xi| \to \infty$, with an exponential rate.

Remark 3.2. *In the $j = 1$ case, we have*

$$\left| C_1^{\rm d}(\ell, m) - C_1 \right| \lesssim e^{-\eta_1 [|\boldsymbol{r}_\ell| + |\boldsymbol{r}_m| - |\boldsymbol{r}_{\ell m}|]}.$$

For higher derivatives, the relationship between ℓ and $\boldsymbol{m}$ is more complicated.

3.4 Numerical Experiments

In the following numerical simulations, we use the NRL tight binding model [32, 91, 99] to test the force-locality in bulk carbon and silicon, both with and without an interstitial defect. Since we are unaware of established codes that compute site energies and their derivatives, these models were implemented in the `Julia` package `SKTB.jl` [28]. The implementation was tested against an NRL tight binding implementation in the QUIP package [13].

3.4.1 The NRL Tight Binding Model

The NRL tight binding model, developed by Cohen, Mehl, and Papaconstantopoulos [32], is slightly more general than our formulation in **(TB)**. Since this model is non-orthogonal, the energy levels are now determined by the following generalised eigenvalue problem

$$\mathcal{H}(\boldsymbol{X})\psi_s = \lambda_s S(\boldsymbol{X})\psi_s \qquad \text{where} \qquad \psi_s^{\mathrm{T}} S(\boldsymbol{X})\psi_s = 1. \tag{3.4.1}$$

Furthermore, the NRL Hamiltonian and overlap matrices are constructed both from hopping elements as in (6.3.1) as well as on-site matrix elements as a function of the local environment. For carbon and silicon they are parameterised as follows (for other elements the parameterisation is similar): To define the on-site terms, each atom ℓ is assigned a pseudo-atomic density

$$\rho_\ell := \sum_k e^{-\lambda^2 r_{\ell k}} f_{\mathrm{c}}(r_{\ell k}),$$

where λ is a fitting parameter, f_{c} is the cutoff function

$$f_c(r) := \frac{\theta(R_{\mathrm{c}} - r)}{1 + \exp\big((r - R_{\mathrm{c}})/l_c + L_c\big)},$$

with θ the Heaviside step function, and the parameters $l_c = 0.5$, $L_c = 5.0$ for most elements. Although, in principle, the on-site terms should have off-diagonal elements, the NRL model follows traditional practice and only include the diagonal terms. Then, the on-site terms for each atomic site ℓ are given by

$$\mathcal{H}(\boldsymbol{X})_{\ell\ell}^{\upsilon\upsilon} := a_\upsilon + b_\upsilon \rho_\ell^{2/3} + c_\upsilon \rho_\ell^{4/3} + d_\upsilon \rho_\ell^2, \tag{3.4.2}$$

where $\upsilon = s, p,$ or d is the index for angular-momentum-dependent atomic orbitals and (a_υ), (b_υ), (c_υ), (d_υ) are fitting parameters. The on-site elements for the overlap matrix are simply taken to be the identity matrix.

The off-diagonal NRL Hamiltonian entries follow the formalism of Slater and Koster who showed in [112] that all two-centre (spd) hopping integrals can

be constructed from ten independent "bond integral" parameters $h_{\upsilon\upsilon'\mu}$, where

$$(\upsilon\upsilon'\mu) = ss\sigma,\ sp\sigma,\ pp\sigma,\ pp\pi,\ sd\sigma,\ pd\sigma,\ pd\pi,\ dd\sigma,\ dd\pi,\ \text{and}\ dd\delta.$$

The NRL bond integrals are given by

$$h_{\upsilon\upsilon'\mu}(r) := \left(e_{\upsilon\upsilon'\mu} + f_{\upsilon\upsilon'\mu}r + g_{\upsilon\upsilon'\mu}r^2\right)e^{-i_{\upsilon\upsilon'\mu}r}f_{\mathrm{c}}(r) \tag{3.4.3}$$

with fitting parameters $e_{\upsilon\upsilon'\mu}, f_{\upsilon\upsilon'\mu}, g_{\upsilon\upsilon'\mu}, i_{\upsilon\upsilon'\mu}$. The matrix elements $\mathcal{H}(\boldsymbol{X})^{\upsilon\upsilon'}_{\ell k}$ are constructed from the $h_{\upsilon\upsilon'\mu}(r)$ by a standard procedure [112].

The bond integral parameterisation of the overlap matrix is given by

$$s_{\upsilon\upsilon'\mu}(r) := \left(\delta_{\upsilon\upsilon'} + j_{\upsilon\upsilon'\mu}r + k_{\upsilon\upsilon'\mu}r^2 + l_{\upsilon\upsilon'\mu}r^3\right)e^{-m_{\upsilon\upsilon'\mu}r}f_{\mathrm{c}}(r) \tag{3.4.4}$$

with the fitting parameters $j_{\upsilon\upsilon'\mu}, k_{\upsilon\upsilon'\mu}, l_{\upsilon\upsilon'\mu}, m_{\upsilon\upsilon'\mu}$.

The fitting parameters in the foregoing expressions are determined by fitting to high-symmetry first-principle calculations. In the NRL method, a database of eigenvalues (band structures) and total energies was constructed for several crystal structures at several volumes. Then the parameters are chosen such that the eigenvalues and energies in the database are reproduced to within some acceptable tolerance. For practical simulations, the parameters for different elements can be found in [99].

3.4.2 Test systems

Our two test systems are diamond cubic bulk carbon and bulk silicon, which provide ideal test cases of our theory due to their clearly defined band gaps. Since carbon has a much larger band gap than silicon we will also be able to test how this affects locality of interaction.

For both elements, we simulate a supercell model consisting of $5 \times 5 \times 5$ diamond cubic unit cells, containing 1000 atoms in total. First, we use the NRL tight binding model to relax the cells to their ground states (this only rescales the cells but does not change their shape). We then compute the band

structures which are, respectively, shown in Figures 3.1 and 3.2. We verified our implementation by comparing the band structure for the silicon model against that published in [100]. The chemical potential is chosen to be the mid-point between the highest occupied state and the lowest unoccupied state of the 1000-atom system. For both systems, we observe clearly defined band gaps, approximately 0.98 eV for Si and 3.83 eV for C.

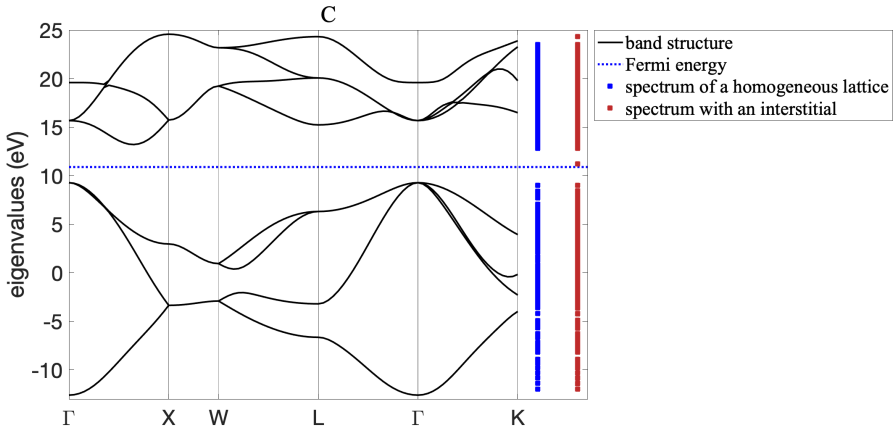


Figure 3.1: Band structure of C; spectrum of the homogeneous lattice (supercell approximation) and defective system.

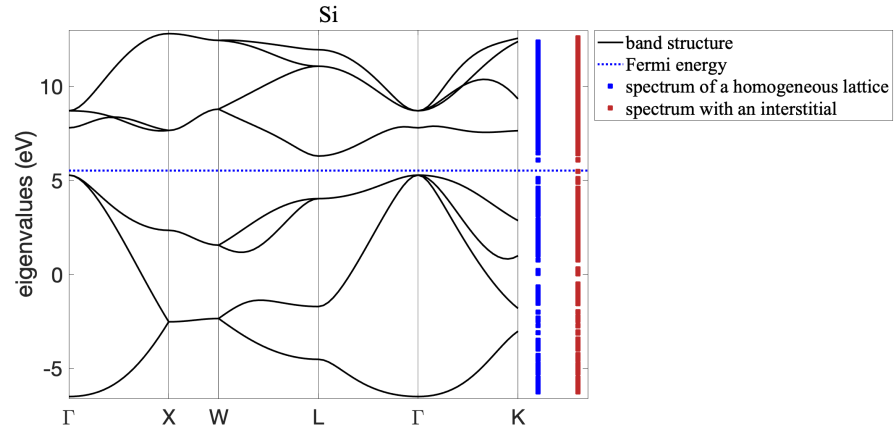


Figure 3.2: Band structure of Si, spectrum of the homogeneous lattice (supercell approximation) and defective system.

Next, we create a self-interstitial near the origin, and observe (in Figures 3.1 and 3.2) the expected pollution of the band gap in the defect system. By tweaking the position of the interstitial we are able to create configurations where an eigenvalue is arbitrarily close to the chemical potential in order to

provide a challenging situation to confirm the result of Theorem 3.2.

3.4.3 Site energy locality

To test the locality of interatomic interaction we evaluate all first and second site energy derivatives $G_{\ell,j} = \partial_{\boldsymbol{r}_j} G_\ell$ and $G_{\ell,ij} = \partial_{\boldsymbol{r}_i}\partial_{\boldsymbol{r}_j} G_\ell$ in both the homogeneous and defective system, and plot the data points

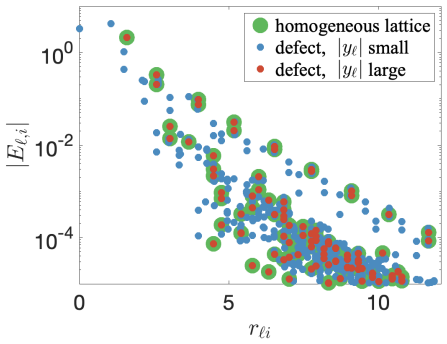
$$\big(r_{\ell j}, |G_{\ell,j}|\big) \qquad \text{and} \qquad \big(r_{\ell i} + r_{\ell j}, |G_{\ell,ij}|\big)$$

in Figures 3.3 and 3.4. For the homogeneous systems all sites are equivalent, hence we only plot the site energy derivatives for a single site. For the defective systems we plot the data points for the interstitial site itself ("$|\boldsymbol{r}_\ell|$ small") as well as for the site in the computational cell that has the largest distance to the interstitial atom ("$|\boldsymbol{r}_\ell|$ large").

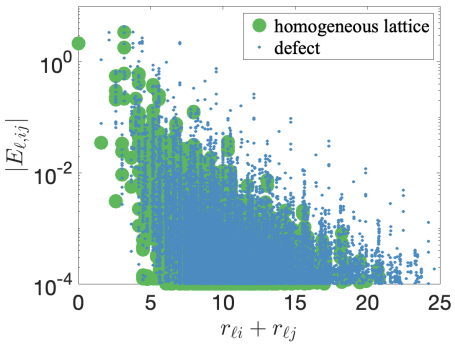
We clearly observe the exponential decay of interaction strength as predicted in Theorem 3.2. Moreover, we also observe that for sites ℓ far from the defect the site derivative decay perfectly matches that of the bulk system.

Two additional observations were unexpected for us: (1) the decay of site derivatives for "near-defect sites" does not exhibit the increased prefactor that we predicted; however we do see this increase in the second derivatives. (2) the decay of interaction in the silicon system is nearly identical (after rescaling by the lattice constants) to the carbon system even though silicon has a much smaller band gap.

These observations suggest that there are further effects leading to improved locality of interaction that our analysis does not fully capture. While a possible explanation is that the locality of the bond integral functions dominates the locality of the resolvents, this does not explain the excellent locality of the Si systems which have a fairly small band gap.

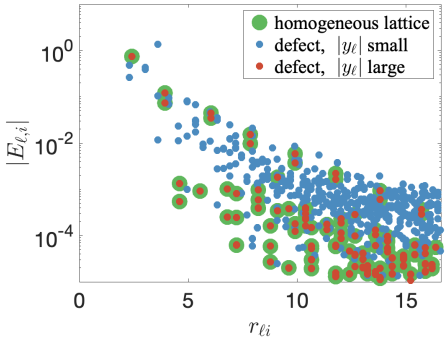


(a) Decay of site energy derivatives.

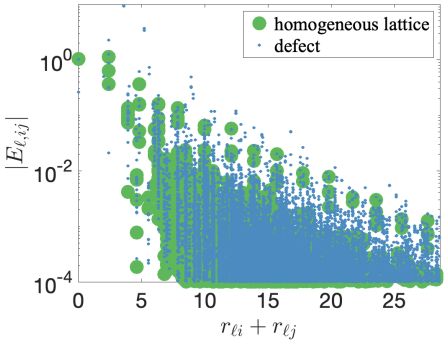


(b) Decay of site energy hessians.

Figure 3.3: Carbon: Locality of site energies in homogeneous lattice and defective system.



(a) Decay of site energy derivatives.



(b) Decay of site energy hessians.

Figure 3.4: Silicon: Locality of site energies in homogeneous lattice and defective system.

3.4.4 Force Locality

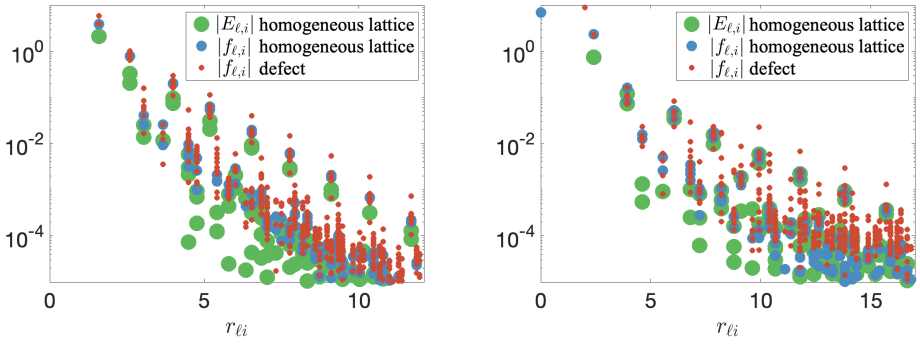
Finally, we compare the decay of site energy derivatives to the decay of force derivatives. The reason for this additional test is that our definition of a site-energy is somewhat arbitrary. Indeed, there are infinitely many possible decompositions of total energy $\mathcal{G} = \sum_\ell G_\ell$ into site energies and each choice may lead to a different rate of decay of the interaction. Forces, on the other hand, are uniquely defined.

In Figure 3.5, we compare the decay of site energy derivatives and force derivatives. We evaluate the force derivatives $f_{\ell,j} = \partial_{\boldsymbol{r}_j} f_\ell$, where the force is defined by the (negative) derivative of the total energy $f_\ell = -\partial_{\boldsymbol{r}_\ell} \mathcal{G}$, and plot

the data points

$$\big(r_{\ell j}, |f_{\ell,j}|\big) \qquad \text{and} \qquad \big(r_{\ell i} + r_{\ell j}, |G_{\ell,ij}|\big)$$

in Figures 3.5. We observe that the site energy locality matches force locality very closely, which suggests that our choice of site energies leads to near-optimal locality of interaction.



(a) Carbon. (b) Silicon.

Figure 3.5: The decay of force derivatives in homogeneous lattice and defective system.

3.5 Conclusions

In this chapter, we have extended existing locality estimates [29] to insulators at zero Fermi-temperature. We have described a site energy decomposition for a zero Fermi-temperature linear tight binding model and shown that the site contributions are exponentially localised. Most importantly, we have shown that the exponents in these estimates are independent of the discrete spectrum inside the band gap caused by point defects, and even the pre-factors converge to the pre-factors that would result from using the homogeneous site energy in the estimates, as the distance of a site to the defect increases. Our numerical results strongly support our analysis, but also point to possible further extensions in particular in the limit of small band gaps where our results may not yet be sharp.

The results of this chapter allow the formulation of zero Fermi-temperature

lattice relaxation as a variational problem on the energy space of displacements analogous to the finite Fermi-temperature problem of [26]. Results regarding the zero Fermi-temperature limit in these geometry optimisation problems are presented in Chapter 6.

3.6 Proof of the Main Results

3.6.1 General Locality Estimates: Proof of Theorem 3.1

Using the resolvent calculus formulation (2.4.1), it suffices to prove that derivatives of the resolvent operators are local. That is, since

$$\left|\frac{\partial^j O_\ell(\boldsymbol{X})}{\partial \boldsymbol{X}_{m_1}\dots\partial \boldsymbol{X}_{m_j}}\right| \leqslant \|O\|_{\mathscr{C}} \sup_{z\in\mathscr{C}}\left|\frac{\partial^j \mathscr{R}_z(\boldsymbol{X})_{\ell\ell}}{\partial \boldsymbol{X}_{m_1}\dots\partial \boldsymbol{X}_{m_j}}\right|, \tag{3.6.1}$$

where $\|O\|_{\mathscr{C}} \coloneqq \frac{\operatorname{len}\mathscr{C}}{2\pi}\sup_{z\in\mathscr{C}}|O(z)|$ and $\mathscr{R}_z(\boldsymbol{X}) \coloneqq \big(\mathcal{H}(\boldsymbol{X})-z\big)^{-1}$.

In order to show that derivatives of the *resolvent* $\mathscr{R}_z(\boldsymbol{X})$ are local, we start by stating the following Combes–Thomas [33] estimate (which we state for general operators because we will later apply it to the stability operator, introduced in Chapter 5):

Lemma 3.3 (Combes–Thomas)**.** *Suppose that $A\colon \ell^2(\Lambda;\mathbb{R}^n)\to\ell^2(\Lambda;\mathbb{R}^n)$ is a invertible bounded linear operator with the off-diagonal decay $|A_{\ell k}|\leqslant c_A e^{-\gamma_A r_{\ell k}}$ for some $c_A,\gamma_A>0$. Then, for $\mathfrak{d}\coloneqq\inf_{\lambda\in\sigma(A)}|\lambda|$, we have*

$$\big|\big[A^{-1}\big]_{\ell k}\big| \leqslant 2\mathfrak{d}^{-1}e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})r_{\ell k}},$$

where $\gamma_{\mathrm{CT}}(\mathfrak{d})\coloneqq c_0\gamma_A\min\Big\{1,\frac{\gamma_A^d}{c_A}\mathfrak{d}\Big\}$ and $c_0>0$ depends only on $\mathfrak{m}$ and d.

Remark 3.3. *We obtain the estimate for the resolvents $\big(\mathcal{H}-z\big)^{-1}$ in* (3.6.1) *by setting $A\coloneqq\mathcal{H}-z$ and $\mathfrak{d}\coloneqq\mathfrak{d}_O$ from* (2.4.2)*.*

Proof. The estimate follows the proof of [29, Lemma 6] (or the main ideas of [45]), however, to obtain the explicit $\mathfrak{d}$-dependence in the exponent, we require sharper bounds. We sketch the argument for completeness.

First, we observe that if $\|I - A^{-1}B\|_{\ell^2\to\ell^2} \leqslant \frac{1}{2}$, then B is necessarily invertible on ℓ^2 with $|[B^{-1}]_{\ell k}| \leqslant \|B^{-1}\|_{\ell^2\to\ell^2} \leqslant 2\|A^{-1}\|_{\ell^2\to\ell^2} \leqslant \frac{2}{\mathfrak{d}}$. The final inequality follows from $\|A^{-1}\|_{\ell^2\to\ell^2} = \sup_{\lambda\in\sigma(A)} |\lambda^{-1}| \leqslant \frac{1}{\mathfrak{d}}$. In particular, if B given by $B_{\ell k} \coloneqq e^{\gamma_{\mathrm{CT}} r_{\ell k_0}} A_{\ell k} e^{-\gamma_{\mathrm{CT}} r_{k k_0}}$ for some $k_0 \in \Lambda$ and $\gamma_{\mathrm{CT}} > 0$ sufficiently small such that $\|B-A\|_{\ell^2\to\ell^2} \leqslant \frac{1}{2}\mathfrak{d}$, then we obtain $|[A^{-1}]_{\ell k}| \leqslant \frac{2}{\mathfrak{d}} e^{-\gamma_{\mathrm{CT}}[r_{\ell k_0} - r_{k k_0}]}$. The result follows by choosing $k_0 = k$.

Proof of $\|B-A\|_{\ell^2\to\ell^2} \leqslant \frac{1}{2}\mathfrak{d}$. We consider the $\ell^\infty \to \ell^\infty$ operator norm and note that the exact same arguments work for $\ell^1 \to \ell^1$, therefore by interpolation, the same bound holds for $\ell^2 \to \ell^2$. We have

$$\|B - A\|_{\ell^\infty\to\ell^\infty} \leqslant c_A \sup_{\ell\in\Lambda} \sum_{k\in\Lambda} e^{-\gamma_A r_{\ell k}} \big(e^{\gamma_{\mathrm{CT}} r_{\ell k}} - 1\big). \tag{3.6.2}$$

Now for fixed ℓ, the function $\theta(\gamma_{\mathrm{CT}}) \coloneqq \sum_{k\in\Lambda} e^{-\gamma_A r_{\ell k}} \big(e^{\gamma_{\mathrm{CT}} r_{\ell k}} - 1\big)$ satisfies $\theta(0) = 0$ and is differentiable on $[0, \frac{1}{2}\gamma_A]$ with $|\theta'| \leqslant \frac{C_{\mathfrak{m},d}^{-1}}{\gamma_A^{d+1}}$ where $C_{\mathfrak{m},d}$ is a constant depending on $\mathfrak{m}$ and d. In particular, we have

$$\|B - A\|_{\ell^2\to\ell^2} \leqslant \frac{c_A}{C_{\mathfrak{m},d}\gamma_A^{d+1}} \gamma_{\mathrm{CT}}$$

for all $\gamma_{\mathrm{CT}} \leqslant \frac{1}{2}\gamma_A$. We conclude by choosing $\gamma_{\mathrm{CT}} \coloneqq \frac{1}{2}\gamma_A \min\Big\{1, \frac{C_{\mathfrak{m},d}\gamma_A^d}{c_A}\mathfrak{d}\Big\} \geqslant c_1\gamma_A \min\{1, c_A^{-1}\gamma_A^d\mathfrak{d}\}$. □

We are now ready to conclude the proof of Theorem 3.1. For $z \in \mathbb{C}$ with $\operatorname{dist}\big(z, \sigma\big(\mathcal{H}(\boldsymbol{X})\big)\big) \geqslant \mathfrak{d} > 0$, we define $\mathscr{R}_z \coloneqq \big(\mathcal{H}(\boldsymbol{X}) - z\big)^{-1}$, and obtain

$$\begin{aligned}
\left|\frac{\partial[\mathscr{R}_z]_{\ell\ell}}{\partial \boldsymbol{X}_m}\right| &= \left|\left[\mathscr{R}_z \frac{\partial \mathcal{H}}{\partial \boldsymbol{X}_m} \mathscr{R}_z\right]_{\ell\ell}\right| \\
&\leqslant C \sum_{kn} \mathfrak{d}^{-2} e^{-\gamma_{\mathrm{CT}}[r_{\ell k} + r_{n\ell}]} e^{-\gamma_1[r_{km} + r_{mn}]} \\
&\leqslant C\mathfrak{d}^{-2}\gamma_1^{-2d} e^{-\min\{\gamma_{\mathrm{CT}},\gamma_1\} r_{\ell m}}.
\end{aligned} \tag{3.6.3}$$

Similarly, for the second derivatives,

$$\frac{\partial^2[\mathscr{R}_z]_{\ell\ell}}{\partial \boldsymbol{X}_{m_1}\partial \boldsymbol{X}_{m_2}} = \Big[\mathscr{R}_z\frac{\partial \mathcal{H}}{\partial \boldsymbol{X}_{m_1}}\mathscr{R}_z\frac{\partial \mathcal{H}}{\partial \boldsymbol{X}_{m_2}}\mathscr{R}_z - \mathscr{R}_z\frac{\partial^2 \mathcal{H}}{\partial \boldsymbol{X}_{m_1}\partial \boldsymbol{X}_{m_2}}\mathscr{R}_z + \mathscr{R}_z\frac{\partial \mathcal{H}}{\partial \boldsymbol{X}_{m_2}}\mathscr{R}_z\frac{\partial \mathcal{H}}{\partial \boldsymbol{X}_{m_1}}\mathscr{R}_z\Big]_{\ell\ell}. \tag{3.6.4}$$

Each of the terms in (3.6.4) can be bounded separately:

$$\begin{aligned}
&\left|\left[\mathscr{R}_z\frac{\partial \mathcal{H}}{\partial \boldsymbol{X}_{m_1}}\mathscr{R}_z\frac{\partial \mathcal{H}}{\partial \boldsymbol{X}_{m_2}}\mathscr{R}_z\right]_{\ell\ell}\right| \\
&\quad\leqslant C\mathfrak{d}^{-3}\sum_{\ell_1,\ell_2,\ell_3,\ell_4\in\Lambda} e^{-\gamma_{\mathrm{CT}}\left(r_{\ell\ell_1}+r_{\ell_2\ell_3}+r_{\ell_4\ell}\right)}e^{-\gamma_1\left(r_{\ell_1 m_1}+r_{m_1\ell_2}+r_{\ell_3 m_2}+r_{m_2\ell_4}\right)} \\
&\quad\leqslant C\mathfrak{d}^{-3}e^{-\frac{1}{2}\min\{\gamma_{\mathrm{CT}},\gamma_1\}\left(r_{\ell m_1}+r_{m_1 m_2}+r_{m_2\ell}\right)}
\end{aligned} \tag{3.6.5}$$

and

$$\begin{aligned}
&\left|\left[\mathscr{R}_z\frac{\partial^2 \mathcal{H}}{\partial \boldsymbol{X}_{m_1}\partial \boldsymbol{X}_{m_2}}\mathscr{R}_z\right]_{\ell\ell}\right| \\
&\quad\leqslant C\mathfrak{d}^{-2}\sum_{\ell_1,\ell_2\in\Lambda} e^{-\gamma_{\mathrm{CT}}\left(r_{\ell\ell_1}+r_{\ell_2\ell}\right)}e^{-\gamma_2\left(r_{\ell_1 m_1}+r_{m_1\ell_2}+r_{\ell_1 m_2}+r_{m_2\ell_2}\right)} \\
&\quad\leqslant C\mathfrak{d}^{-2}e^{-\frac{1}{2}\min\{\gamma_{\mathrm{CT}},\gamma_2\}\left(r_{\ell m_1}+r_{m_1 m_2}+r_{m_2\ell}\right)}.
\end{aligned} \tag{3.6.6}$$

For higher derivatives the same arguments can be made and analogous estimates hold.

To conclude the proof of Theorem 3.1 for $O = F^\beta$ or G^β, we apply (3.6.1) with an appropriately chosen contour $\mathscr{C}$ (depending on β and the spectral gap g). Provided the limit $\mathsf{g}\to 0$ is approached symmetrically about μ, the distance $\mathfrak{d}$ may be chosen to be linear in both β^{-1} and g as $\beta^{-1}+\mathsf{g}\to 0$, see Figure 2.3. Here, we apply Lemma 2.5 to conclude that the prefactor $\|O\|_{\mathscr{C}}$ may be chosen to be β independent in the zero Fermi-temperature limit for both $O = F^\beta$ and G^β.

3.6.2 Point Defects: Proof of Theorem 3.2

We first prove an improved Combes–Thomas resolvent estimate for finite rank updates (which, in particular, applies to $\mathcal{H}(\boldsymbol{X}) + P_\varepsilon$ from Lemma 2.3 and thus

gives improved resolvent estimates for $\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})$):

Lemma 3.4 (Improved Combes–Thomas)**.** *Suppose that $A, P\colon \ell^2(\Lambda;\mathbb{R}^n) \to \ell^2(\Lambda;\mathbb{R}^n)$ are bounded linear operators such that A and $A+P$ are invertible, $|A_{\ell k}| \leqslant c_A e^{-\gamma_A r_{\ell k}}$, and $P_{\ell k} = 0$ if $|\boldsymbol{r}_\ell| > R$ or $|\boldsymbol{r}_k| > R$ for some $R > 0$. Then, for $\mathfrak{d} \coloneqq \inf_{\lambda\in\sigma(A)} |\lambda|$ and $\mathfrak{d}^{\mathrm{d}} \coloneqq \inf_{\lambda\in\sigma(A+P)} |\lambda|$, we have*

$$\left|\left[(A+P)^{-1}\right]_{\ell k}\right| \leqslant 2\mathfrak{d}^{-1} e^{-\gamma_{\mathrm{CT}}(\mathfrak{d}) r_{\ell k}} + c_P e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})[|\boldsymbol{r}_\ell| + |\boldsymbol{r}_k|]}, \tag{3.6.7}$$

where $\gamma_{\mathrm{CT}}(\mathfrak{d})$ is the constant from Lemma 3.3 when applied to A and $c_P > 0$ depends on $\mathfrak{d}^{\mathrm{d}}$.

Remark 3.4. *This result applies to $A \coloneqq \mathcal{H}(\boldsymbol{X}) + P_\varepsilon - z$ and $P \coloneqq P_{\mathrm{FR}}$ where $P_\varepsilon, P_{\mathrm{FR}}$ are from Lemma 2.3. Since $A + P = \mathcal{H}(\boldsymbol{X}^{\mathrm{d}}) - z$, we may choose $\mathfrak{d}$ and $\mathfrak{d}^{\mathrm{d}}$ as in Definition 2.4.*

Proof. First, we note that $(A+P)^{-1} - A^{-1} = (A+P)^{-1}[A - (A+P)]A^{-1}$, $I + PA^{-1}$ is invertible with inverse $A(A+P)^{-1}$, and $I + A^{-1}P$ is invertible with inverse $(A+P)^{-1}A$. In particular, we have

$$(A+P)^{-1} = A^{-1} - A^{-1}(I + PA^{-1})^{-1} PA^{-1} \tag{3.6.8}$$

$$= A^{-1} - A^{-1}P(I + A^{-1}P)^{-1} A^{-1}, \tag{3.6.9}$$

and $[(I+PA^{-1})^{-1}P]_{\ell k} = [P(I+A^{-1}P)^{-1}]_{\ell k} = 0$ if $|\boldsymbol{r}_\ell| > R$ or $|\boldsymbol{r}_k| > R$.

Therefore, applying the standard Combes–Thomas estimate (Lemma 3.3) to A, we obtain

$$\begin{aligned}\left|\left[(A+P)^{-1}\right]_{\ell k}\right| &\leqslant 2\mathfrak{d}^{-1} e^{-\gamma_{\mathrm{CT}}(\mathfrak{d}) r_{\ell k}} \\ &\quad + 4\mathfrak{d}^{-2} \left\|(I + PA^{-1})^{-1}P\right\|_{\max} \sum_{\substack{\ell_1,\ell_2\colon \\ |\boldsymbol{r}_\ell|, |\boldsymbol{r}_k| \leqslant R}} e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})\left[r_{\ell\ell_1} + r_{\ell_2 k}\right]}.\end{aligned}$$

We conclude by bounding $\left\|(I + PA^{-1})^{-1}P\right\|_{\max} = \left\|A(A+P)^{-1}P\right\|_{\max}$: for

fixed ℓ, k, we have

$$\begin{aligned}\left|\left[A(A+P)^{-1}P\right]_{\ell k}\right| &\leqslant 2c_A(\mathfrak{d}^{\mathrm{d}})^{-1} \sum_{\ell_1,\ell_2\colon |\boldsymbol{r}_{\ell_2}|\leqslant R} e^{-\gamma_A r_{\ell\ell_1}} e^{-\gamma_{\mathrm{CT}}(\mathfrak{d}^{\mathrm{d}})r_{\ell_1\ell_2}} |P_{\ell_2 k}| \\ &\lesssim_R c_A(\mathfrak{d}^{\mathrm{d}})^{-1}\gamma_A^{-d}\|P\|_{\max}, \end{aligned} \tag{3.6.10}$$

where $\gamma_{\mathrm{CT}}(\mathfrak{d}^{\mathrm{d}})$ is the Combes–Thomas exponent from Lemma 3.3 when applied to $A+P$. □

We are now ready to combine Lemma 3.4 (applied to $A \coloneqq \mathcal{H}(\boldsymbol{X}) + P_\varepsilon - z$ and $P \coloneqq P_{\mathrm{FR}}$ as in Remark 3.4) together with the general estimate (4.2.2) to prove Theorem 3.2. Directly applying Lemma 3.4, we have

$$\left|\left[\left(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}}) - z\right)^{-1}\right]_{\ell k}\right| \leqslant \left(2\mathfrak{d}^{-1} + c_P\right) e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})r_{\ell k}}$$

In particular, we may apply the exact same arguments as in §3.6.1 to obtain locality estimates with defect-independent exponents but with increased prefactors.

We now show that the prefactors in these improved estimates converge to the corresponding defect-free prefactors as the subsystem containing ℓ and $m_1, \ldots, m_j$ move away from the defect core.

The improved resolvent estimate of Lemma 3.4 is given as the sum of the resolvent estimate from the defect-free case $2\mathfrak{d}^{-1}e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})r_{\ell k}}$ and the additional term $c_P e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_k|]}$. Therefore, we may bound quantities such as (3.6.3), (3.6.5), and (3.6.6) for $\mathscr{R}_z \coloneqq \left(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}}) - z\right)^{-1}$ by the sum of the corresponding quantity in the defect-free case, and terms that arise by replacing estimates of the form $2\mathfrak{d}^{-1}e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})r_{\ell k}}$ with $c_P e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_k|]}$. That is, we replace an exponential depending on the length of the path between $\boldsymbol{r}_\ell$ and $\boldsymbol{r}_k$ with an exponential depending on the length of the path between $\boldsymbol{r}_\ell$ and $\boldsymbol{r}_k$ which also visits $0 \in \mathbb{R}^d$ in-between.

For example, first derivatives of the resolvent $\mathscr{R}_z \coloneqq \left(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}}) - z\right)^{-1}$ may be bounded above by the sum of (3.6.3) and a constant multiple (depending

on c_P and $\mathfrak{d}$ but independent of ℓ, m) of

$$\sum_{kn}\Big[e^{-\eta_1[|\boldsymbol{r}_k|+r_{n\ell}]}+e^{-\eta_1[r_{\ell k}+|\boldsymbol{r}_n|]}+e^{-\eta_1[|\boldsymbol{r}_k|+|\boldsymbol{r}_n|+|\boldsymbol{r}_\ell|]}\Big]e^{-\eta_1[|\boldsymbol{r}_\ell|+r_{km}+r_{mn}]}$$
$$\lesssim\Big(e^{-\frac{1}{2}\eta_1[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_m|-r_{\ell m}]}+e^{-\eta_1[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_m|-r_{\ell m}]}\Big)e^{-\eta_1 r_{\ell m}}, \tag{3.6.11}$$

where $\eta_1 \coloneqq \min\{\gamma_{\mathrm{CT}}(\mathfrak{d}), \gamma_1\}$. In particular, the constant prefactor in (3.6.11) vanishes and thus the prefactor in the locality estimate (3.2.1) converges to the corresponding defect-free prefactor as the subsystem (ℓ, m) moves away from the defect core: that is, $C_1^{\mathrm{d}}(\ell, m) \to C_1$ as $|\boldsymbol{r}_\ell| + |\boldsymbol{r}_m| - r_{\ell m} \to \infty$.

The same argument may be applied for second derivatives. First, we write (3.6.4) and consider each term in turn. The exponent in (3.6.5) is the length of the path starting at $\boldsymbol{r}_\ell$, visiting $\boldsymbol{r}_{m_1}$ and $\boldsymbol{r}_{m_2}$ in that order, and returning to $\boldsymbol{r}_\ell$. Each time a resolvent is applied in the line above (3.6.5), we now need to also consider an additional $c_P e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_k|]}$ term. Therefore, we may bound (3.6.5) above by the sum of the defect-free quantity and all paths starting and ending at $\boldsymbol{r}_\ell$, visiting $\boldsymbol{r}_{m_1}$ and $\boldsymbol{r}_{m_2}$ in that order, and visiting 0 at least once in-between. The latter is a constant multiple (independent of ℓ, m_1, m_2) of

$$\Big[e^{-\frac{1}{2}\eta[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_{m_1}|-r_{\ell m_1}]}+e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_1}|+|\boldsymbol{r}_{m_2}|-r_{m_1m_2}]}+e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_2}|+|\boldsymbol{r}_\ell|-r_{\ell m_2}]}$$
$$+e^{-\frac{1}{2}\eta[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_{m_1}|-r_{\ell m_1}]}e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_1}|+|\boldsymbol{r}_{m_2}|-r_{m_1m_2}]}e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_2}|+|\boldsymbol{r}_\ell|-r_{\ell m_2}]}$$
$$+e^{-\frac{1}{2}\eta[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_{m_1}|-r_{\ell m_1}]}\Big(e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_1}|+|\boldsymbol{r}_{m_2}|-r_{m_1m_2}]}+e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_2}|+|\boldsymbol{r}_\ell|-r_{\ell m_2}]}\Big)$$
$$+e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_1}|+|\boldsymbol{r}_{m_2}|-r_{m_1m_2}]}e^{-\frac{1}{2}\eta[|\boldsymbol{r}_{m_2}|+|\boldsymbol{r}_\ell|-r_{\ell m_2}]}\Big]e^{-\frac{1}{2}\eta[r_{\ell m_1}+r_{m_1m_2}+r_{m_2\ell}]}.$$

Similarly, the second term in (3.6.4) may be bounded by the sum of (3.6.6) in the defect-free case, and a constant multiple of

$$\Big[e^{-\frac{1}{2}\eta_2[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_{m_1}|-r_{\ell m_1}]}+e^{-\frac{1}{2}\eta_2[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_{m_2}|-r_{\ell m_2}]}$$
$$+e^{-\frac{1}{2}\eta_2[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_{m_1}|-r_{\ell m_1}]}e^{-\frac{1}{2}\eta_2[|\boldsymbol{r}_\ell|+|\boldsymbol{r}_{m_2}|-r_{\ell m_2}]}\Big]e^{-\frac{1}{2}\eta_2[r_{\ell m_1}+r_{m_1m_2}+r_{m_2\ell}]},$$

where $\eta_2 \coloneqq \min\{\gamma_{\mathrm{CT}}(\mathfrak{d}), \gamma_2\}$. Therefore the prefactor in the improved estimates

converges to the corresponding defect-free prefactor as the subsystem moves away from the defect core together: that is, $C_2^{\mathrm{d}}(\ell, m_1, m_2) \to C_2$ as $|\boldsymbol{r}_k| + |\boldsymbol{r}_m| - r_{km} \to \infty$ for all distinct $k, m \in \{\ell, m_1, m_2\}$.

CHAPTER 4

Body-ordered Approximations

of the Potential Energy Landscape

This chapter is based on the article [123] "Rigorous body-order approximations of an electronic structure potential energy landscape" submitted to the arXiv preprint server, arXiv:2106.12572 (2021). This paper is co-authored by Huajie Chen and Christoph Ortner.

4.1 Introduction

In this Chapter, we construct body-ordered approximations (1.4.2) to local analytic observables (2.4.1) and prove an exponential rate of convergence. That is, for fixed body-order $N \in \mathbb{N}$, we construct

$$O_\ell^N(\boldsymbol{X}) \coloneqq \sum_{n=0}^{N-1} \sum_{\substack{k_1,\dots,k_n \neq \ell \\ k_1<\cdots<k_n}} V_{nN}(\boldsymbol{X}_\ell; \boldsymbol{X}_{\ell k_1}, \dots, \boldsymbol{X}_{\ell k_n}) \tag{4.1.1}$$

(for some $(n+1)$-*body potentials* V_{nN}), and show $\left|O_\ell(\boldsymbol{X}) - O_\ell^N(\boldsymbol{X})\right| \lesssim e^{-\gamma N}$ for some $\gamma > 0$ depending on the Fermi-temperature and band gap of the material. Moreover, we show that related nonlinear approximation schemes lead to

superior theoretical properties, with convergence rates only weakly depending on defect states within the band gap, similarly to the locality estimates in Chapter 3.

In addition to justifying and supporting the development of new models for general atomic properties, our results establish generic properties of *ab initio* models that have broader consequences, e.g. for the study of the mechanical properties of atomistic materials [27, 48, 98, 122].

Recall from Chapter 3 that we have decomposed the PEL into local contributions from each atomic site (1.4.1). In practise, one may therefore truncate the interaction introducing a finite cutoff radius. However, as we have seen in Chapter 1, the site energy E_ℓ is still an extremely high-dimensional object, and so in order to control the dimensionality of the representation, we consider the body-ordered approximation (1.4.2).

The vacuum cluster expansion (which we review in §4.5) is the traditional and, arguably, the most natural many-body expansion of a potential energy landscape. However, in many systems, it converges extremely slowly with respect to the body-order and is thus computationally impractical. An intuitive explanation for this slow convergence is that, when defining the body-order expansion in this way, we are building an interaction law for a condensed system from clusters in vacuum where the bonding chemistry is significantly different.

The approach considered here uses an entirely different mechanism where environment information is incorporated. In the simplest scheme, we approximate the local observables $O_\ell(\boldsymbol{X}) = \operatorname{tr} O\big(\mathcal{H}(\boldsymbol{X})\big)_{\ell\ell}$ (2.4.1) by approximating O with a polynomial p on the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$. This approach results in the approximation $\operatorname{tr} p\big(\mathcal{H}(\boldsymbol{X})\big)_{\ell\ell}$, which is naturally body-ordered. To obtain quasi-optimal approximation results, naive polynomial approximation schemes (e.g. Chebyshev) are suitable only in the simplest scenarios. For the insulating case we leverage potential theory techniques which in particular yield quasi-optimal approximation rates on unions of disconnected domains (the occupied and unoccupied bands). Our main results are obtained by converting these into

approximation results on atomic properties, analysing their qualitative features, and taking care to obtain sharp estimates in the zero Fermi-temperature limit.

These initial results provide strong evidence for the accuracy of a linear body-order approximation in relatively simple scenarios, and would for example be useful in a study of the mechanical response of single crystals with a limited selection of possible defects. However, they come with limitations that we discuss in the main text. In response, we then explore a much more general framework, generalizing the theory of bond order potentials [74], that incorporates our linear body-ordered model as well as a range of nonlinear models. We will highlight a specific nonlinear construction with significantly improved theoretical properties over the linear scheme.

4.2 A General Framework

Before we consider two specific body-ordered approximations, we present a general framework which illustrates the key features needed for a convergent scheme: To that end, we introduce the *local density of states* (LDOS) [53] which is the (positive) measure D_ℓ supported on $\sigma(\mathcal{H})$ such that

$$\int x^n \mathrm{d}D_\ell(x) = \mathrm{tr}[\mathcal{H}^n]_{\ell\ell}, \qquad \text{for } n \in \mathbb{N}_0. \tag{4.2.1}$$

Existence and uniqueness follows from the spectral theorem for normal operators (e.g. see [1, Theorem 6.3.3] or [121]). In particular, (2.4.1) may be written as the integral $O_\ell(\boldsymbol{X}) = \int O \, \mathrm{d}D_\ell$.

Since the moments $[\mathcal{H}^n]_{\ell\ell}$ have finite body order (see Proposition 4.1), on constructing a (possibly signed) measure D_ℓ^N with $\int x^n \mathrm{d}D_\ell^N(x) = \mathrm{tr}[\mathcal{H}^n]_{\ell\ell}$ for $n = 0, 1, \ldots, N$, we may define the body-ordered approximate local observable $O_\ell^N(\boldsymbol{X}) \coloneqq \int O \, \mathrm{d}D_\ell^N$. Now, the conditions on the moments of D_ℓ^N imply that $\int P_N \mathrm{d}(D_\ell - D_\ell^N) = 0$ for all polynomials P_N of degree at most N, and thus

we obtain the following general error estimates:

$$\begin{aligned}\big|O_\ell(\boldsymbol{X}) - O_\ell^N(\boldsymbol{X})\big| &= \inf_{P_N\in\mathcal{P}_N}\Big|\int \big(O-P_N\big)\mathrm{d}\big(D_\ell - D_\ell^N\big)\Big| \\ &\leqslant \big\|D_\ell - D_\ell^N\big\|_{\mathrm{op}} \inf_{P_N\in\mathcal{P}_N}\big\|O-P_N\big\|_\infty \end{aligned} \tag{4.2.2}$$

where $\mathcal{P}_N$ denotes the set of polynomials of degree at most N, and $\|\cdot\|_{\mathrm{op}}$ is the operator norm on a function space $(\mathcal{S}, \|\cdot\|_\infty)$. For example, we may take $\mathcal{S}$ to be the set of functions analytic on an open set containing $\mathscr{C}$, a contour encircling $\mathrm{supp}\big(D_\ell - D_\ell^N\big)$ and satisfying (2.4.1), and consider

$$\|O\|_{\mathscr{C}} \coloneqq \frac{\mathrm{len}(\mathscr{C})}{2\pi}\|O\|_{L^\infty(\mathscr{C})}.$$

Alternatively, we may consider $\mathcal{S} = L^\infty\big(\mathrm{supp}(D_\ell - D_\ell^N)\big)$ leading to the total variation operator norm. Equation (4.2.2) highlights the key generic features that are crucial ingredients in obtaining convergence results:

- *Analyticity.* The potential theory results of §4.8.1 connect the asymptotic convergence rates for polynomial approximation to the size and shape of the region of analyticity of O.

- *Spectral Pollution.* While $\mathrm{supp}\, D_\ell \subseteq \sigma(\mathcal{H})$, this need not be true for D_ℓ^N. Indeed, if $\mathrm{supp}\, D_\ell^N$ introduces additional points within the band gap, this may significantly slow the convergence of the polynomial approximation; cf. §4.5.

- *Regularity of D_ℓ^N.* Roughly speaking, the first term of (4.2.2) measures how "well-behaved" D_ℓ^N is. In particular, if D_ℓ^N is positive, then this term is bounded independently of N, whereas, if D_ℓ^N is a general signed measure, then this factor contributes to the asymptotic convergence behaviour.

In the following sections, we introduce linear (§4.3) and nonlinear (§4.4) approximation schemes that fit into this general framework. Moreover, in §4.5, we also write the vacuum cluster expansion as an integral against an

approximate LDOS and investigate which of the requirements listed above fail. This analysis complements the intuitive explanation for the slow convergence of the vacuum cluster expansion.

In the appendices, we review other approximation schemes that fit into this general framework such as the quadrature method (Appendix C.3), numerical bond order potentials (Appendix C.4), and the kernel polynomial method (Appendix C.5).

4.3 Linear Body-ordered Approximation

To construct our first model we exploit the observation that polynomial approximations of an analytic function correspond to body-order expansions of an observable.

An intuitive approach is therefore to write the local observable in terms of its Chebyshev expansion and truncate to some maximal polynomial degree. The corresponding projection operator is a simple example of the kernel polynomial method (KPM) [110] and the basis for analytic bond order potentials (BOP) [101]. We discuss in Appendix C.5 that these schemes put more emphasis on the approximation of the local density of states (LDOS) and, in particular, exploit particular features of the Chebyshev polynomials to obtain a positive approximate LDOS. Since our focus is instead on the approximation of observables, we employ a different approach that is tailored to specific properties of the band structure and leads to superior convergence rates for these quantities.

For a set of $N+1$ distinct interpolation points $\mathcal{X} = \mathcal{X}_N$, and a complex-valued function O defined on $\mathcal{X}$, we denote by $I_{\mathcal{X}}O(z)$ the degree N polynomial interpolant of $z \mapsto O(z)$ on $\mathcal{X}$. This gives rise to the body-ordered approximation

$$I_{\mathcal{X}}O_\ell(\boldsymbol{X}) \coloneqq \operatorname{tr}\big[I_{\mathcal{X}}O\big(\mathcal{H}(\boldsymbol{X})\big)_{\ell\ell}\big]. \tag{4.3.1}$$

We may connect (4.3.1) to the general framework in §4.2 by writing

$$I_{\mathcal{X}} O_\ell(\boldsymbol{X}) = \int O \mathrm{d}D_\ell^{N,\mathrm{lin}} \quad \text{where} \quad D_\ell^{N,\mathrm{lin}} := \mathrm{tr} \sum_j \ell_j(\mathcal{H})_{\ell\ell}\, \delta(\cdot - \varepsilon_j) \quad (4.3.2)$$

and ℓ_j are the node polynomials corresponding to the interpolation set $\mathcal{X} = \{\varepsilon_j\}$ (that is, $\ell_j(\varepsilon_i) = \delta_{ij}$).

Proposition 4.1. *$I_{\mathcal{X}} O_\ell(\boldsymbol{X})$ has finite body-order. More specifically, there exists a maximal body order $M \in \mathbb{N}$ and $(n+1)$-body potentials V_{nN} for $n = 0, \dots, M-1$ such that*

$$I_{\mathcal{X}} O_\ell(\boldsymbol{X}) = \sum_{n=0}^{M-1} \sum_{\substack{k_1,\dots,k_n \neq \ell \\ k_1 < \cdots < k_n}} V_{nN}(\boldsymbol{X}_\ell; \boldsymbol{X}_{\ell k_1}, \dots, \boldsymbol{X}_{\ell k_n}). \quad (4.3.3)$$

For two-centre tight binding models $M = N$, whereas $M = 2N$ in the three-centre case.

Sketch of the Proof. Since (4.3.1) is a linear combination of the monomials $[\mathcal{H}^n]_{\ell\ell}$, it is enough to show that, for each $n \in \mathbb{N}$,

$$[\mathcal{H}^n]_{\ell\ell} = \sum_{\ell_1,\dots,\ell_{n-1}} \mathcal{H}_{\ell\ell_1} \mathcal{H}_{\ell_1\ell_2} \cdots \mathcal{H}_{\ell_{n-1}\ell} \quad (4.3.4)$$

has finite body order. Each term in (4.3.4) depends on the central atom ℓ, the $n-1$ neighbouring sites $\ell_1, \dots, \ell_{n-1}$, and the at most n additional sites arising from the three-centre summation in the tight binding Hamiltonian **(TB)**. In particular, (4.3.1) has body order at most $2N$ for three-centre tight binding models, and at most N for two-centre models. See §4.8.2 for a complete proof including an explicit definition of the V_{nN}. □

If one uses Chebyshev points as the basis for the body-ordered approximation (4.3.1), the rates of convergence depend on the size of the largest *Bernstein ellipse* (that is, ellipses with foci points ± 1) contained in the region of analyticity of $z \mapsto O(z)$ [124]. This leads to a exponentially convergent body-order expansion in the metallic finite-temperature case (see §4.8.1 for the

details).

However, the resulting estimates depend on β^{-1} and deteriorate in the zero-temperature limit. Instead, we apply results of potential theory to construct interpolation sets $\mathcal{X}$ that are adapted to the spectral properties of the system (see §4.8.1 for examples) and *(i)* do not suffer from spectral pollution, and *(ii)* (asymptotically) minimise the total variation of $D_\ell^{N,\mathrm{lin}}$ which, in this context, is the Lebesgue constant [124] for the interpolation operator $I_\mathcal{X}$. This leads to rapid convergence of the body-ordered approximation based on (4.3.1). The interpolation sets $\mathcal{X}_N$ depend only on the intervals I_-, I_+ from Definition 2.2 (see also Figure 2.2) and can be chosen independently of $\boldsymbol{X}$ as long as $B_\varepsilon\big(\sigma\big(\mathcal{H}(\boldsymbol{X})\big)\big) \subseteq I_- \cup I_+$.

Theorem 4.2. *Suppose $\boldsymbol{X}$ satisfies Definition 2.2. Fix $0 < \beta \leqslant \infty$ and suppose that, either $\beta < \infty$ or $\mathsf{g} > 0$. Then, there exist constants $\gamma_N > 0$ and interpolation operators $I_N \coloneqq I_{\mathcal{X}_N}$ satisfying* (4.3.3) *and with $\mathcal{X}_N \subseteq I_- \cup I_+$ such that*

$$\begin{aligned} \big|O_\ell^\beta(\boldsymbol{X}) - I_N O_\ell^\beta(\boldsymbol{X})\big| &\leqslant C_1 e^{-\gamma_N N}, \qquad \textit{and} \\ \left|\frac{\partial O_\ell^\beta(\boldsymbol{X})}{\partial \boldsymbol{X}_m} - \frac{\partial I_N O_\ell^\beta(\boldsymbol{X})}{\partial \boldsymbol{X}_m}\right| &\leqslant C_2 e^{-\frac{1}{2}\gamma_N N} e^{-\eta\, r_{\ell m}}, \end{aligned}$$

where $O^\beta = F^\beta$ or G^β and $C_1, C_2 > 0$ are independent of N. The asymptotic convergence rate $\gamma \coloneqq \lim_{N\to\infty} \gamma_N$ is positive and exhibits the asymptotic behaviour

$$C_1 \sim (\mathsf{g} + \beta^{-1})^{-1},\ C_2 \sim (\mathsf{g} + \beta^{-1})^{-3},\ \textit{and}\ \gamma, \eta \sim \mathsf{g} + \beta^{-1} \quad \textit{as}\ \mathsf{g} + \beta^{-1} \to 0.$$

In this asymptotic relation, we assume that the limit $\mathsf{g} \to 0$ is approached symmetrically about the chemical potential μ.

Remark 4.1. *Higher derivatives may be treated similarly under the assumption that higher derivatives of the tight binding Hamiltonian* **(TB)** *exist and are short ranged.*

Remark 4.2 (Locality)**.** *(i) By Theorem 4.3, and the locality estimates for the exact observables O_ℓ^β (Theorem 3.2), we immediately obtain corresponding locality estimates for the approximate quantities:*

$$\left| \frac{\partial I_N O_\ell^\beta(\boldsymbol{X})}{\partial \boldsymbol{X}_m} \right| \lesssim e^{-\eta r_{\ell m}}. \tag{4.3.5}$$

(ii) We investigate another type of locality in Appendix C.1 where we show that various truncation operators result in approximation schemes that only depend on a small atomic neighbourhood of the central site. An exponential rate of convergence as the truncation radius tends to infinity is obtained.

4.3.1 The role of the point spectrum

We now turn towards the important scenario when a localised defect is embedded within a homogeneous crystalline solid. Recall from §2.3 (see in particular Fig. 2.2) that this gives rise to a discrete spectrum, which "pollutes" the band gap [95]. Thus, the spectral gap is reduced and a naive application of Theorem 4.2 leads to a reduction in the convergence rate of the body-ordered approximation. We now improve these estimates by showing that, away from the defect, we obtain improved pre-asymptotics, reminiscent of similar results for locality of interaction (Chapter 3).

In the following, we suppose that $(\boldsymbol{X}, \boldsymbol{X}^{\rm d})$ satisfies Definition 2.2. While improved estimates may be obtained by choosing $\{\lambda_j\}$ as interpolation points, leading to asymptotic exponents that are independent of the defect, in practice, this requires full knowledge of the point spectrum. Since the point spectrum within the spectral gap depends on the whole atomic configuration, the approximate quantities of interest corresponding to these interpolation operators would no longer satisfy Proposition 4.1.

Remark 4.3. *This phenomenon has been observed in the context of Krylov subspace methods for solving linear equations $Ax = b$ where outlying eigenvalues delay the convergence by $O(1)$ steps without affecting the asymptotic rate [43]. Indeed, since the residual after n steps may be written as $r_n = p_n(A)r_0$*

where p_n is a polynomial of degree n, there is a close link between polynomial approximation and convergence of Krylov methods.

On the other hand, we may use the exponential localisation of the eigenvectors corresponding to isolated eigenvalues to obtain pre-factors that decay exponentially as $|\boldsymbol{r}_\ell| \to \infty$:

Theorem 4.3. *Suppose $(\boldsymbol{X}, \boldsymbol{X}^{\mathrm{d}})$ satisfies Definition 2.2 with $\mathsf{g} > 0$. Fix $0 < \beta \leqslant \infty$ and suppose that, if $\beta = \infty$, then $\mathsf{g}^{\mathrm{def}} > 0$, and let $C_1, C_2, \gamma_N, \gamma, \eta$, and $I_N \coloneqq I_{\mathcal{X}_N}$ with $\mathcal{X}_N \subseteq I_- \cup I_+$ given by Theorem 4.2. Then,*

$$\begin{aligned} \left|O_\ell^\beta(\boldsymbol{X}^{\mathrm{d}}) - I_N O_\ell^\beta(\boldsymbol{X}^{\mathrm{d}})\right| &\leqslant C_1 e^{-\gamma_N N} + C_3 e^{-\gamma_{\mathrm{CT}}|\boldsymbol{r}_\ell|} e^{-\frac{1}{2}\gamma_N^{\mathrm{def}} N} \\ \left|\frac{\partial O_\ell^\beta(\boldsymbol{X}^{\mathrm{d}})}{\partial \boldsymbol{X}_m^{\mathrm{d}}} - \frac{\partial I_N O_\ell^\beta(\boldsymbol{X}^{\mathrm{d}})}{\partial \boldsymbol{X}_m^{\mathrm{d}}}\right| &\leqslant \left(C_2 e^{-\frac{1}{2}\gamma_N N} + C_4 e^{-\gamma_{\mathrm{CT}}|\boldsymbol{r}_\ell|} e^{-\frac{1}{2}\gamma_N^{\mathrm{def}} N}\right) e^{-\eta\, r_{\ell m}} \end{aligned} \tag{4.3.6}$$

where $O^\beta = F^\beta$ or G^β and $C_3, C_4 > 0$ are independent of N. The asymptotic convergence rate $\gamma^{\mathrm{def}} \coloneqq \lim_{N\to\infty} \gamma_N^{\mathrm{def}}$ is positive and we have

$$\begin{aligned} \gamma^{\mathrm{def}} &\sim \mathsf{g}^{\mathrm{def}} + \beta^{-1} \qquad \text{as } \mathsf{g}^{\mathrm{def}} + \beta^{-1} \to 0, \\ \gamma_{\mathrm{CT}}, \eta &\sim \mathsf{g} + \beta^{-1} \qquad \text{as } \mathsf{g} + \beta^{-1} \to 0. \end{aligned}$$

In these asymptotic relations, we assume that the limits $\mathsf{g}^{\mathrm{def}}, \mathsf{g} \to 0$ are approached symmetrically about the chemical potential μ.

In practice, Theorem 4.3 means that, for atomic sites ℓ away from the defect-core, the observed pre-asymptotic error estimates may be significantly better than the asymptotic convergence rates obtained in Theorem 4.2.

Remark 4.4 (Connection to the General Framework §4.2)**.** *The fact that the exponents in Theorem 4.3 depend on the discrete eigenvalues of $\mathcal{H}(\boldsymbol{X})$ can be seen from the general estimate* (4.2.2) *applied to the approximate LDOS $D_\ell^{N,\mathrm{lin}}$ from* (4.3.2)*:*

- *Spectral Pollution. We choose the interpolation points so that the support*

of $D_\ell^{N,\mathrm{lin}}$ lies within $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ and so spectral pollution does not play a role,

- *Regularity. The total variation of $D_\ell^{N,\mathrm{lin}}$ can be estimated by the Lebesgue constant [124] for the interpolation operator I_N:*

$$\begin{aligned}\|D_\ell^{N,\mathrm{lin}}\|_{\mathrm{TV}} &\coloneqq \sup_{\|f\|_{L^\infty(\sigma(\mathcal{H}))}=1} |I_N f(\mathcal{H})_{\ell\ell}| \\ &\leqslant \sup_{\|f\|_{L^\infty(\sigma(\mathcal{H}))}=1} \sup_{x\in\sigma(\mathcal{H})} |I_N f(x)| \\ &= \sup_{x\in\sigma(\mathcal{H})} \sum_j |\ell_j(x)|. \end{aligned} \tag{4.3.7}$$

This quantity depends on the discrete eigenvalues within the band gap.

4.4 Nonlinear Body-ordered Approximation

The method presented in §4.3 approximates local quantities of interest by approximating the integrand $O\colon \mathbb{C}\to\mathbb{C}$ with polynomials. As we have seen, this leads to approximation schemes that are linear functions of the spatial correlations $\{[\mathcal{H}^n]_{\ell\ell}\}_{n\in\mathbb{N}}$. In this section, we construct a non-linear approximation related to bond-order potentials (BOP) [39, 54, 74] and show that the added non-linearity leads to improved asymptotic error estimates that are independent of the discrete spectra lying within the band gap. In this way, the nonlinearity captures "spectral information" from $\mathcal{H}$ rather than only approximating $O\colon \mathbb{C}\to\mathbb{C}$ without reference to the Hamiltonian.

Applying the recursion method [66, 67], a reformulation of the Lanczos process [81], we obtain a tri-diagonal (Jacobi) operator T on $\ell^2(\mathbb{N}_0)$ whose spectral measure is the LDOS D_ℓ [120] (see §4.8.3 for the details). We then truncate T by taking the principal $\frac{1}{2}(N+1)\times\frac{1}{2}(N+1)$ submatrix $T_{\frac{1}{2}(N-1)}$, diagonalise $T_{\frac{1}{2}(N-1)}$ to find the normalised eigenpairs (λ_s,ψ_s), and define the

spectral measure

$$D_\ell^{N,\mathrm{nonlin}} \coloneqq \sum_s [\psi_s]_0^2 \delta(\,\cdot - \lambda_s) \qquad \text{and} \tag{4.4.1}$$

$$\Theta\big(\mathcal{H}_{\ell\ell}, [\mathcal{H}^2]_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big) \coloneqq O(T_{\frac{1}{2}(N-1)})_{00} = \int O \mathrm{d} D_\ell^{N,\mathrm{nonlin}}. \tag{4.4.2}$$

By showing that the first N moments of $D_\ell^{N,\mathrm{nonlin}}$ are exact, we are able to apply (4.2.2) to obtain the following error estimates. The asymptotic behaviour of the exponent in these estimates follows by proving that the spectral pollution of $D_\ell^{N,\mathrm{nonlin}}$ in the band gap is sufficiently mild.

Theorem 4.4. *Suppose $(\boldsymbol{X}, \boldsymbol{X}^{\mathrm{d}})$ satisfies Definition 2.2 and $\mathcal{H} \coloneqq \mathcal{H}(\boldsymbol{X}^{\mathrm{d}})$. Fix $0 < \beta \leqslant \infty$ and suppose that, if $\beta = \infty$, then $\mathsf{g} > 0$. Then, for N odd, there exists an open set $U \subseteq \mathbb{C}^N$ such that* (4.4.2) *extends to an analytic function $\Theta\colon U \to \mathbb{C}$, independent of $\mathcal{H}$, such that*

$$\Big| O_\ell(\boldsymbol{X}^{\mathrm{d}}) - \Theta\big(\mathcal{H}_{\ell\ell}, [\mathcal{H}^2]_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big) \Big| \lesssim e^{-\gamma_N N} \tag{4.4.3}$$

where $O = F^\beta$ or G^β. The asymptotic convergence rate $\gamma \coloneqq \lim_{N\to\infty} \gamma_N$ is positive and $\gamma \sim \mathsf{g} + \beta^{-1}$ as $\mathsf{g} + \beta^{-1} \to 0$ where the $\mathsf{g} \to 0$ limit is approached symmetrically about the chemical potential.

Remark 4.5. *It is important to note that $\Theta\colon U \to \mathbb{C}$ can be constructed without knowledge of $\mathcal{H}$ because, as we have seen, if the discrete eigenvalues are known* a priori*, then Theorem 4.4 is immediate from Theorem 4.3 by adding finitely many additional interpolation points on the discrete spectrum.*

In particular, the fact that Θ is a material-agnostic *nonlinearity has potentially far-reaching consequences for material modelling.*

Remark 4.6 (Connection to the General Framework §4.2)**.** *The fact that the exponents in Theorem 4.4 are independent of the discrete eigenvalues of $\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})$ can be seen from the general estimate* (4.2.2) *applied to the approximate LDOS $D_\ell^{N,\mathrm{nonlin}}$ from* (4.4.2)*:*

- *Spectral Pollution. We prove that if $[a, b] \cap \sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big) = \emptyset$, then the*

number of points in $[a,b] \cap \operatorname{supp} D_\ell^{N,\mathrm{nonlin}}$ *is at most one (see Lemma 4.5). In particular, the spectral pollution within the band gap is sufficiently mild to ensure that the asymptotic error estimates in the polynomial approximation problem in* (4.2.2) *are independent of the discrete points in the band gap,*

- *Regularity. By construction,* $D_\ell^{N,\mathrm{nonlin}}$ *is a positive measure and thus the first term of* (4.2.2) *is bounded independently of* N*.*

Remark 4.7 (Quadrature Method)**.** *Alternatively, we may use the sequence of orthogonal polynomials [55] corresponding to* D_ℓ *as the basis for a Gauss quadrature rule to evaluate local observables. This procedure, called the* Quadrature Method *[68, 93], is a precursor of the bond order potentials. Outlined in Appendix C.3, we show that it produces an alternative scheme also satisfying Theorem 4.4.*

Remark 4.8 (Convergence of Derivatives)**.** *In this more complicated nonlinear setting, obtaining results such as* (4.3.6) *is more subtle. We require an additional assumption on* D_ℓ*, which we believe may be typically satisfied, but we currently cannot justify it and have therefore postponed this discussion to Appendix C.2. We briefly mention, however, that if* D_ℓ *is absolutely continuous (e.g., in periodic systems), we obtain*

$$\left| \frac{\partial}{\partial \boldsymbol{X}_m} \Big(O_\ell^\beta(\boldsymbol{X}) - \Theta\big(\mathcal{H}_{\ell\ell}, [\mathcal{H}^2]_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big) \Big) \right| \lesssim e^{-\frac{1}{2}\gamma_N N} e^{-\eta\, r_{\ell m}}.$$

4.5 Vacuum Cluster Expansion

The vacuum cluster expansion is a many-body expansion of the form (1.4.2) where the $(n+1)$-body potentials $V^{(n)}$ are constructed by considering all isolated clusters of $j \leqslant n$ atoms. That is, on defining the restriction of the Hamiltonian matrix $\mathcal{H}\big|_{\ell;K}$ corresponding to the finite system $\{\ell\} \cup K \subseteq \Lambda$,

$$\big[\mathcal{H}\big|_{\ell;K}\big]_{k_1 k_2} \coloneqq h(\boldsymbol{X}_{k_1 k_2}) + \sum_{m \in \{\ell\} \cup K} t(\boldsymbol{X}_{k_1 m}, \boldsymbol{X}_{k_2 m}) + \delta_{k_1 k_2} v_{k_1} \mathrm{Id}_{N_\mathrm{b}}, \quad (4.5.1)$$

we define

$$O_\ell^{N,\mathrm{vac}}(\boldsymbol{X}) \coloneqq \sum_{n=0}^{N-1} \sum_{\substack{k_1,\dots,k_n \neq \ell \\ k_1<\dots<k_n}} V^{(n)}(\boldsymbol{X}_\ell; \boldsymbol{X}_{\ell k_1}, \dots, \boldsymbol{X}_{\ell k_n}), \quad \text{where} \tag{4.5.2}$$

$$V^{(n)}(\boldsymbol{X}_\ell; \boldsymbol{X}_{\ell k_1}, \dots, \boldsymbol{X}_{\ell k_n}) = \sum_{K \subseteq \{k_1,\dots,k_n\}} (-1)^{n-|K|} O\big(\mathcal{H}\big|_{\ell;K}\big)_{\ell\ell}. \tag{4.5.3}$$

For a system of N particles, this expansion is exact.

Therefore, on defining the measure $D_{\ell;K} \coloneqq \sum_s \delta\big(\,\cdot\, - \lambda_s(K)\big)|[\psi_s(K)]_\ell|^2$ where $\big(\lambda_s(K), \psi_s(K)\big)$ the are normalised eigenpairs of $\mathcal{H}\big|_{\ell;K}$, we may write the vacuum cluster expansion as in §4.2:

$$\begin{aligned} O_\ell^{N,\mathrm{vac}}(\boldsymbol{X}) &= \int O \,\mathrm{d}D_\ell^{N,\mathrm{vac}} \qquad \text{where} \\ D_\ell^{N,\mathrm{vac}} &\coloneqq \sum_{n=0}^{N-1} \sum_{\substack{k_1,\dots,k_n \neq \ell \\ k_1<\dots<k_n}} \sum_{K \subseteq \{k_1,\dots,k_n\}} (-1)^{n-|K|} D_{\ell;K}. \end{aligned} \tag{4.5.4}$$

While $D_\ell^{N,\mathrm{vac}}$ is a generalised signed measure (with values in $\mathbb{R} \cup \{\pm\infty\}$), all moments are finite:

$$\int x^j \,\mathrm{d}D_\ell^{N,\mathrm{vac}}(x) = \sum_{\substack{\ell_1,\dots,\ell_{j-1} \\ |\{\ell,\ell_1,\dots,\ell_{j-1}\}| \leqslant N}} \mathcal{H}_{\ell\ell_1}\mathcal{H}_{\ell_1\ell_2}\dots\mathcal{H}_{\ell_{j-1}\ell}. \tag{4.5.5}$$

Equation (4.5.5) follows from the proof of Proposition 4.1, see (4.8.17). In particular, the first N moments of $D_\ell^{N,\mathrm{vac}}$ are exact. Therefore, we may apply the general error estimate (4.2.2) and describe the various features of $D_\ell^{N,\mathrm{vac}}$ which provide mathematical intuition for the slow convergence of the vacuum cluster expansion:

- *Spectral Pollution.* When splitting the system up into arbitrary subsystems as is the case in the vacuum cluster expansion, one expects significant spectral pollution in the band gaps, leading to a reduction in the convergence rate,

- *Regularity.* The approximate LDOS is a linear combination of countably many Dirac deltas and does not have bounded variation. Moreover,

$D_\ell^{N,\mathrm{vac}}$ has values in $\mathbb{R} \cup \{\pm\infty\}$.

4.6 Pre-asymptotic Regime

Possibly the most significant limitation of our analysis of the linear body-ordered approximation scheme is that the estimates deteriorate when defects cause a pollution of the point spectrum. Here, we briefly demonstrate that this appears to be an asymptotic effect, while in the pre-asymptotic regime this deterioration is not noticeable.

To explore this we choose a union of intervals $E \supseteq \sigma(\mathcal{H})$ and a polynomial P_N of degree N and note

$$\begin{aligned}\Big|\big[O(\mathcal{H}) - P_N(\mathcal{H})\big]_{\ell\ell}\Big| &\leqslant \big\|O(\mathcal{H}) - P_N(\mathcal{H})\big\|_{\ell^2\to\ell^2} = \big\|O - P_N\big\|_{L^\infty(\sigma(\mathcal{H}))} \\ &\leqslant \big\|O - P_N\big\|_{L^\infty(E)}. \end{aligned} \tag{4.6.1}$$

We then construct interpolation sets (Fejér sets) such that the corresponding polynomial interpolant gives the optimal asymptotic approximation rates (for details of this construction, see §4.8.1). We then contrast this with a best $L^\infty(E)$-approximation, and with the nonlinear approximation scheme from Theorem 4.4. We will observe that the non-linearity leads to improved asymptotic but comparable pre-asymptotic approximation errors.

As a representative scenario we consider the Fermi-Dirac distribution $F^\beta(z) = (1 + e^{\beta z})^{-1}$ with $\beta = 100$ and both the "defect-free" case $E_1 \coloneqq [-1, a] \cup [b, 1]$ and $E_2 \coloneqq [-1, a] \cup [c, d] \cup [b, 1]$ with the parameters $a = -0.2, b = 0.2, c = -0.06$, and $d = -0.03$. Then, for fixed polynomial degree N and $j \in \{1, 2\}$, we construct the $(N+1)$-point Fejér set for E_j and the corresponding polynomial interpolant $I_{j,N}F^\beta$. Moreover, we consider a polynomial $P^\star_{j,N}$ of degree N minimising the right hand side of (4.6.1) for $E = E_j$. Then, we plot the errors $\|F^\beta - I_{j,N}F^\beta\|_{L^\infty(E_j)}$ and $\|F^\beta - P^\star_{j,N}\|_{L^\infty(E_j)}$ for both $j = 1$ (Fig. 4.1) and $j = 2$ (Fig. 4.2) against the polynomial degree N together with the theoretical asymptotic convergence rates for best $L^\infty(E_j)$ polynomial

approximation (4.8.13).

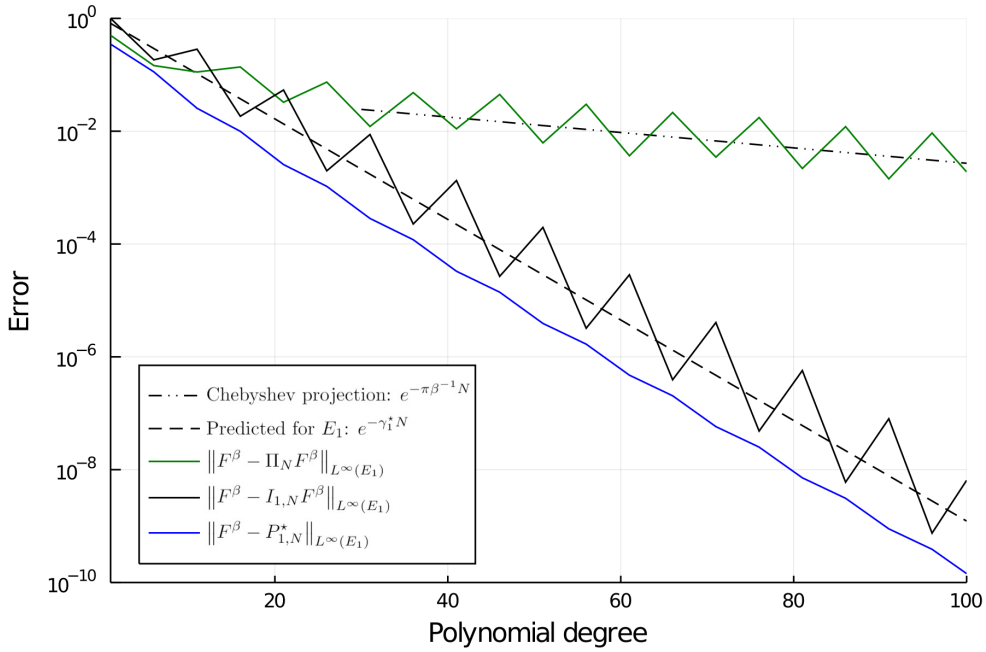


Figure 4.1: Approximation errors for Chebyshev projection (green), polynomial interpolation in Fejér sets on E_1 (black), and best $L^\infty(E_1)$ polynomial approximation (blue) for $E_1 = [-1, a] \cup [b, 1]$. We also plot the corresponding predicted asymptotic rates (from (4.8.3) and (4.8.13)). Here, we only plot data points for $N \in \{1, 6, 11, 16, \dots\}$.

What we observe is that, as expected, introducing the interval $[c, d]$ into the approximation domain drastically affects the asymptotic convergence rate and the errors in the approximation based on interpolation. While the best approximation errors follow the asymptotic rate for larger polynomial degree, it appears that, pre-asymptotically, the errors are significantly reduced. We also see that the approximation errors are significantly better than the general error estimate $\|F^\beta - \Pi_N F^\beta\|_{L^\infty} \lesssim e^{-\pi\beta^{-1}N}$ where Π_N is the Chebyshev projection operator (see §4.8.1).

Moreover, in Figure 4.2, we plot the errors when using a nonlinear approximation scheme satisfying Theorem 4.4. In this simple experiment, we consider the Gauss quadrature rule $\Theta \coloneqq \int I_{\mathcal{X}_N} F^\beta \mathrm{d}D_\ell$ where $\mathcal{X}_N$ are the zeros of the degree $N+1$ orthogonal polynomial (see Appendix C.3) with respect to $\mathrm{d}D_\ell(x) \coloneqq \big(\chi_{E_0}(x) + \sum_j \delta(x - \lambda_j)\big)\mathrm{d}x$, for a finite set $\{\lambda_j\} \subseteq [c, d]$. While D_ℓ does not correspond to a physically relevant Hamiltonian, the same procedure

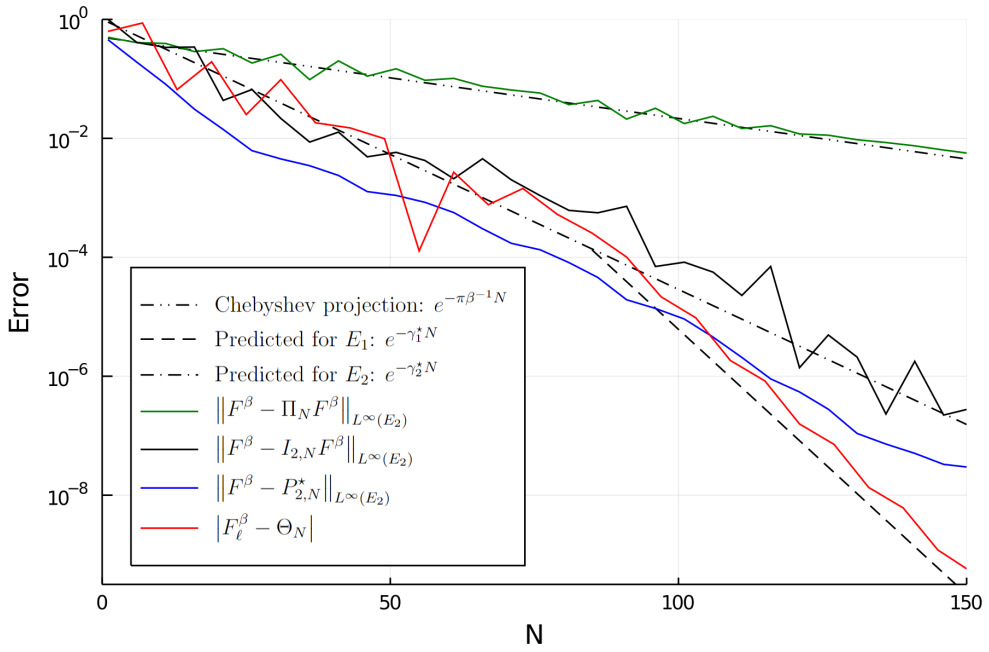


Figure 4.2: Approximation errors for Chebyshev projection (green), polynomial interpolation in Fejér sets on E_2 (black), best $L^\infty(E_2)$ polynomial approximation (blue), and errors in the nonlinear approximation scheme (red) for $E_2 = [-1, a] \cup [c, d] \cup [b, 1]$ and $\{\lambda_j\} = \{c, \frac{c+d}{2}, d\}$. We also plot the corresponding predicted asymptotic rates (from (4.8.3), (4.8.13), and Theorem 4.2). Here, we only plot data points for $N \in \{1, 6, 11, 16, \dots\}$ in the linear schemes (which captures the oscillatory behaviour), and $N \in \{1, 7, 13, 19, \dots\}$ for the nonlinear scheme (since N must be odd).

may be carried out for any measure supported on E_1 with $\operatorname{supp} D_\ell \cap [c, d]$ finite. Then plotting the upper bounds $\int |F^\beta - I_{\mathcal{X}_N} F^\beta| \mathrm{d}D_\ell$, we observe improved asymptotic convergence rates that agree with that of the "defect-free" case from Figure 4.1. However, the improvement is only observed in the asymptotic regime which corresponds to body-orders never reached in practice.

4.7 Conclusions

In this chapter we have seen a sequence of rigorous results about body-ordered approximations of a wide class of properties extracted from tight-binding models for condensed phase systems, the primary example being the potential energy landscape. Our results demonstrate that exponentially fast convergence can be obtained, provided that the chemical environment is taken into account. In the spirit of the results in Chapter 3 on the locality of interaction [29, 98, 122],

this chapter provides further theoretical justification — albeit qualitative — for widely assumed properties of atomic interactions. More broadly, the analysis illustrates how to construct general low-dimensional but systematic representations of high-dimensional complex properties of atomistic systems.

4.8 Proofs of the Main Results

4.8.1 Preliminaries

Here, we briefly introduce the concepts needed in the proofs of the main results.

Hermite integral formula

For a finite interpolation set $\mathcal{X} \subseteq \mathbb{C}$, we let $\ell_{\mathcal{X}}(z) \coloneqq \prod_{x\in\mathcal{X}}(z-x)$ be the corresponding *node polynomial*.

For fixed $z \in \mathbb{C}\backslash\mathcal{X}$, we suppose that O is analytic on an open neighbourhood of $\mathcal{X} \cup \{z\}$. Then, for a simple closed positively oriented contour (or system of contours) $\mathscr{C}$ contained in the region of analyticity of O, encircling $\mathcal{X}$, and avoiding $\{z\}$, we have

$$I_{\mathcal{X}}O(z) = \oint_{\mathscr{C}} \frac{\ell_{\mathcal{X}}(\xi) - \ell_{\mathcal{X}}(z)}{\ell_{\mathcal{X}}(\xi)} \frac{O(\xi)}{\xi - z} \frac{\mathrm{d}\xi}{2\pi i}. \tag{4.8.1}$$

If, in addition, $\mathscr{C}$ encircles $\{z\}$, then

$$O(z) - I_{\mathcal{X}}O(z) = \oint_{\mathscr{C}} \frac{\ell_{\mathcal{X}}(z)}{\ell_{\mathcal{X}}(\xi)} \frac{O(\xi)}{\xi - z} \frac{\mathrm{d}\xi}{2\pi i}. \tag{4.8.2}$$

The proof of these facts is a simple application of Cauchy's integral formula, [3, 124].

Chebyshev Projection and Interpolation in Chebyshev Points

We denote by $\{T_n\}$ the *Chebyshev polynomials* (of the first kind) satisfying $T_n(\cos\theta) = \cos n\theta$ on $[-1, 1]$ and, equivalently, the recurrence $T_0 = 1, T_1 = x$, and $T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$.

For O Lipshitz continuous on $[-1,1]$, there exists an absolutely convergent Chebyshev series expansion: there exists c_n such that $O(z) = \sum_{n=0}^{\infty} c_n T_n(z)$. For maximal polynomial degree N, the corresponding projection operator is denoted $\Pi_N O(z) \coloneqq \sum_{n=0}^{N} c_n T_n(z)$. This approach is a special case of the Kernel Polynomial Method (KPM) which we briefly review in Appendix C.5.

On the other hand, supposing that the interpolation set is given by the *Chebyshev points* $\mathcal{X} = \{\cos \frac{j\pi}{N}\}_{0 \leqslant j \leqslant N}$, we may expand the polynomial interpolant $I_N O \coloneqq I_{\mathcal{X}} O$ in terms of the Chebyshev polynomials: there exists c'_n such that $I_N O(z) = \sum_{n=0}^{N} c'_n T_n(z)$.

For functions O that can be analytically continued to the *Bernstein ellipse* $E_\rho \coloneqq \{\frac{1}{2}(z + z^{-1}) \colon |z| = \rho\}$ for $\rho > 1$, the corresponding coefficients $\{c_n\}$, $\{c'_n\}$ decay exponentially ($|c_n|, |c'_n| \lesssim \|O\|_{L^\infty(E_\rho)} \rho^{-n}$), which leads to the following error estimates

$$\|O - \Pi_N O\|_{L^\infty([-1,1])} + \|O - I_N O\|_{L^\infty([-1,1])} \lesssim \|O\|_{L^\infty(E_\rho)} \frac{\rho^{-N}}{\rho - 1}. \tag{4.8.3}$$

For $O^\beta = F^\beta$ or G^β, these estimates give an exponential rate of convergence with exponent depending on $\sim \beta^{-1}$. Indeed, after scaling $\mathcal{H}$ so that the spectrum is contained in $[-1,1]$, we obtain

$$\begin{aligned} \left| O^\beta_\ell(\boldsymbol{X}) - \Pi_N O^\beta_\ell(\boldsymbol{X}) \right| &\leqslant \left\| O^\beta(\mathcal{H}) - \Pi_N O^\beta(\mathcal{H}) \right\|_{\ell^2 \to \ell^2} \\ &\leqslant \|O^\beta - \Pi_N O^\beta\|_{L^\infty([-1,1])}, \end{aligned} \tag{4.8.4}$$

and we conclude by directly applying (4.8.3). The same estimate also holds for I_N (or any polynomial).

For full details of all the statements made in this subsection, see [124].

Classical logarithmic potential theory

In this section, we give a very brief introduction to classical potential theory in order to lay out the key notation. For a more thorough treatment, see [103] or [52, 82, 104, 124].

It can be seen from the Hermite integral formula (4.8.2) that the approximation error for polynomial interpolation may be determined by taking the ratio of the size of the node polynomial $\ell_{\mathcal{X}}$ at the approximation points to the size of $\ell_{\mathcal{X}}$ along an appropriately chosen contour. Logarithmic potential theory provides an elegant mechanism for choosing the interpolation points so that the asymptotic behaviour of $\ell_{\mathcal{X}}$ can be described.

We suppose that $E \subseteq \mathbb{C}$ is a compact set. We will see that choosing the interpolation nodes as to maximise the geometric mean of pairwise distances provides a particularly good approximation scheme:

$$\delta_n(E) \coloneqq \max_{z_1,\dots,z_n \in E} \Big(\prod_{1 \leqslant i < j \leqslant n} |z_i - z_j| \Big)^{\frac{2}{n(n-1)}}. \tag{4.8.5}$$

Any set $\mathcal{F}_n \subseteq E$ attaining this maximum is known as a *Fekete set*. It can be shown that the quantities $\delta_n(E)$ form a decreasing sequence and thus converges to what is known as the *transfinite diameter*: $\tau(E) \coloneqq \lim_{n\to\infty} \delta_n(E)$.

We let $\ell_{\mathcal{X}_n}(z) \coloneqq \prod_{x \in \mathcal{X}_n}(z - x)$ denote the node polynomial corresponding to a Fekete set $\mathcal{X}_n$ and note that

$$\begin{aligned} |\ell_{\mathcal{X}_n}(z)| \delta_n(E)^{\frac{n(n-1)}{2}} &= \prod_{x \in \mathcal{X}_n} |z - x| \cdot \max_{z_1,\dots,z_n \in E} \prod_{1 \leqslant i < j \leqslant n} |z_i - z_j| \\ &= \max_{z_0,\dots,z_n \in E:\ z_0 = z} \prod_{0 \leqslant i < j \leqslant n} |z_i - z_j| \\ &\leqslant \max_{z_0,\dots,z_n \in E} \prod_{0 \leqslant i < j \leqslant n} |z_i - z_j| = \delta_{n+1}(E)^{\frac{n(n+1)}{2}}. \end{aligned} \tag{4.8.6}$$

Therefore, rearranging (4.8.6), we obtain $\lim_{n\to\infty} \|\ell_{\mathcal{X}_n}\|_{L^\infty(E)}^{1/n} \leqslant \tau(E)$. In fact, this inequality can be replaced with equality, showing that Fekete sets allow us to describe the asymptotic behaviour of the node polynomials on the domain of approximation.

To extend these results, it is useful to recast the maximisation problem (4.8.5) into the following minimisation problem, describing the minimal logarithmic energy attained by n particles lying in E with the repelling force

$1/|z_i - z_j|$ between particles i and j lying at positions z_i and z_j, respectively:

$$\mathcal{E}_n(E) \coloneqq \min_{z_1,\ldots,z_n \in E} \sum_{1 \leqslant i < j \leqslant n} \log \frac{1}{|z_i - z_j|} = \frac{n(n-1)}{2} \log \frac{1}{\delta_n(E)}. \tag{4.8.7}$$

Fekete sets can therefore be seen as minimal energy configurations and described by the normalised counting measure $\nu_n \coloneqq \frac{1}{n} \sum_{j=1}^{n} \delta_{z_j}$ where $\mathcal{F}_n = \{z_j\}_{j=1}^{n}$.

The minimisation problem (4.8.7) may be extended for general unit Borel measures μ supported on E by defining the logarithmic potential and corresponding total energy by

$$U^{\mu}(z) \coloneqq \int \log \frac{1}{|z-\xi|} \mathrm{d}\mu(\xi) \qquad \text{and} \qquad I(\mu) \coloneqq \iint \log \frac{1}{|z-\xi|} \mathrm{d}\mu(\xi)\mathrm{d}\mu(z).$$

The infimum of the energy over the space of unit Borel measures supported on E, known as the *Robin constant* for E, will be denoted $-\infty < V_E \leqslant +\infty$. The *capacity* of E is defined as $\operatorname{cap}(E) \coloneqq e^{-V_E}$ and is equal to the transfinite diameter [50]. Using a compactness argument, it can be shown that there exists an *equilibrium measure* ω_E with $I(\omega_E) = V_E$ and, in the case $V_E < \infty$, by the strict convexity of the integral, ω_E is unique [105]. Moreover, if $V_E < \infty$ (equivalently, if $\operatorname{cap}(E) > 0$), then $U^{\omega_E}(z) \leqslant V_E$ for all $z \in \mathbb{C}$, with equality holding on E except on a set of capacity zero (we say this property holds *quasi-everywhere*).

Moreover, if $\operatorname{cap} E > 0$, then it can be shown that the normalised counting measures, ν_n, corresponding to a sequence of Fekete sets weak-$\star$ converges to ω_E. Since $U^{\nu_n}(z) = \frac{1}{n} \log \frac{1}{|\ell_n(z)|}$, the weak-$\star$ convergence allows one to conclude that

$$\begin{aligned} &\lim_{n\to\infty} \|\ell_n\|_{L^\infty(E)}^{1/n} = \operatorname{cap}(E), \quad \text{and} \\ &\lim_{n\to\infty} |\ell_n(z)|^{1/n} = e^{-U^{\omega_E}(z)} =: \operatorname{cap}(E) e^{g_E(z)} \end{aligned} \tag{4.8.8}$$

uniformly on compact subsets of $\mathbb{C} \setminus E$. Here, we have defined the *Green's function* $g_E(z) \coloneqq V_E - U^{\omega_E}(z)$, which describes the asymptotic behaviour

of the node polynomials corresponding to Fekete sets. We therefore wish to understand the Green's function g_E.

Construction of the Green's function

Now we restrict our attention to the particular case where $E \subseteq \mathbb{R}$ is a union of finitely many compact intervals of non-zero length.

It can be shown that the Green's function g_E satisfies the following Dirichlet problem on $\mathbb{C} \setminus E$ [103]:

$$\Delta g_E(z) = 0 \quad \text{on } \mathbb{C} \setminus E, \tag{4.8.9a}$$

$$g_E(z) \sim \log|z| \quad \text{as } |z| \to \infty, \tag{4.8.9b}$$

$$g_E(z) = 0 \quad \text{on } E. \tag{4.8.9c}$$

In fact, it can be shown that (4.8.9) admits a unique solution [103] and thus (4.8.9) is an alternative definition of the Green's function. Using this characterisation, it is possible to explicitly construct the Green's function g_E as follows.

In the upper half plane, $g_E(z) = \operatorname{Re}(G_E(z))$ where

$$G_E \colon \{z \in \mathbb{C} \colon \operatorname{Im}(z) \geqslant 0\} \to \{z \in \mathbb{C} \colon \operatorname{Re}(z) \geqslant 0, \operatorname{Im}(z) \in [0, \pi]\}$$

is a conformal mapping on $\{z \colon \operatorname{Im}(z) > 0\}$ with $G_E(E) = i[0, \pi]$, $G_E(\min E) = i\pi$, and $G_E(\max E) = 0$. Using the symmetry of E with respect to the real axis, we may extend $\operatorname{Re}(G_E(z))$ to the whole complex plane via the Schwarz reflection principle. Then, one can easily verify that this analytic continuation satisfies (4.8.9). Since the image of G_E is a (generalised) polygon, $z \mapsto G_E(z)$ is an example of a Schwarz-–Christoffel mapping [42]. See Figure 4.3 for the case $E = [-1, -\varepsilon] \cup [\varepsilon, 1]$.

We shall briefly discuss the construction of the Schwarz-–Christoffel mapping G_E for $E = [-1, \varepsilon_-] \cup [\varepsilon_+, 1]$. We define the *pre-vertices* $z_1 = -1, z_2 = \varepsilon_-, z_4 = \varepsilon_+, z_5 = 1$ and wish to construct a conformal map G_E with $G_E(z_k) = \omega_k$ as in

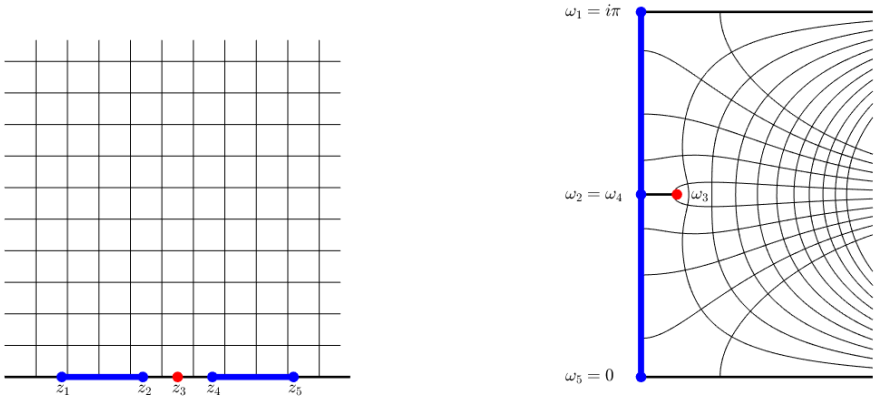


Figure 4.3: The Schwarz–Christoffel mapping G_E with $E = [z_1, z_2] \cup [z_4, z_5]$ which maps the upper half plane (left) onto the infinite slit strip $\{\omega \in \mathbb{C}\colon \operatorname{Re}\omega > 0, \operatorname{Im}\omega \in (0,\pi)\}$ (right), is continuous on $\{z \in \mathbb{C}\colon \operatorname{Re} z \geqslant 0\}$ and maps the intervals $[z_1, z_2]$, $[z_4, z_5]$ to $[\omega_1, \omega_2], [\omega_4, \omega_5] \subseteq i[0,\pi]$, respectively. We also plot the image of an 10×10 equi-spaced grid. A parameter problem is solved in order to obtain z_3 and thus ω_3 and $\omega_2 = \omega_4$ whereas the other constants are fixed. Here, we take $z_1 = -1, z_2 = -\varepsilon, z_4 = \varepsilon, z_5 = 1, \omega_1 = i\pi, \omega_5 = 0$ with $\varepsilon = 0.3$.

Figure 4.3. For simplicity, we also define $z_0 \coloneqq -\infty$ and $z_6 \coloneqq \infty$ and observe that because the image is a polygon, $\arg G_E'(z)$ must be constant on each interval (z_{k-1}, z_k) and

$$\arg G_E'(z_k^+) - \arg G_E'(z_k^-) = (1 - \alpha_k)\pi \tag{4.8.10}$$

where $z_k^- \in (z_{k-1}, z_k)$, $z_k^+ \in (z_k, z_{k+1})$, and $\alpha_k \pi$ is the interior angle of the infinite slit strip at vertex ω_k (that is, $\alpha_1 = \alpha_2 = \alpha_4 = \alpha_5 = \frac{1}{2}$ and $\alpha_3 = 2$). After defining $z^\alpha \coloneqq |z|^\alpha e^{i\alpha \arg z}$ where $\arg z \in (-\pi, \pi]$, we can see that for $z \in (z_{k-1}, z_k)$, we have $\arg \prod_{j=k}^5 (z - z_j)^{\alpha_j - 1} = \sum_{j=k}^5 (\alpha_j - 1)\pi$ and so the jump in the argument of $z \mapsto \prod_{j=1}^5 (z - z_j)^{\alpha_j - 1}$ is $(1 - \alpha_k)\pi$ at z_k as in (4.8.10). Therefore, integrating this expression, we obtain

$$G_E(z) = A + B \int_1^z \frac{\zeta - z_3}{\sqrt{\zeta + 1}\sqrt{\zeta - \varepsilon_-}\sqrt{\zeta - \varepsilon_+}\sqrt{\zeta - 1}} \mathrm{d}\zeta. \tag{4.8.11}$$

Since $G_E(1) = A$, we take $A = 0$ (to ensure (4.8.9c) holds). Moreover, since the real part of the integral is $\sim \log|z|$ as $|z| \to \infty$, we apply (4.8.9b) to conclude $B = 1$. Finally, we can choose z_3 such that $\operatorname{Re} G_E(z) = 0$ for all $z \in E$. That

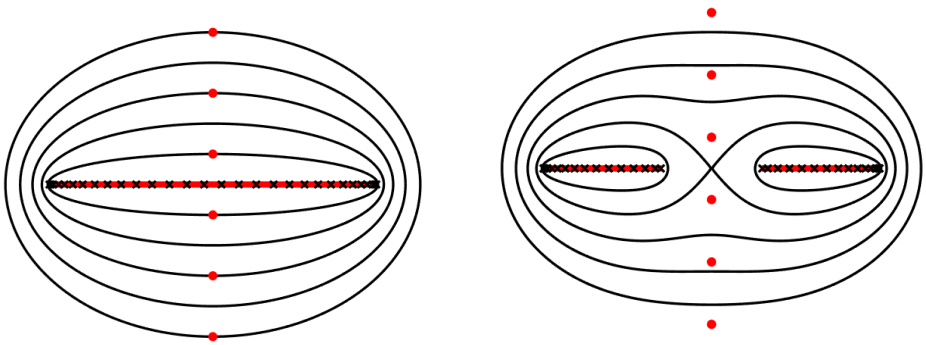
is,

$$z_3 \in (\varepsilon_-, \varepsilon_+): \qquad \int_{\varepsilon_-}^{\varepsilon_+} \frac{\zeta - z_3}{\sqrt{\zeta+1}\sqrt{\zeta-\varepsilon_-}\sqrt{\varepsilon_+-\zeta}\sqrt{1-\zeta}}\mathrm{d}\zeta = 0. \quad (4.8.12)$$

For more details, see [52]. We use the Schwarz-–Christoffel toolbox [42] in MATLAB to evaluate (4.8.11) and plot Figure 4.4.

For the simple case $E \coloneqq [-1,1]$, by the same analysis, we can disregard z_2, z_3, z_4 and $\omega_2, \omega_3, \omega_4$ and integrate the corresponding expression to obtain the closed form $G_{[-1,1]}(z) = \log(z + \sqrt{z-1}\sqrt{z+1})$.

A similar analysis allows one to construct conformal maps from the upper half plane to the interior of any polygon. For further details, rigorous proofs and numerical considerations, see [44].



(a) Metal: $E = [-1,1]$.

(b) Insulator: $E = [-1,-\varepsilon]\cup[\varepsilon,1]$, $\varepsilon = 0.30$ (2 s.f.).

Figure 4.4: Equi-potential curves $\mathscr{C}_{r_k} \coloneqq \{z \in \mathbb{C}\colon e^{g_E(z)} = r_k\}$ for both metals (a) and insulators (b) where $\frac{1}{2}(r_k - r_k^{-1}) = \frac{k\pi}{\beta}$ for $k \in \{1,2,3,4,5\}$ and $\beta = 10$. In the case of metals (a), the equi-potential curves agree with Bernstein ellipses. We also plot the poles of $F^\beta(\,\cdot\,)$ which determine the maximal admissible integration contours: for (a), we can take contours $\mathscr{C}_r$ for all $r < r_1$ and, for (b), the contour $\mathscr{C}_{r_2}$ can be used for all positive Fermi-temperatures (we have chosen the gap carefully so that $\mathscr{C}_{r_2}$ self-intersects at μ). Shown in black crosses are 30 Fejér points in each case. To create these plots we consider an integral formula for the Green's function $z \mapsto g_E(z)$ [52] and use the Schwarz-Christoffel MATLAB toolbox [41, 42] to approximate these integrals.

Interpolation nodes

The only difficulty in obtaining (4.8.8) in practice is the fact that Fekete sets are difficult to compute. An alternative, based on the Schwarz-–Christoffel

mapping G_E, are *Fejér points*. For equally spaced points $\{\zeta_j\}_{j=1}^n$ on the interval $i[0,\pi]$, the n^{th} Fejér set is defined by $\{G_E^{-1}(\zeta_j)\}_{j=1}^n$. Fejér sets are also *asymptotically optimal* in the sense that (4.8.8) is satisfied where ℓ_n is now the node polynomial corresponding to n-point Fejér set.

Another approach is to use *Leja points* which are generated by the following algorithm: for fixed $z_1,\dots,z_n$, the next interpolation node z_{n+1} is constructed by maximising $\prod_{j=1}^n |z_j - z|$ over all $z \in E$. Sets of this form are also asymptotically optimal [119] for any choice of $z_1 \in E$. Since we have fixed the previous nodes $z_1,\dots,z_n$, the maximisation problem for constructing z_{n+1} is much simpler than that of (4.8.5).

More generally, if the normalised counting measure corresponding to a sequence of sets $\{z_j\}_{j=1}^n \subseteq E$ weak-$\star$ converges to the equilibrium measure ω_E, then the corresponding node polynomials satisfy (4.8.8).

For the simple case where $E = [-1,1]$, many systems of zeros or maxima of sequences of orthogonal polynomials are asymptotically optimal in the sense of (4.8.8). In fact, since the equilibrium measure for $[-1,1]$ is the arcsine measure [104]

$$\mathrm{d}\mu_{[-1,1]}(x) = \frac{1}{\pi}\frac{1}{\sqrt{1-x^2}}\mathrm{d}x,$$

any sequence of sets with this limiting distribution is asymptotically optimal. An example of particular interest are the *Chebyshev points* $\{\cos\frac{j\pi}{n}\}_{0\leqslant j\leqslant n}$ given by the $n+1$ extreme points of the Chebyshev polynomials defined by $T_n(\cos\theta) = \cos n\theta$.

Asymptotically optimal polynomial approximations

Suppose that E is the union of finitely many compact intervals of non-zero length and $O\colon E \to \mathbb{C}$ extents to an analytic function in an open neighbourhood of E. On defining $\mathscr{C}_\gamma := \{z \in \mathbb{C}\colon g_E(z) = \gamma\}$, we denote by $\gamma^\star$ the maximal constant for which O is analytic on the interior of $\mathscr{C}_{\gamma^\star}$. We let $P_N^\star$ be the best $L^\infty(E)$-approximation to O in the space of polynomials of degree at most N and suppose that I_N is a polynomial interpolation operator in $N+1$ points

satisfying (4.8.9). Then, the Green's function g_E determines the asymptotic rate of approximation for not only polynomial interpolation but also for best approximation:

$$\lim_{N\to\infty} \|O - P_N^\star\|_{L^\infty(E)}^{1/N} = \lim_{N\to\infty} \|O - I_N O\|_{L^\infty(E)}^{1/N} = e^{-\gamma^\star}. \tag{4.8.13}$$

For a proof that the asymptotic rate of best approximation is given by the Green's function see [104]. The result for polynomial interpolation uses the Hermite integral formula and (4.8.8), see (4.8.18) and (4.8.19), below.

4.8.2 Linear body-order approximation

In this section, we use the classical logarithmic potential theory from §4.8.1 to prove the approximation error bounds for interpolation. However, we first show in more detail that polynomial approximations lead to body-order approximations:

Proof of Proposition 4.1. We first simplify the notation by absorbing the effective potential and two-centre terms into the three-centre summation:

$$\begin{aligned} \mathcal{H}(\boldsymbol{X})_{k_1k_2} &= \sum_m \mathcal{H}_{k_1k_2m}, \quad \text{where} \\ \mathcal{H}_{k_1k_2m} &\coloneqq \begin{cases} \frac{1}{2}h(\boldsymbol{X}_{k_1k_2}) + \delta_{k_1k_2}v_{k_1}\mathrm{Id}_{N_\mathrm{b}}, & \text{if } m \in \{k_1,k_2\}, \\ t(\boldsymbol{X}_{k_1m}, \boldsymbol{X}_{k_2m}), & \text{if } m \notin \{k_1,k_2\}. \end{cases} \end{aligned} \tag{4.8.14}$$

Now, supposing that $I_{\mathcal{X}}O(z) = \sum_{j=0}^{|\mathcal{X}|-1} c_j z^j$, we obtain

$$\begin{aligned} I_{\mathcal{X}}O_\ell(\boldsymbol{X}) &= \mathrm{tr} \sum_{j=0}^{|\mathcal{X}|-1} c_j \sum_{\ell_1,\ldots,\ell_{j-1}} \mathcal{H}_{\ell\ell_1}\mathcal{H}_{\ell_1\ell_2}\ldots\mathcal{H}_{\ell_{j-1}\ell} \\ &= \mathrm{tr} \sum_{j=0}^{|\mathcal{X}|-1} c_j \sum_{\substack{\ell_1,\ldots,\ell_{j-1} \\ m_1,\ldots,m_j}} \mathcal{H}_{\ell\ell_1m_1}\mathcal{H}_{\ell_1\ell_2m_2}\ldots\mathcal{H}_{\ell_{j-1}\ell m_j}, \end{aligned} \tag{4.8.15}$$

where the first two terms in the outer summation are c_0 and $c_1\mathcal{H}_{\ell\ell}$. Now, for a fixed body-order $(n+1)$, and $k_1 < \cdots < k_n$ with $k_l \neq \ell$, we construct

$V_{nN}(\boldsymbol{X}_\ell; \boldsymbol{X}_{\ell k_1}, \dots, \boldsymbol{X}_{\ell k_n})$ by collecting all terms in (4.8.15) with $0 \leqslant j \leqslant |\mathcal{X}|-1$ and $\{\ell, \ell_1, \dots, \ell_{j-1}, m_1, \dots, m_j\} = \{\ell, k_1, \dots, k_n\}$. In particular, the maximal body-order in this expression is $2(|\mathcal{X}|-1)$ for three-centre models and $|\mathcal{X}|-1$ in the two-centre case.

More explicitly, using the notation (4.5.1), we have

$$
\begin{aligned}
&V_{nN}(\boldsymbol{X}_\ell; \boldsymbol{X}_{\ell k_1}, \dots, \boldsymbol{X}_{\ell k_n}) \\
&= \operatorname{tr} \sum_{j=0}^{|\mathcal{X}|-1} c_j \sum_{\substack{\ell_1,\dots,\ell_{j-1},m_1,\dots,m_j \\ \{\ell,\ell_1,\dots,\ell_{j-1},m_1,\dots,m_j\}=\{\ell,k_1,\dots,k_n\}}} \mathcal{H}_{\ell\ell_1 m_1} \mathcal{H}_{\ell_1 \ell_2 m_2} \dots \mathcal{H}_{\ell_{j-1}\ell m_j} \qquad (4.8.16) \\
&= \operatorname{tr} \sum_{K \subseteq \{k_1,\dots,k_n\}} (-1)^{n-|K|} I_{\mathcal{X}} O\big(\mathcal{H}\big|_{\ell;K}\big)_{\ell\ell}. \qquad (4.8.17)
\end{aligned}
$$

Here, we have applied an inclusion-exclusion principle to ensure that we are not only summing over sites in $\{k_1, \dots, k_n\}$ but we select at least one of each site in this set. Indeed, if we choose $\ell_1, \dots, \ell_{j-1}, m_1, \dots, m_j$ such that $\{\ell, \ell_1, \dots, \ell_{j-1}, m_1, \dots, m_j\} = \{\ell\} \cup K_0$, then the expression $\mathcal{H}_{\ell\ell_1 m_1} \cdots \mathcal{H}_{\ell_{j-1}\ell m_j}$ appears in each term of (4.8.17) with $K \supseteq K_0$ exactly once (with a $\pm$ sign). Therefore, the number of times $\mathcal{H}_{\ell\ell_1 m_1} \mathcal{H}_{\ell_1 \ell_2 m_2} \dots \mathcal{H}_{\ell_{j-1}\ell m_j}$ appears is exactly

$$
\sum_{l=0}^{n-|K_0|} (-1)^{n-|K_0|-l} \binom{n-|K_0|}{l} = \begin{cases} 1 & \text{if } |K_0| = n, \\ 0 & \text{otherwise.} \end{cases}
$$

That is, (4.8.17) only contains the terms in the summation (4.8.16). □

Proof of Theorem 4.2. We let $\ell_N(x) \coloneqq \prod_j (x - x_j^N)$ be the node polynomial for $\mathcal{X}_N \coloneqq \{x_j^N\}_{j=0}^N$. Again, we fix the configuration $\boldsymbol{X}$ and consider $\mathcal{H} \coloneqq \mathcal{H}(\boldsymbol{X})$.

Supposing that $\mathscr{C}$ is a simple closed positively oriented contour encircling

$\sigma(\mathcal{H})$, we apply the Hermite integral formula (4.8.2) to obtain:

$$\begin{aligned}\left|O_\ell^\beta(\boldsymbol{X}) - I_{\mathcal{X}_N} O_\ell^\beta(\boldsymbol{X})\right| &\leqslant \|O^\beta(\mathcal{H}) - I_{\mathcal{X}_N} O^\beta(\mathcal{H})\|_{\ell^2\to\ell^2} \\ &= \sup_{z\in\sigma(\mathcal{H})} \left|O^\beta(z) - I_{\mathcal{X}_N} O^\beta(z)\right| \\ &\leqslant \sup_{z\in\sigma(\mathcal{H})} \left|\frac{1}{2\pi i}\oint_{\mathscr{C}} \frac{\ell_N(z)}{\ell_N(\xi)}\frac{O^\beta(\xi)}{\xi - z}\mathrm{d}\xi\right| \\ &\leqslant \frac{\|O^\beta\|_{\mathscr{C}}}{\operatorname{dist}\big(\mathscr{C}, \sigma(\mathcal{H})\big)} \sup_{z\in\sigma(\mathcal{H}),\,\xi\in\mathscr{C}} \left|\frac{\ell_N(z)}{\ell_N(\xi)}\right|. \end{aligned} \tag{4.8.18}$$

At this point we apply standard results of classical logarithmic potential theory (see, §4.8.1 or [82]) and conclude by noting that if the interpolation points are asymptotically distributed according to the equilibrium distribution corresponding to $E \coloneqq I_- \cup I_+$, then after applying (4.8.8), we have

$$\lim_{N\to\infty} \left|\frac{\ell_N(z)}{\ell_N(\xi)}\right|^{\frac{1}{N}} = e^{g_E(z) - g_E(\xi)}. \tag{4.8.19}$$

Here, the equilibrium distribution and the Green's function $g_E(z)$ are concepts introduced in §4.8.1.

Therefore, by choosing the contour $\mathscr{C} \coloneqq \{\xi \in \mathbb{C}\colon g_E(\xi) = \gamma\}$ for $0 < \gamma < g_E(\mu + i\pi\beta^{-1})$, the asymptotic exponents in the approximation error is γ. The maximal asymptotic convergence rate is given by $g_E(\mu + i\pi\beta^{-1})$ since $\mathscr{C}$ must be contained in the region of analyticity of O^β and the first singularity of O^β is at $\mu + i\pi\beta^{-1}$ (for $O^\beta = F^\beta$ or G^β). Examples of the equi-potential level sets $\mathscr{C}$ are given in Figure 4.4.

Using the Green's function results of §4.8.1, we have $g_E(\mu + i\pi\beta^{-1}) = \operatorname{Re} G_E(\mu + i\pi\beta^{-1})$ where G_E is the integral (4.8.11). The asymptotic behaviour of this maximal asymptotic convergence rate for the separate $\beta \to \infty$ and $\mathsf{g} \to 0$ limits can be found in [52, 109]. Here, we consider the $\beta^{-1} + \mathsf{g} \to 0$ limit where the gap remains symmetric about the chemical potential μ.

To simplify the notation we consider $I_- \cup I_+ = [-1, \varepsilon_-] \cup [\varepsilon_+, 1]$ where $\varepsilon_\pm = \mu \pm \frac{1}{2}\mathsf{g}$. By choosing to integrate (4.8.11) along the contour composed of

the intervals $[1, \mu]$ and $[\mu, \mu + i\pi\beta^{-1}]$, we obtain

$$G_E(\mu + i\pi\beta^{-1}) = G_E(\mu) + \int_{\mu}^{\mu+i\pi\beta^{-1}} \frac{\zeta - z_3}{\sqrt{\zeta+1}\sqrt{\zeta-\varepsilon_-}\sqrt{\zeta-\varepsilon_+}\sqrt{\zeta-1}} \mathrm{d}\zeta. \tag{4.8.20}$$

Since $g_E(\mu) \sim \mathsf{g}$ as $\mathsf{g} \to 0$ [52], we only consider the remaining term in (4.8.20).

For $\zeta \in \mu + i[0, \pi\beta^{-1}]$, we have $c^{-1} \leqslant |\sqrt{\zeta \pm 1}| \leqslant c$, and so the integral in (4.8.20) has the same asymptotic behaviour as the following

$$\begin{aligned} &\int_{\mu}^{\mu+i\pi\beta^{-1}} \frac{\zeta - z_3}{\sqrt{\zeta-\varepsilon_-}\sqrt{\zeta-\varepsilon_+}} \mathrm{d}\zeta \\ &\quad = \mathsf{g} \int_{\frac{1}{2}}^{\frac{1}{2}+\frac{i\pi\beta^{-1}}{\mathsf{g}}} \frac{\sqrt{\zeta}}{\sqrt{\zeta-1}} \mathrm{d}\zeta + (\varepsilon_- - z_3) \int_{\frac{1}{2}}^{\frac{1}{2}+\frac{i\pi\beta^{-1}}{\mathsf{g}}} \frac{1}{\sqrt{\zeta}\sqrt{\zeta-1}} \mathrm{d}\zeta, \end{aligned} \tag{4.8.21}$$

where we have used the change of variables $\frac{\zeta-\varepsilon_-}{\varepsilon_+-\varepsilon_-} \to \zeta$. Since the integrands are uniformly bounded along the domain of integration, (4.8.21) is $\sim \beta^{-1}$ as $\beta \to \infty$.

The constant pre-factor in (4.8.18) is inversely proportional to the distance $\mathrm{dist}\big(\mathscr{C}, \sigma(\mathcal{H})\big)$ between the contour $\mathscr{C} = \{g_E = \gamma\}$ and the spectrum $\sigma(\mathcal{H})$. In particular, since g_E is uniformly Lipschitz with some constant $L > 0$ on the compact region bounded by $\mathscr{C}$, we have: there exists $\lambda \in \sigma(\mathcal{H})$ and $\xi \in \mathscr{C}$ such that

$$\mathrm{dist}\big(\mathscr{C}, \sigma(\mathcal{H})\big) = |\xi - \lambda| \geqslant \frac{1}{L} |g_E(\xi) - g_E(\lambda)| = \frac{1}{L}\gamma.$$

Therefore, choosing γ to be a constant multiple of $g_E(\mu + i\pi\beta^{-1})$, we conclude that the constant pre-factor C satisfies $C \sim (\mathsf{g} + \beta^{-1})^{-1}$ as $\mathsf{g} + \beta^{-1} \to 0$.

To extend the body-order expansion results to derivatives (in particular, to forces), we write the quantities of interest using resolvent calculus, apply (3.6.3) to bound the derivatives of the resolvent, and use the Hermite integral formula (4.8.18) to conclude: for $\mathscr{C}_1$, $\mathscr{C}_2$ simple closed positively oriented contours

encircling the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ and $\mathscr{C}_1$, respectively, we have

$$\begin{aligned}\left|\frac{\partial O_\ell(\boldsymbol{X})}{\partial \boldsymbol{X}_m}-\frac{\partial I_{\mathcal{X}_N} O_\ell(\boldsymbol{X})}{\partial \boldsymbol{X}_m}\right| &= \frac{1}{2\pi}\left|\oint_{\mathscr{C}_1}\big(O(z)-I_{X_N}O(z)\big)\frac{\partial\big(\mathcal{H}(\boldsymbol{X})-z\big)^{-1}_{\ell\ell}}{\partial \boldsymbol{X}_m}\mathrm{d}z\right| \\ &= \frac{1}{4\pi^2}\left|\oint_{\mathscr{C}_1}\oint_{\mathscr{C}_2}\frac{\ell_N(z)}{\ell_N(\xi)}\frac{O(\xi)}{\xi-z}\frac{\partial\big(\mathcal{H}(\boldsymbol{X})-z\big)^{-1}_{\ell\ell}}{\partial \boldsymbol{X}_m}\mathrm{d}\xi\mathrm{d}z\right| \\ &\leqslant Ce^{-\eta r_{\ell m}}\sup_{z\in\mathscr{C}_1,\xi\in\mathscr{C}_2}\left|\frac{\ell_N(z)}{\ell_N(\xi)}\right|. \end{aligned} \tag{4.8.22}$$

We conclude by choosing appropriate contours $\mathscr{C}_l=\{g_E=\gamma_l\}$ for $l=1,2$ and applying (4.8.19). □

Role of the Point Spectrum

Proof of Theorem 4.3. Suppose that $\mathscr{C}$ is a simple closed contour encircling the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big)$ and (λ_s,ψ_s) are normalised eigenpairs corresponding to the finitely many eigenvalues outside $I_-\cup I_+$. Therefore, we have

$$\begin{aligned}O^\beta_\ell(\boldsymbol{X}^{\mathrm{d}})-I_{\mathcal{X}_N}O^\beta_\ell(\boldsymbol{X}^{\mathrm{d}}) = \mathrm{tr}\oint_{\mathscr{C}}\big(O^\beta(z)-I_{\mathcal{X}_N}O^\beta(z)\big)\big(z-\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big)^{-1}_{\ell\ell}\frac{\mathrm{d}z}{2\pi i} \\ +\sum_s\big(O^\beta(\lambda_s)-I_{\mathcal{X}_N}O^\beta(\lambda_s)\big)\big|[\psi_s]_\ell\big|^2.\end{aligned} \tag{4.8.23}$$

The first term of (4.8.23) may be treated in the same way as in the proof of Theorem 4.2. Moreover, derivatives of this term may be treated in the same way as in (4.8.22). It is therefore sufficient to bound the remaining term and its derivative.

Firstly, we note that the eigenvectors corresponding to isolated eigenvalues in the spectral gap have the following decay [98]: for $\mathscr{C}'$ a simple closed positively oriented contour (or system of contours) encircling $\{\lambda_s\}$, we have

$$\begin{aligned}\sum_s\big|[\psi_s]_\ell\big|^2 &= \frac{1}{2\pi}\left|\oint_{\mathscr{C}'}\big[\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big)-z\big)^{-1}\big]_{\ell\ell}\mathrm{d}z\right| \\ &= \frac{1}{2\pi}\left|\oint_{\mathscr{C}'}\big[\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big)-z\big)^{-1}-\big(\mathcal{H}(\boldsymbol{X})-z\big)^{-1}\big]_{\ell\ell}\mathrm{d}z\right| \\ &\leqslant Ce^{-\gamma_{\mathrm{CT}}[|\boldsymbol{r}_\ell|-R_{\mathrm{d}}]},\end{aligned} \tag{4.8.24}$$

where γ_{CT} is the Combes–Thomas constant from Lemma 3.3 depending on the constant $\mathfrak{d} = \operatorname{dist}\big(\mathscr{C}', \sigma(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}}))\big)$. The constant pre-factor in (4.8.24) depends on the distance between the contour and the defect spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{d}})\big)$. Similar estimates hold for the derivatives. For full details on the derivation of (4.8.24), see [98, (5.18)–(5.21)] or the proof of Theorem 3.2.

Therefore, combining (4.8.24) and the Hermite integral formula (4.8.2), we conclude as in the proof of Theorem 4.2. □

4.8.3 Non-linear body-order approximation

Recursion method

In the following we briefly introduce the recursion method [66, 67], a reformulation of the Lanczos process [81], which generates a tri-diagonal (Jacobi) operator T [120] whose spectral measure is D_ℓ and the corresponding sequence of orthogonal polynomials [55]. This process provides the basis for constructing approximations to the LDOS giving rise to nonlinear approximation schemes satisfying Theorem 4.4.

Recall that D_ℓ is the LDOS satisfying (4.2.1). We start by defining $p_0 \coloneqq 1$, $a_0 \coloneqq \int x \mathrm{d}D_\ell(x)$ and $b_1 p_1(x) \coloneqq x - a_0$ where b_1 is the normalising constant to ensure $\int p_1(x)^2 \mathrm{d}D_\ell(x) = 1$. Then, supposing we have defined $a_0, a_1, b_1, \ldots, a_n, b_n$ and the polynomials $p_0(x), \ldots, p_n(x)$, we set

$$b_{n+1} p_{n+1}(x) \coloneqq (x - a_n) p_n(x) - b_n p_{n-1}(x), \qquad \text{with} \tag{4.8.25}$$

$$\int p_{n+1}(x)^2 \mathrm{d}D_\ell(x) = 1, \qquad a_{n+1} \coloneqq \int x p_{n+1}(x)^2 \mathrm{d}D_\ell(x). \tag{4.8.26}$$

Moreover, for each N, we define

$$T_N \coloneqq \begin{pmatrix} a_0 & b_1 & & \\ b_1 & a_1 & \ddots & \\ & \ddots & \ddots & b_N \\ & & b_N & a_N \end{pmatrix}, \tag{4.8.27}$$

and let $T_\infty = T$ to be the infinite symmetric tridiagonal matrix on $\mathbb{N}_0$ with diagonal $(a_n)_{n\in\mathbb{N}_0}$ and off-diagonal $(b_n)_{n\in\mathbb{N}}$.

Then, we have the following key preliminary result (the proof of which follows the proof of Theorem 4.4):

Lemma 4.5. *The sequence of polynomials p_n generated by the recursion* (4.8.25) *and T_N defined by* (4.8.27) *satisfy*

(i) $\{p_n\}$ are orthonormal with respect to D_ℓ. That is,

$$\int p_n p_m \mathrm{d}D_\ell = [p_n(\mathcal{H})p_m(\mathcal{H})]_{\ell\ell} = \delta_{nm},$$

(ii) D_ℓ is the spectral measure of T corresponding to $\boldsymbol{e}_0 \coloneqq (1,0,0,\dots)^{\mathrm{T}}$,

(iii) If $[a,b]\cap\sigma(\mathcal{H}) = \emptyset$, then $[a,b]\cap\sigma(T_N)$ contains at most a single point.

Remark 4.9. *It will also prove convenient for us to renormalise the orthogonal polynomials by defining $P_n(x) \coloneqq b_n p_n(x)$ and $b_0 \coloneqq 1$. That is,*

$$P_0(x) = 1, \quad P_1(x) = x - a_0,$$

$$P_{n+1}(x) = \frac{x-a_n}{b_n}P_n(x) - \frac{b_n}{b_{n-1}}P_{n-1}(x), \quad \textit{for } n \geqslant 1 \tag{4.8.28}$$

$$b_{n+1}^2 = \int P_{n+1}(x)^2 \mathrm{d}D_\ell(x), \quad \textit{and} \quad a_{n+1} = \frac{\int x P_{n+1}(x)^2 \mathrm{d}D_\ell(x),}{b_{n+1}^2}. \tag{4.8.29}$$

One advantage of this formulation is that the coefficients $\{b_n\}$ are explicit.

Therefore, if we have the first $2N+1$ moments $\mathcal{H}_{\ell\ell},\dots,(\mathcal{H}^{2N+1})_{\ell\ell}$, it is possible to evaluate $Q_{2N+1}(\mathcal{H})_{\ell\ell}$ (that is, $\int Q_{2N+1}\mathrm{d}D_\ell$) for all polynomials Q_{2N+1} of degree at most $2N+1$, and thus compute T_N. In particular, for a fixed observable of interest O, we may write

$$\Theta\big(\mathcal{H}_{\ell\ell},\dots,[\mathcal{H}^{2N+1}]_{\ell\ell}\big) \coloneqq O(T_N)_{00}. \tag{4.8.30}$$

Remark 4.10. *In Appendix C.4 we introduce more complex bond order potential (BOP) schemes based on the recursion method and show that they also satisfy Theorem 4.4.*

Error estimates

Equation (4.8.30) states that the nonlinear approximation scheme given by Θ simply approximates the LDOS with the spectral measure of T_N corresponding to $\boldsymbol{e}_0 \coloneqq (1, 0, \dots, 0)^{\mathrm{T}}$. Since $[(T_N)^n]_{00} = [T^n]_{00}$ for all $n \leqslant 2N+1$ and $[T^n]_{00} = [\mathcal{H}^n]_{\ell\ell}$ for all n (Lemma 4.5 *(ii)*), we may apply the general error estimate (4.2.2) to conclude

$$\big|O_\ell - \Theta\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big)\big| \leqslant 2 \inf_{P_{2N+1} \in \mathcal{P}_{2N+1}} \|O - P_{2N+1}\|_{L^\infty(\sigma(\mathcal{H}) \cup \sigma(T_N))}. \tag{4.8.31}$$

Now, applying Lemma 4.5 *(iii)*, we may conclude that there are at most finitely many points in $\sigma(T_N)$ outside $I_- \cup I_+$, independently of N. In particular, these points do not affect the asymptotic error estimates for best L^∞ polynomial approximation on $I_- \cup \{\lambda_j\} \cup I_+$.

Analyticity

To conclude the proof of Theorem 4.4, we show that Θ as in (4.8.30) extents to an analytic function on some open set $U \subseteq \mathbb{C}^{2N+1}$. Throughout this section, we use the rescaled orthogonal polynomials $\{P_n\}$ from Remark 4.9.

For a polynomial $P(x) = \sum_{j=0}^m c_j x^j$, we use the notation $\mathcal{L}P(z_1, \dots, z_m) \coloneqq c_0 + \sum_{j=1}^m c_j z_j$ for the linear function satisfying $P(x) = \mathcal{L}P(x, x^2, \dots, x^m)$. To extend the recurrence coefficients from Remark 4.9, we start by defining

$$\begin{aligned} b_0 = 1, \quad a_0(z_1) &\coloneqq z_1, \quad P_1(x; z_1) \coloneqq x - a_0(z_1) = x - z_1, \\ b_1^2(z_1, z_2) &\coloneqq \mathcal{L}\big(x \mapsto P_1(x; z_1)^2\big)(z_1, z_2) = z_2 - z_1^2, \\ a_1(z_1, z_2, z_3) &\coloneqq \frac{\mathcal{L}\big(x \mapsto x P_1(x; z_1)^2\big)(z_1, z_2, z_3)}{b_1^2(z_1, z_2)} = \frac{z_3 - 2z_1 z_2 + z_1^3}{z_2 - z_1^2}. \end{aligned} \tag{4.8.32}$$

To simplify the notation, we write $\boldsymbol{z}_{1:m}$ for the m-tuple $(z_1, \dots, z_m)$. Given $a_0(z_1), \dots, a_n(\boldsymbol{z}_{1:2n+1})$ and $b_1(\boldsymbol{z}_{1:2}), \dots, b_n(\boldsymbol{z}_{1:2n})$, we define $P_{n+1}(x; \boldsymbol{z}_{1:2n+1})$ to be the polynomial in x satisfying the same recursion as Remark 4.9 but as

a function of $\boldsymbol{z}_{1:2n+1}$:

$$P_{n+1}(x;\boldsymbol{z}_{1:2n+1}) = \frac{x-a_n(\boldsymbol{z}_{1:2n+1})}{b_n(\boldsymbol{z}_{1:2n})}P_n(x;\boldsymbol{z}_{1:2n-1}) - \frac{b_n(\boldsymbol{z}_{1:2n})}{b_{n-1}(\boldsymbol{z}_{1:2n-2})}P_{n-1}(x;\boldsymbol{z}_{1:2n-3}).$$

With this notation, we define

$$b_{n+1}^2(\boldsymbol{z}_{1:2n+2}) \coloneqq \mathcal{L}\big(x \mapsto P_{n+1}(x;\boldsymbol{z}_{1:2n+1})^2\big)(\boldsymbol{z}_{1:2n+2}), \tag{4.8.33}$$

$$a_{n+1}(\boldsymbol{z}_{1:2n+3}) \coloneqq \frac{\mathcal{L}\big(x \mapsto xP_{n+1}(x;\boldsymbol{z}_{1:2n+1})^2\big)(\boldsymbol{z}_{1:2n+3})}{b_{n+1}^2(\boldsymbol{z}_{1:2n+2})}. \tag{4.8.34}$$

Since $P_{n+1}(x) = P_{n+1}(x;\mathcal{H}_{\ell\ell},\ldots,[\mathcal{H}^{2n+1}]_{\ell\ell})$, we have extended the definition of the recursion coefficients (4.8.29) to functions of multiple complex variables.

We now show that $a_n(\boldsymbol{z}_{1:2n+1})$ and $b_n^2(\boldsymbol{z}_{1:2n})$ are rational functions. As a preliminary step, we show that both P_{n+1}^2 and $\frac{P_{n+1}P_n}{b_n}$ are polynomials in x with coefficients given by rational functions of a_n, b_n^2 and all previous recursion coefficients. This statement is clearly true for $n=0$: $P_1^2 = (x-a_0)^2$ and $\frac{P_1P_0}{b_0} = x - a_0$. Therefore, by induction and noting that

$$P_{n+1}^2 = \left(\frac{x-a_n}{b_n}P_n\right)^2 - 2(x-a_n)\frac{P_nP_{n-1}}{b_{n-1}} + \frac{b_n^2}{b_{n-1}^2}P_{n-1}^2 \tag{4.8.35}$$

$$\frac{P_{n+1}P_n}{b_n} = \frac{x-a_n}{b_n^2}P_n^2 - \frac{P_nP_{n-1}}{b_{n-1}}, \tag{4.8.36}$$

we can conclude. Therefore, by (4.8.32) and (4.8.33) and (4.8.34), we can apply another induction argument to conclude that $a_{n+1}(\boldsymbol{z}_{1:2n+3})$ and $b_{n+1}^2(\boldsymbol{z}_{1:2(n+1)})$ are rational functions.

We fix N and define the following complex valued tri-diagonal matrix

$$T_N(\boldsymbol{z}) \coloneqq \begin{pmatrix} a_0(z_1) & b_1^2(\boldsymbol{z}_{1:2}) & & & \\ 1 & a_1(\boldsymbol{z}_{1:3}) & b_2^2(\boldsymbol{z}_{1:4}) & & \\ & 1 & \ddots & \ddots & \\ & & \ddots & \ddots & b_N^2(\boldsymbol{z}_{1:2N}) \\ & & & 1 & a_N(\boldsymbol{z}_{1:2N+1}) \end{pmatrix}. \tag{4.8.37}$$

If $z_j = [\mathcal{H}^j]_{\ell\ell}$ for each $j = 1, \dots, N$, (4.8.37) is similar to T_N from (4.8.27).

Now, on defining $U \coloneqq \{\boldsymbol{z} \in \mathbb{C}^{2N+1} \colon b_n^2(\boldsymbol{z}_{1:2n}) \neq 0 \ \forall n = 1, \dots, N\}$, the mapping $U \to \mathbb{C}^{(N+1)\times(N+1)}$ given by $\boldsymbol{z} \mapsto T_N(\boldsymbol{z})$ is analytic. Therefore, for appropriately chosen contours $\mathscr{C}_{\boldsymbol{z}}$ encircling $\sigma\big(T_N(\boldsymbol{z})\big)$, we have

$$\Theta(\boldsymbol{z}) \coloneqq O\big(T_N(\boldsymbol{z})\big)_{00} = \oint_{\mathscr{C}_{\boldsymbol{z}}} O(\omega)\Big[\big(\omega - T_N(\boldsymbol{z})\big)^{-1}\Big]_{00} \frac{\mathrm{d}\omega}{2\pi i}. \tag{4.8.38}$$

In particular, Θ is an analytic function on

$$\big\{\boldsymbol{z} \in U \colon O \text{ analytic in an open neighbourhood of } \sigma\big(T_N(\boldsymbol{z})\big)\big\}.$$

Remark 4.11. *Since $\mathbb{C}^{2N+1} \setminus U$ is the zero set for some (non-zero) polynomial P in $2N+1$ variables, it has $(2N+1)$-dimensional Lebesgue measure zero [63].*

Remark 4.12. *In Appendix C.3 we show that the eigenvalues of $T_N(\boldsymbol{z})$ are distinct for $\boldsymbol{z}$ in some open neighbourhood, $U_0 \subseteq U$, of $\mathbb{R}^{2N+1}$, which leads to the following alternative proof. On U_0, the eigenvalues and corresponding left and right eigenvectors can be chosen to be analytic: there exist analytic functions $\varepsilon_j, \psi_j, \phi_j^\star$ for $j = 0, \dots, N$ such that $\phi_i^\star(\boldsymbol{z})\psi_j(\boldsymbol{z}) = \delta_{ij}$ and*

$$T_N(\boldsymbol{z})\psi_j(\boldsymbol{z}) = \varepsilon_j(\boldsymbol{z})\psi_j(\boldsymbol{z}) \qquad \text{and} \qquad \phi_j^\star(\boldsymbol{z})T_N(\boldsymbol{z}) = \varepsilon_j(\boldsymbol{z})\phi_j^\star(\boldsymbol{z}).$$

(More precisely, we apply [62, Theorem 2] to obtain analytic functions $\psi_j, \phi_j^\star$ of each variable $z_1, \dots, z_{2N+1}$ separately and then apply Hartog's theorem [80] to conclude that $\psi_j, \phi_j^\star$ are analytic as functions on $U \subseteq \mathbb{C}^{2N+1}$). Therefore, the nonlinear method discussed in this section can also be written in the following form

$$\Theta = \sum_{j=0}^{N} [\psi_j]_0 [\phi_j^\star]_0 \cdot \big(O \circ \varepsilon_j\big) \tag{4.8.39}$$

which is an analytic function on $\{\boldsymbol{z} \in U_0 \colon O \text{ analytic at } \varepsilon_j(\boldsymbol{z}) \text{ for each } j\}$ (as it is a finite combination of analytic functions only involving products, compositions and sums).

Proof of Lemma 4.5

The idea behind the proofs are standard in the theory of Gauss quadrature (e.g. see [55]) and collected here for convenience of the reader.

Proof of (i). First note that $\int p_0 p_1 \mathrm{d}D_\ell = 0$. We assume that $p_0, \ldots, p_n$ are mutually orthogonal with respect to D_ℓ, and note that,

$$\begin{aligned} b_1 = b_1 \int p_1^2 \mathrm{d}D_\ell &= \int (x - a_0) p_1(x) \mathrm{d}D_\ell(x) = \int x p_0(x) p_1(x) \mathrm{d}D_\ell(x), \qquad \text{and} \\ b_n = b_n \int p_n^2 \mathrm{d}D_\ell &= \int \big((x - a_{n-1}) p_{n-1}(x) p_n(x) - b_{n-1} p_{n-2}(x) p_n(x) \big) \mathrm{d}D_\ell(x) \\ &= \int x p_{n-1}(x) p_n(x) \mathrm{d}D_\ell(x) \qquad \text{for } n \geqslant 2. \end{aligned} \tag{4.8.40}$$

Therefore, we conclude by noting

$$\begin{aligned} b_{n+1} \int p_{n+1} p_j \mathrm{d}D_\ell &= \int \big((x - a_n) p_n(x) p_j(x) - b_n p_{n-1}(x) p_j(x) \big) \mathrm{d}D_\ell(x) \\ &= \begin{cases} \int x p_n(x)^2 \mathrm{d}D_\ell - a_n & \text{if } j = n, \\ \int x p_n(x) p_{n-1}(x) \mathrm{d}D_\ell - b_n & \text{if } j = n-1 \\ 0 & \text{if } j \leqslant n-2, \end{cases} \end{aligned} \tag{4.8.41}$$

and applying (4.8.40).

Proof of (ii). By the orthogonality, we have

$$[T^0]_{ij} = \int p_i(x) x^0 p_j(x) \mathrm{d}D_\ell(x) = \delta_{ij}.$$

Therefore, assuming $[T^n]_{ij} = \int p_i(x) x^n p_j(x) \mathrm{d}D_\ell(x)$, we can conclude

$$\begin{aligned} [T^{n+1}]_{ij} &= \sum_k [T^n]_{ik} T_{kj} \\ &= \int p_i(x) x^n \big[b_j p_{j-1}(x) + a_j p_j(x) + b_{j+1} p_{j+1}(x) \big] \mathrm{d}D_\ell(x) \\ &= \int p_i(x) x^{n+1} p_j(x) \mathrm{d}D_\ell(x). \end{aligned}$$

Here, we have applied (4.8.25) directly. In particular, if $i = j = 0$, we obtain $[T^n]_{00} = [\mathcal{H}^n]_{\ell\ell}$ for all n.

Proof of (iii). First, we note that the recurrence relation (4.8.25) may be written as $x\boldsymbol{p}(x) = T_N\boldsymbol{p}(x) + b_{N+1}p_{N+1}(x)\boldsymbol{e}_N$ where T_N is the tri-diagonal matrix (4.8.27), $\boldsymbol{p}(x) \coloneqq \big(1, p_1(x), \ldots, p_N(x)\big)^T$, and $[\boldsymbol{e}_N]_j = \delta_{jN}$. In particular, the spectrum of T_N is exactly the set of zeros of p_{N+1}.

Now, suppose that $[a,b] \cap \sigma(\mathcal{H}) = \emptyset$ and $\sigma(T_N) = \{\varepsilon_j\}_{j=0}^N$ with $\varepsilon_0, \varepsilon_1 \in \sigma(T_N) \cap [a,b]$. Then, after defining $R(x) \coloneqq \prod_{j=2}^N (x - \varepsilon_j)$, a polynomial of degree $N-1$, and noting $(x-\varepsilon_0)(x-\varepsilon_1) > 0$ on $\sigma(\mathcal{H})$, we obtain

$$\int p_{N+1}(x)R(x)\mathrm{d}D_\ell(x) = \int R(x)^2(x-\varepsilon_0)(x-\varepsilon_1)\mathrm{d}D_\ell(x) > 0,$$

contradicting the orthogonality property (part *(i)*).

CHAPTER 5

Locality & Body-ordered Approximations: Self-consistent Tight Binding

- *Sections §5.3 and §5.4 are based on the article [122] "Locality of interatomic interactions in self-consistent tight binding models" published in the Journal of Nonlinear Science, 30(6): 3293–3319 (2020). However, the locality estimates for point defects in this thesis are sharper than those of [122]. Full details of the improvements are given in Remark 5.3,*
- *The results presented in §5.5.1 are from [123, §2.7] "Rigorous body-order approximations of an electronic structure potential energy landscape" submitted to the arXiv preprint server, arXiv:2106.12572 (2021). This paper is co-authored by Huajie Chen and Christoph Ortner,*
- *The content of §5.5.2 was previously unpublished.*

5.1 Introduction

In contrast to Chapter 3 and the previous works [26, 29], in this chapter we let the on-site Hamiltonian matrix entries depend on the local electron density through an effective potential. This results in a class of nonlinear tight

binding models encompassing for example DFTB [49,79,106], since the electron density itself depends on the Hamiltonian via a self-consistency condition. This approach therefore represents a key stepping stone between linear tight binding and more accurate nonlinear models such as Kohn–Sham density functional theory.

The self-consistency introduces the interesting issue of stability of the electronic structure problem; the main additional technical difficulty when compared to the linear model. Under a natural stability condition [45], stating that the linearised operator is invertible, we show that the potential energy landscape in this model can be decomposed into exponentially localised site contributions, thus justifying many classical interatomic potential (IP) and multiscale methods.

Again, we also consider point defects and show improved estimates which only weakly depend on the defect states within the band gap.

The highly nonlinear charge-equilibration leads *in principle* to arbitrarily complex intermixing of the nuclei information, and thus arbitrarily high body-order. However, the results on the body-ordered approximations for linear tight-binding models mean that each iteration of the self-consistent field (SCF) iteration can be expressed in terms of a low body-ordered and local interaction scheme. This leads us to propose a self-similar compositional representation of atomic properties that is highly reminiscent of recurrant neural network architectures. Each "layer" of this representation remains local and low-dimensional in the sense of Chapter 4.

We present a related approach by constructing a mapping between the configuration $(\boldsymbol{r}, \rho)$ and energies whose Euler–Lagrange equation is the self-consistency equation. Therefore, approximation of this energy by "simple" components yields an alternative approximation scheme that is both low-dimensional and short-ranged.

5.2 Self-consistency and Stability

For fixed $(\boldsymbol{r}, Z)$ and electron density ρ, we consider the following effective potential: for an infinitely differentiable function $v_0 \colon \mathbb{R} \to \mathbb{R}$, we define

$$v(\rho)_\ell \coloneqq v_0(\rho_\ell) + \sum_{m \neq \ell} \frac{\rho_m - Z_m}{r_{\ell m}} e^{-\gamma_v r_{\ell m}} \tag{5.2.1}$$

for some $\gamma_v > 0$. Of course $v(\rho)$ also depends on the positions and species of the atoms $(\boldsymbol{r}, Z)$, but for notational simplicity, we omit this dependence in the notation.

Taking $\gamma_v = \infty$, we obtain the simplest abstract nonlinear tight binding models as discussed in [45, 122]. If $\gamma_v \in (0, \infty)$, (5.2.1) is a (short-ranged) Yukawa potential which covers many important modelling scenarios and also serves as a crucial stepping stone towards charge equilibration under full Coulomb interaction (i.e. with $\gamma_v = 0$). This latter case goes beyond the mathematical results of this thesis but is discussed in more detail in §5.5.1, below.

For a given configuration $\boldsymbol{X}$, we consider corresponding *self-consistent* electron densities, giving rise to the nonlinearity of the problem:

(SC). *We say ρ is a self-consistent electronic density if $\rho = F^\beta\big(\boldsymbol{X}(\rho)\big)$ where $\boldsymbol{X}(\rho) \coloneqq \big(\boldsymbol{r}, v(\rho), Z\big)$, $z \mapsto F^\beta(z)$ is the Fermi–Dirac distribution* (2.4.4)*, and $F^\beta(\boldsymbol{X})$ is defined in* (2.4.1)*.*

In this chapter, the configuration will be written as a function of the variable of interest. For example, in **(SC)** the electron density ρ is essential in the definition and so we write $\boldsymbol{X}(\rho)$. In (5.2.3) below, we instead write the configuration as a function of the atomic positions $\boldsymbol{r}$ locally about a self-consistent configuration. This slight abuse of notation significantly simplifies the presentation.

Remark 5.1. *For a finite system, the self-consistency equation* **(SC)** *takes*

the following form:

$$\rho_\ell = \sum_s F^\beta(\lambda_s)\big|[\psi_s]_\ell\big|^2 \tag{5.2.2}$$

where $\mathcal{H}\big(\boldsymbol{X}(\rho)\big) = \sum_s \lambda_s |\psi_s\rangle \langle\psi_s|$ *for normalised eigenpairs* (λ_s, ψ_s)*. That is, the electronic structure of the system is obtained by assigning electrons to the eigenstates of lowest energy, according to the Fermi–Dirac occupation distribution and subject to Pauli's exclusion principle.*

We wish to show that, for fixed $\boldsymbol{X}$ and associated self-consistent electronic density ρ, the quantities $O_\ell\big(\boldsymbol{X}(\rho)\big)$ are exponentially localised. As shown in Chapter 3 for the linear model, the exponent in these locality results are linear in the distance between the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ and the integration contour $\mathscr{C}$ from (2.4.1). For the nonlinear model that we consider here, the locality result also depends on the *stability* of the model; discussed below.

Supposing that $\big(\overline{\boldsymbol{r}}, v(\overline{\rho}), Z\big)$ is self-consistent and satisfies a natural stability condition (see **(Stab)**, below), it is possible to rewrite the local observables as a function of the atomic configuration. That is, for $\boldsymbol{r}$ in a small neighbourhood of $\overline{\boldsymbol{r}}$, there exists a locally unique $\rho = \rho(\boldsymbol{r})$ in a neighbourhood of $\overline{\rho}$ such that $\boldsymbol{X}(\boldsymbol{r}) \coloneqq \big(\boldsymbol{r}, v\big(\rho(\boldsymbol{r})\big), Z\big)$ satisfies **(SC)**. See Lemma 5.9 for the rigorous statement. Therefore,

$$O_\ell^{\mathrm{sc}}(\boldsymbol{r}) \coloneqq O_\ell\big(\boldsymbol{X}(\boldsymbol{r})\big) \tag{5.2.3}$$

is a well-defined $\nu-$times continuously differentiable mapping in a neighbourhood of $\overline{\boldsymbol{r}}$.

We may now consider the derivatives of the local observables with respect to the perturbation of atomic positions. Using the resolvent calculus approach (2.4.1), it is sufficient to consider derivatives of the resolvent operators. Since the linear part has already been studied in Chapter 3, we only consider the additional nonlinear contribution, which involves derivatives of the electronic

density. Due to the self-consistency, we obtain

$$\frac{\partial \rho_\ell}{\partial \boldsymbol{r}_n} = \Big[\big(I - \mathscr{L}(\rho)\big)^{-1} \phi^n\Big]_\ell, \tag{5.2.4}$$

where the *stability operator* $\mathscr{L}(\rho)$ is the Jacobian of $F^\beta\big(\boldsymbol{X}(\rho)\big)$ with respect to ρ and $\phi^n \in \ell^2(\Lambda)$. Therefore, the following stability condition, which we take from [45, 46], is the minimal starting assumption required for the analysis:

(Stab). *We say $\boldsymbol{X}(\rho)$ is stable if $I - \mathscr{L}(\rho)\colon \ell^2(\Lambda) \to \ell^2(\Lambda)$ is an invertible bounded linear operator.*

5.3 General Locality Estimates

We are now in a position to state general locality estimates:

Theorem 5.1. *Suppose that $\boldsymbol{X}(\boldsymbol{r})$ satisfies* **(SC)**, **(Stab)**, *and Definition 2.2 and that O, F^β satisfy Definition 2.4. Then, for $1 \leqslant j \leqslant \nu$, there exists $C_j, \eta_j > 0$ such that*

$$\left| \frac{\partial^j O_\ell^{\rm sc}(\boldsymbol{r})}{\partial \boldsymbol{r}_{m_1} \dots \partial \boldsymbol{r}_{m_j}} \right| \leqslant C_j \|O\|_{\mathscr{C}} e^{-\eta_j \sum_{l=1}^j r_{\ell m_l}}$$

for any $\ell, m_1, \dots, m_j \in \Lambda$. Moreover, $\eta_j \coloneqq c_j \min\{1, \mathfrak{d}_O, \mathfrak{d}_{F^\beta}, c_{F^\beta} \mathsf{d}_{\mathscr{L}}\}$ where $\mathsf{d}_{\mathscr{L}} \coloneqq \operatorname{dist}\big(1, \sigma\big(\mathscr{L}(\rho)\big) > 0$, $c_{F^\beta} \coloneqq \mathfrak{d}_{F^\beta}^2 \min\{1, \mathfrak{d}_{F^\beta}^{d+1}\}$, and $c_j > 0$ is independent of $\mathfrak{d}_O, \mathfrak{d}_{F^\beta}$, and $\mathsf{d}_{\mathscr{L}}$.

Sketch of the Proof. The proof follows the analogous proof in the linear case, together with bounds on the nonlinear contribution (5.2.4). Locality of the nonlinear term not only depends on $\mathfrak{d}_O$, as in the linear case, but also on the stability. Full details are presented in §5.6.1. □

5.4 Locality Estimates for Point Defects

Now we consider the specific example of point defect reference configurations. In this case we show improved locality estimates in which, away from the defect

core, the pre-factors and exponents behave like the corresponding defect-free case.

Fix a reference configuration $\boldsymbol{X} = \big(\overline{\boldsymbol{r}}, v, Z\big)$ and, for a point defect $(\overline{\boldsymbol{r}}^{\mathrm{d}}, Z^{\mathrm{d}})$, we let $v^{\mathrm{d}} \colon \ell^\infty(\Lambda^{\mathrm{d}}) \to \ell^\infty(\Lambda^{\mathrm{d}})$ be the corresponding Yukawa potential (5.2.1) and consider $\boldsymbol{X}^{\mathrm{d}} \coloneqq (\overline{\boldsymbol{r}}^{\mathrm{d}}, v^{\mathrm{d}}, Z^{\mathrm{d}})$. Moreover, we suppose there exist stable, self-consistent electron densities $\rho = \rho(\overline{\boldsymbol{r}})$ and $\rho^{\mathrm{d}} = \rho^{\mathrm{d}}(\overline{\boldsymbol{r}}^{\mathrm{d}})$ corresponding to $\boldsymbol{X}$ and $\boldsymbol{X}^{\mathrm{d}}$, respectively. In particular, we may define the self-consistent configurations $\boldsymbol{X}(\boldsymbol{r})$ and $\boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})$ for $\boldsymbol{r}$ and $\boldsymbol{r}^{\mathrm{d}}$ in neighbourhoods of $\overline{\boldsymbol{r}}$ and $\overline{\boldsymbol{r}}^{\mathrm{d}}$, respectively, as in (5.2.3). We simplify notation by writing $\mathscr{L}$ and $\mathscr{L}^{\mathrm{d}}$ for the stability operators for $\boldsymbol{X}$ and $\boldsymbol{X}^{\mathrm{d}}$, respectively.

Now, if $\big(\boldsymbol{X}(\boldsymbol{r}),\, \boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})\big)$ satisfies $\mathbf{(P}_\delta\mathbf{)}$, we may approximate the Hamiltonian $\mathcal{H}\big(\boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})\big)$ with a finite rank update of $\mathcal{H}\big(\boldsymbol{X}(\boldsymbol{r})\big)$ (Proposition 2.3) and thus apply the improved resolvent estimates from Lemma 3.4 as in the linear setting. Analogously, showing that the stability operator $\mathscr{L}^{\mathrm{d}}$ may be approximated by a finite rank update of $\mathscr{L}$, leads to improved estimates for the stability operator:

Proposition 5.2 (Decomposition of the Stability Operator)**.** *Fix $\varepsilon > 0$. Then, there exists $\delta > 0$ such that if $\big(\boldsymbol{X}(\boldsymbol{r}), \boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})\big)$ satisfies $\mathbf{(P}_\delta\mathbf{)}$ and*

$$\limsup_{|\boldsymbol{r}_k| \to \infty} \big| v_0'(\rho_k^{\mathrm{d}}) - v_0'(\rho_k) \big| < \delta, \tag{5.4.1}$$

then there exists $R > 0$ and operators $Q_\varepsilon, Q_{\mathrm{FR}}$ such that

$$\mathscr{L}^{\mathrm{d}} = \mathscr{L} + Q_{\mathrm{FR}} + Q_\varepsilon, \tag{5.4.2}$$

$[Q_{\mathrm{FR}}]_{\ell k} = 0$ if $|\boldsymbol{r}_\ell| > R$ or $|\boldsymbol{r}_k| > R$, and $\|Q_\varepsilon\|_{\ell^2 \to \ell^2} < \varepsilon$. Moreover, we have $\big|\sigma\big(\mathscr{L}^{\mathrm{d}}\big) \setminus B_\varepsilon\big(\sigma(\mathscr{L})\big)\big| < \infty$.

Remark 5.2. *In particular, for $\big(\boldsymbol{X}(\boldsymbol{r}), \boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})\big)$ to satisfy $\mathbf{(P}_\delta\mathbf{)}$, we require*

$$\limsup_{|\boldsymbol{r}_k| \to \infty} \Big| \Big[v_0(\rho_k^{\mathrm{d}}) - v_0(\rho_k) + \sum_{m \in \Lambda^{\mathrm{ff}}} \frac{\rho_k^{\mathrm{d}} - \rho_k}{r_{km}} e^{-\gamma_v r_{km}} \Big] \Big| < \delta. \tag{5.4.3}$$

This is the minimal technical assumption required for the analysis. Indeed, if (5.4.3) *does not hold, then the defect Hamiltonian cannot be approximated by a finite rank update of the defect-free Hamiltonian, and the method of proof used in this chapter cannot be applied. Moreover,* (5.4.1) *is the minimal assumption needed for* (5.4.2)*.*

Theorem 5.3. *Fix* $\varepsilon > 0$ *such that* $\mathsf{d}_{\mathscr{L}} \coloneqq \operatorname{dist}\big(1, B_\varepsilon\big(\sigma(\mathscr{L})\big)\big) > 0$ *and suppose* $\boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})$ *satisfies* (5.4.1) *and* $\mathbf{(P}_\delta\mathbf{)}$ *with* $\delta > 0$ *sufficiently small such that Propositions 2.3 and 5.2 hold with the constant* $\varepsilon > 0$*. Moreover, suppose* (C_j, η_j) *are the constants from Theorem 5.1 when applied to* $\boldsymbol{X}(\boldsymbol{r})$ *and with the constant* $\mathsf{d}_{\mathscr{L}}$*, and* O, F^β *satisfy Definition 2.4. Then, for* $1 \leqslant j \leqslant \nu$*,* $\ell \in \Lambda^{\mathrm{d}}$*, and* $\boldsymbol{m} = (m_1, \dots, m_j) \in (\Lambda^{\mathrm{d}})^j$*, there exists* $C_j^{\mathrm{d}} = C_j^{\mathrm{d}}(\ell, \boldsymbol{m})$*, such that*

$$\left| \frac{\partial^j O_\ell^{\mathrm{sc}}(\boldsymbol{r}^{\mathrm{d}})}{\partial \boldsymbol{r}^{\mathrm{d}}_{m_1} \dots \partial \boldsymbol{r}^{\mathrm{d}}_{m_j}} \right| \leqslant C_j^{\mathrm{d}} \|O\|_{\mathscr{C}} e^{-\eta_j \sum_{l=1}^{j} r_{\ell m_l}}.$$

Moreover, $C_j^{\mathrm{d}}(\ell, \boldsymbol{m})$ *is uniformly bounded independently of* $(\ell, \boldsymbol{m})$ *and, if* $\ell, m_1, \dots, m_j \in B_R(\xi)$ *for some* $R > 0$*, then* $C_j^{\mathrm{d}}(\ell, \boldsymbol{m}) \to C_j$*, with an exponential rate.*

Remark 5.3. *Theorem 5.3 is an improved version of the published estimate. In the published version, the exponent depends on the defect and is given as a function of the relevant atomic positions:* $\eta_j^{\mathrm{d}} = \eta_j^{\mathrm{d}}(\ell, \boldsymbol{m})$*. Similarly to the prefactor, it is shown that* $\eta_j^{\mathrm{d}} \to \eta_j$ *as the subsystem* $(\ell, \boldsymbol{m})$ *moves away from the defect core together, with an exponential rate. In the published version, improved resolvent estimates are used to obtain estimates on* $\mathscr{L}$ *with prefactors depending on the atomic positions which, in turn, leads to estimates on* $(I - \mathscr{L})^{-1}$ *in which the exponents depend on the atomic positions. Instead of this approach, the present work directly uses the low rank update formula* (5.4.2) *to obtain improved estimates on* $(I - \mathscr{L})^{-1}$*.*

5.5 Body-ordered Approximations

We present two related methods for incorporating electronic information in a self-consistent manner into the body-ordered approximation schemes presented in Chapter 4.

5.5.1 Approximate Self-consistent Equations

Perhaps the most natural approach is to to first approximate self-consistent electron densities $\rho^\star = F^\beta\big(\boldsymbol{X}(\rho^\star)\big)$ with self-consistent solutions to the following approximate self-consistency equation:

$$\rho_N = I_N F^\beta\big(\boldsymbol{X}(\rho_N)\big), \tag{5.5.1}$$

where I_N is an interpolation operator given by (4.3.1), and then use ρ_N in the definition of the approximate quantities. That is, the fixed point mapping for the exact electron density $\rho^\star$ is replaced with an approximate fixed point mapping based on the body-ordered approximation schemes of Chapter 4. This approach leads to the following two results:

Theorem 5.4. *Suppose that $\rho^\star$ satisfies* **(SC)** *and* **(Stab)**. *Then, for N sufficiently large, there exist self-consistent solutions ρ_N of* (5.5.1) *such that*

$$\big\|\rho_N - \rho^\star\big\|_{\ell^\infty} \leqslant Ce^{-\gamma_N N}, \tag{5.5.2}$$

where γ_N are the constants from Theorem 4.2 applied to $\boldsymbol{X}(\rho^\star)$.

Corollary 5.5. *Suppose that $\rho^\star$ and ρ_N are as in Theorem 5.4. Then,*

$$\big|O_\ell\big(\boldsymbol{X}(\rho^\star)\big) - I_N O_\ell\big(\boldsymbol{X}(\rho_N)\big)\big| \leqslant Ce^{-\gamma_N N},$$

where γ_N are the constants from Theorem 4.2 applied to $\boldsymbol{X}(\rho^\star)$.

In order for this result to be of any practical use, we need to solve the non-linear equation (5.5.1) for the electron density via a self-consistent field

(SCF) procedure. Supposing we have the electron density ρ^i and corresponding state $\boldsymbol{X}^i \coloneqq \boldsymbol{X}(\rho^i)$ after i iterations, we diagonalise the Hamiltonian $\mathcal{H}(\boldsymbol{X}^i)$ and hence evaluate the output density $\rho^{\text{out}} = I_N F^\beta(\boldsymbol{X}^i)$. At this point, since the simple iteration $\rho^{i+1} = \rho^{\text{out}}$ does not converge in general, a mixing strategy, possibly combined with Anderson acceleration [31], is used in order to compute the next iterate. The analysis of such mixing schemes is a major topic in electronic structure and numerical analysis in general and so we only present a small step in this direction.

In particular, solving (5.5.1) via a SCF iteration motivates the use of compositional models, reminiscent of artificial neural networks.

Proposition 5.6 (Stability)**.** *The approximate electron densities ρ_N arising from Theorem 5.4 are* stable *in the following sense: $I - \mathscr{L}_N(\rho_N)\colon \ell^2 \to \ell^2$ is an invertible bounded linear operator where $\mathscr{L}_N$ is the Jacobian of $\rho \mapsto I_N F^\beta\big(\boldsymbol{X}(\rho)\big)$. Moreover, $\big(I - \mathscr{L}_N(\rho_N)\big)^{-1}$ is uniformly bounded in N in operator norm.*

Theorem 5.7. *For $\boldsymbol{X}$ satisfying Definition 2.2, suppose that ρ_N is a corresponding approximate self-consistent electron density stable in the sense of Proposition 5.6. For fixed ρ^0, we define $\{\rho^i\}_{i=0}^\infty$ via the Newton iteration*

$$\rho^{i+1} = \rho^i - \big(I - \mathscr{L}_N(\rho^i)\big)^{-1}\Big(\rho^i - I_N F^\beta\big(\boldsymbol{X}(\rho^i)\big)\Big).$$

Then, for $\|\rho^0 - \rho_N\|_{\ell^\infty}$ sufficiently small, the Newton iteration converges quadratically to ρ_N.

A more thorough treatment of these SCF results is beyond the scope of this work. See [20, 70, 83] for recent results in the context of Hartree-Fock and Kohn-Sham density functional theory. For a recent review of SCF in the context density functional theory, see [129].

Remark 5.4. *It is clear from the proofs of Theorems 5.4 and 5.7 that as long*

as an approximate scheme $F^{\beta,N}$, e.g. $F^{\beta,N} = I_N F^\beta$, satisfies

$$\left|F_\ell^\beta(\boldsymbol{X}) - F_\ell^{\beta,N}(\boldsymbol{X})\right| \lesssim e^{-\gamma_N N} \qquad \text{and} \tag{5.5.3}$$

$$\left|\frac{\partial F_\ell^\beta(\boldsymbol{X})}{\partial v_m} - \frac{\partial F_\ell^{\beta,N}(\boldsymbol{X})}{\partial v_m}\right| \lesssim e^{-\frac{1}{2}\gamma_N N} e^{-\eta r_{\ell m}}, \tag{5.5.4}$$

then we may approximate self-consistent electron densities with approximate self-consistent solutions $\rho_N = F^{\beta,N}\big(\boldsymbol{X}(\rho_N)\big)$. In particular, as long as we have the estimate from Remark 4.8 (see Appendix C.2 for the technical details), then we may use the nonlinear approximation scheme Θ from Theorem 4.4 in Theorems 5.4 and 5.7. In this case, we obtain error estimates that are (asymptotically) independent of the discrete spectrum.

Remark 5.5 (Coulomb interactions)**.** *In principle, one could solve* (5.5.1) *for finite systems under full Coulomb interactions (i.e. with $\gamma_v = 0$). However, following the proofs of this section, we would only obtain Theorem 5.4 with the prefactor and choice of N in* (5.5.2) *depending on system size. Indeed, the error estimates in* (5.5.2) *depend on the operator norm of $\big(I - \mathscr{L}(\rho^\star)\big)^{-1} \colon \ell^\infty \to \ell^\infty$, which* a priori *depends on the size of the system (and the stability constant $\big\|\big(I - \mathscr{L}(\rho^\star)\big)^{-1}\big\|_{\ell^2\to\ell^2}$). In the $\gamma_v > 0$ case, we are able to use the exponential off-diagonal decay of $\mathscr{L}$ to show that $\big\|\big(I - \mathscr{L}(\rho^\star)\big)^{-1}\big\|_{\ell^\infty\to\ell^\infty}$ may be bounded above by a constant depending on γ_v but independent of system size.*

5.5.2 Outlook: Energy Minimisation Approach

The self-consistency equation $\rho^\star = F^\beta\big(\boldsymbol{X}(\rho^\star)\big)$ can be seen as the Euler–Lagrange equation for minimising the following energy for the one particle density matrix P, a self-adjoint bounded linear operator with $0 \leqslant P \leqslant 1$ and diagonal $\rho_\ell = P_{\ell\ell}$. For fixed chemical potential μ and $[\mathcal{H}_0]_{\ell k} \coloneqq h(\boldsymbol{X}_{\ell k}) + \sum_{m\notin\{\ell,k\}} t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km})$ the linear part of the Hamiltonian, we consider

$$\mathcal{G}[P] \coloneqq \mathrm{Tr}\Big[\mathcal{H}_0 P + \beta^{-1} S\big(P\big) - \mu P\Big] + \sum_\ell \rho_\ell W(\rho_\ell) + \frac{1}{2}\sum_{\ell,k\neq\ell} \frac{q_\ell q_k}{r_{\ell k}} e^{-\gamma_v r_{\ell k}}, \tag{5.5.5}$$

where $S(f) = f\log(f) + (1-f)\log(1-f)$ is the Fermi–Dirac entropy, the term $-\mu \mathrm{Tr}\, P$ comes from the fact that we are in the grand canonical ensemble and so we subtract the contribution resulting from varying the particle number, and $q_\ell = \rho_\ell - Z_\ell$ are the partial charges.

Minimising (5.5.5) yields the Euler–Lagrange equation $P = F^\beta\big(\mathcal{H}_0 + v(\rho)\big)$ where $v(\rho)$ is given by (5.2.1) with $v_0(x) = W(x) + xW'(x)$. Therefore, the energy (at a critical point P) can be written as a function of the electron density alone:

$$\begin{aligned}\mathcal{G}[\rho] &= \mathrm{Tr}\Big[(\mathcal{H}_0 - \mu)F^\beta\big(\mathcal{H}_0 + v(\rho)\big) + \beta^{-1}S\big(F^\beta\big(\mathcal{H}_0 + v(\rho)\big)\big)\Big] \\ &\qquad + \sum_\ell \rho_\ell W(\rho_\ell) + \frac{1}{2}\sum_{\ell,k\neq\ell} \frac{q_\ell q_k}{r_{\ell k}} e^{-\gamma_v r_{\ell k}} \\ &= \sum_\ell G^\beta\big(\mathcal{H}_0 + v(\rho)\big)_{\ell\ell} - \sum_\ell \rho_\ell v(\rho)_\ell + \sum_\ell \rho_\ell W(\rho_\ell) + \frac{1}{2}\sum_{\ell,k\neq\ell} \frac{q_\ell q_k}{r_{\ell k}} e^{-\gamma_v r_{\ell k}},\end{aligned} \tag{5.5.6}$$

where G^β is the grand canonical potential function (2.4.5).

Therefore, we have constructed a mapping from $(\boldsymbol{r}, \rho)$ to energy whose critical points satisfy the self-consistency equation $\rho^\star = F^\beta\big(\boldsymbol{X}(\rho^\star)\big)$. In §5.5.1 we approximated this nonlinear equation with the body-ordered approximation presented in Chapter 4. Here, we propose an alternative approach where the following approximate energy

$$\mathcal{G}_N[\rho] \coloneqq \sum_\ell I_N G^\beta\big(\mathcal{H}_0 + v(\rho)\big)_{\ell\ell} + \sum_\ell \rho_\ell\big(W(\rho_\ell) - v(\rho)_\ell\big) + \sum_{\ell<k} \frac{q_\ell q_k}{r_{\ell k}} e^{-\gamma_v r_{\ell k}}. \tag{5.5.7}$$

(where I_N is an interpolation operator from Chapter 4) is minimised over ρ producing a ρ_N analogous to (5.5.1). Mathematical results concerning the convergence $\rho_N \to \rho^\star$ as $N \to \infty$ are left for future work.

In this approximate energy, the first term is the sum of atom centred contributions that are "simple" in the sense described in Chapter 4. That is, the site contributions are body-ordered and depend only on the configuration

$\{(\boldsymbol{r}_{\ell k}, v(\rho)_k)\}$ in a small atomic neighbourhood of the central site ℓ. Moreover, the second term is the sum of local functions of the density and effective potential. In particular, (5.5.7) is a systematic variant of the BpopNN (Becke Population Neural Network) [130] where the first term of (5.5.7) is replaced by the sum of atomic neural networks depending on the configuration via various SOAP-like atomistic descriptors. Therefore, a key difference between (5.5.7) and the BpopNN is that we explicitly include the site effective potential as features in the neural network architecture.

5.6 Proofs of the Main Results

We start with the following preliminary lemma:

Lemma 5.8. *Suppose that $T\colon \ell^2(\Lambda) \to \ell^2(\Lambda)$ is an invertible bounded linear operator with matrix entries $T_{\ell k}$ satisfying $|T_{\ell k}| \leqslant c_T e^{-\gamma_T r_{\ell k}}$ for some positive constants c_T, γ_T. Then, there exists an invertible bounded linear operator $\overline{T}\colon \ell^\infty(\Lambda) \to \ell^\infty(\Lambda)$ extending $T\colon \ell^2(\Lambda) \to \ell^2(\Lambda)$ (that is, $\overline{T}|_{\ell^2(\Lambda)} = T$).*

Proof. First, we denote the inverse of T and its matrix entries by $T^{-1}\colon \ell^2(\Lambda) \to \ell^2(\Lambda)$ and $T^{-1}_{\ell k}$, respectively. Then, applying the Combes–Thomas estimate (Lemma 3.3) to T yields the off-diagonal decay estimate $|T^{-1}_{\ell k}| \leqslant Ce^{-\gamma_{\mathrm{CT}} r_{\ell k}}$ for some $C, \gamma_{\mathrm{CT}} > 0$.

Due to the off-diagonal decay properties of the matrix entries, the operators $\overline{T}, \overline{T}^{-1}\colon \ell^\infty(\Lambda) \to \ell^\infty(\Lambda)$ given by

$$[\overline{T}\phi]_\ell \coloneqq \sum_{k\in\Lambda} T_{\ell k}\phi_k \qquad \text{and} \qquad [\overline{T}^{-1}\phi]_\ell \coloneqq \sum_{k\in\Lambda} T^{-1}_{\ell k}\phi_k$$

are well defined bounded linear operators with norms $\sup_\ell \sum_{k\in\Lambda} |T_{\ell k}|$ and $\sup_\ell \sum_{k\in\Lambda} |T^{-1}_{\ell k}|$, respectively. To conclude, we note that

$$[\overline{T}\overline{T}^{-1}\phi]_\ell = \sum_k \sum_m T_{\ell k} T^{-1}_{km}\phi_m = \sum_m [TT^{-1}]_{\ell m}\phi_m = \phi_\ell \tag{5.6.1}$$

and so $\overline{T}^{-1}$ is the inverse of $\overline{T}$. Here, we have exchanged the summations over

k and m by applying the dominated convergence theorem: $\big|\sum_k T_{\ell k}T^{-1}_{km}\phi_m\big| \leqslant Ce^{-\frac{1}{2}\min\{\gamma_T,\gamma_{\mathrm{CT}}\}r_{\ell m}}\|\phi\|_{\ell^\infty}$ is summable over $m \in \Lambda$. □

5.6.1 General Locality Estimates: Proof of Theorem 5.1

Firstly, we note that for self-consistent configurations $\boldsymbol{X}(\rho)$, the corresponding stability operator is given by $\mathscr{L}(\rho) = \mathscr{F}(\rho)\nabla v(\rho)$ where

$$\mathscr{F}(\rho)_{\ell k} \coloneqq \mathrm{tr}\oint_{\mathscr{C}} F^\beta(z)[\mathscr{R}_{z,\ell k}]^{\mathrm{T}}\mathscr{R}_{z,\ell k}\frac{\mathrm{d}z}{2\pi i} \tag{5.6.2}$$

and $\mathscr{R}_z \coloneqq \big(\mathcal{H}(\boldsymbol{X}(\rho)) - z\big)^{-1}$.

In particular, by applying the Combes–Thomas estimate (Lemma 3.3) to $\mathcal{H}\big(\boldsymbol{X}(\rho)\big) - z$ for $z \in \mathscr{C}$, we obtain

$$\big|\mathscr{L}(\rho)_{\ell k}\big| \leqslant \sum_m \big|\mathscr{F}(\rho)_{\ell m}\big|\big|\nabla v(\rho)_{mk}\big| \tag{5.6.3}$$

$$\leqslant C\big\|F^\beta\big\|_{\mathscr{C}}\mathfrak{d}_{F^\beta}^{-2}\sum_m e^{-2\gamma_{\mathrm{CT}}(\mathfrak{d})r_{\ell m}}e^{-\gamma_v r_{mk}} \leqslant c_{\mathscr{L}}e^{-\gamma_{\mathscr{L}}r_{\ell k}}, \tag{5.6.4}$$

where $\mathfrak{d}_{F^\beta} \coloneqq \mathrm{dist}\big(z, \sigma\big(\mathcal{H}(\boldsymbol{X}(\rho))\big)\big)$, $c_{\mathscr{L}} \coloneqq C\big\|F^\beta\big\|_{\mathscr{C}}\mathfrak{d}_{F^\beta}^{-2}\gamma_v^{-d}$, and the exponent is $\gamma_{\mathscr{L}} \coloneqq \min\{\gamma_{\mathrm{CT}}(\mathfrak{d}_{F^\beta}), \frac{1}{2}\gamma_v\}$.

Therefore, the operator $I - \mathscr{L}(\rho)$ has off-diagonal decay and we can apply the Combes–Thomas estimate to obtain

$$\Big|\big[\big(I - \mathscr{L}(\rho)\big)^{-1}\big]_{\ell k}\Big| \leqslant 2\mathsf{d}_{\mathscr{L}}^{-1}e^{-\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}})r_{\ell k}}, \tag{5.6.5}$$

where $\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}}) = c_0\gamma_{\mathscr{L}}\min\Big\{1, \frac{\gamma_{\mathscr{L}}^d}{1+c_{\mathscr{L}}}\mathsf{d}_{\mathscr{L}}\Big\}$. Therefore, for z contained in a bounded set, $\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}}) \geqslant c_1\min\Big\{1, \mathfrak{d}_{F^\beta}, \mathfrak{d}_{F^\beta}^2\min\{1, \mathfrak{d}_{F^\beta}^{d+1}\}\mathsf{d}_{\mathscr{L}}\Big\}$ for some constant $c_1 > 0$ independent of $\mathfrak{d}_{F^\beta}$ and $\mathsf{d}_{\mathscr{L}}$.

Using the off-diagonal decay estimate (5.6.5), we may apply Lemma 5.8 to conclude that $I - \mathscr{L}(\rho)$ is also an invertible operator on $\ell^\infty(\Lambda)$:

Lemma 5.9. *For stable self-consistent $\boldsymbol{X}(\rho)$, $I-\mathscr{L}(\rho)\colon \ell^2(\Lambda) \to \ell^2(\Lambda)$ extends to an invertible bounded linear operator on $\ell^\infty(\Lambda)$.*

In the following, we denote by $B_\delta(\rho)$ and $B_\delta(\boldsymbol{r})$ the open balls of radius δ

centred on ρ and $\boldsymbol{r}$ with respect to the $\ell^\infty(\Lambda)$ and $\ell^\infty(\Lambda;\mathbb{R}^d)$ norms, respectively. We now show that locally about a stable configuration, there is a unique choice of self-consistent electron density:

Lemma 5.10. *Suppose that* $\big(\overline{\boldsymbol{r}}, v(\overline{\rho}), Z\big)$ *satisfies* **(SC)** *and* **(Stab)**. *Then, there exists* $\delta_1, \delta_2 > 0$ *such that for all* $\boldsymbol{r} \in B_{\delta_1}(\overline{\boldsymbol{r}})$, *there exists a unique electron density* $\rho = \rho(\boldsymbol{r}) \in B_{\delta_2}(\overline{\rho})$ *satisfying* $\rho = F^\beta\big((\boldsymbol{r}, v(\rho), Z)\big)$. *Moreover, the mapping* $\boldsymbol{r} \mapsto \rho$ *is* ν*-times continuously Frechet differentiable at* $\overline{\boldsymbol{r}}$.

Proof. We define $T\colon \ell^\infty(\Lambda;\mathbb{R}^d) \times \ell^\infty(\Lambda) \to \ell^\infty(\Lambda)$ to be the mapping $(\boldsymbol{r}, \rho) \mapsto \rho - F^\beta\big((\boldsymbol{r}, v(\rho), Z)\big)$ and apply the implicit function theorem about $(\overline{\boldsymbol{r}}, \overline{\rho})$.

By **(SC)**, we have $T(\overline{\boldsymbol{r}}, \overline{\rho}) = 0$ and, by **(Stab)**, the Frechet derivative of T at $(\overline{\boldsymbol{r}}, \overline{\rho})$ in the $\rho-$direction is given by the operator $I - \mathscr{L}(\overline{\rho})\colon \ell^\infty(\Lambda) \to \ell^\infty(\Lambda)$, invertible by Lemma 5.9. Therefore, there exists $\delta_1, \delta_2 > 0$ and a Frechet differentiable function $\rho\colon B_{\delta_1}(\overline{\boldsymbol{r}}) \to B_{\delta_2}(\overline{\rho})$ such that $T\big(\boldsymbol{r}, \rho(\boldsymbol{r})\big) = 0$ for all $\boldsymbol{r} \in B_{\delta_1}(\overline{\boldsymbol{r}})$. □

Applying Lemma 5.10, we can conclude that the self-consistent local observables $O_\ell^{\mathrm{sc}}(\boldsymbol{r}) \coloneqq O_\ell\big(\boldsymbol{X}(\boldsymbol{r})\big)$ from (5.2.3) are well-defined, $\nu-$times continuously differentiable functions of the atomic configuration in a neighbourhood of $\overline{\boldsymbol{r}}$.

To simplify notation in the following, we will define

$$\mathcal{H}^{\mathrm{L}}(\boldsymbol{X})_{\ell k} \coloneqq h(\boldsymbol{X}_{\ell k}) + \sum_{m \notin \{\ell, k\}} t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km}) \qquad \text{and} \tag{5.6.6}$$

$$\mathcal{H}^{\mathrm{NL}}(\boldsymbol{X})_{\ell k} \coloneqq \delta_{\ell k} v(\rho)_\ell \mathrm{Id}_{N_{\mathrm{b}}}. \tag{5.6.7}$$

We apply (2.4.1) to write O_ℓ^{sc} as a contour integral in the complex plane, and so it is sufficient to apply (3.6.1) and bound the derivatives of the resolvent operators.

We start with the first derivatives: for $z \in \mathbb{C}$ with $\mathfrak{d}_O \coloneqq \mathrm{dist}\big(z, \sigma(\mathcal{H}(\boldsymbol{X}))\big) > 0$ (the constant $\mathfrak{d}_O$ depends on the region on which O is analytic, and may

differ from $\mathfrak{d}_{F^\beta}$), and $\mathscr{R}_z \coloneqq \big(\mathcal{H}\big(\boldsymbol{X}(\boldsymbol{r})\big) - z\big)^{-1}$, we have

$$\begin{aligned}\frac{\partial[\mathscr{R}_z]_{\ell\ell}}{\partial \boldsymbol{r}_m} &= -\left[\mathscr{R}_z \frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_m}\mathscr{R}_z\right]_{\ell\ell} \\ &= -\left[\mathscr{R}_z \frac{\partial \mathcal{H}^{\mathrm{L}}}{\partial \boldsymbol{r}_m}\mathscr{R}_z\right]_{\ell\ell} - \sum_{k,n}[\mathscr{R}_{z,\ell k}]^{\mathrm{T}}\mathscr{R}_{z,\ell k}\nabla v(\rho)_{kn}\frac{\partial \rho_n}{\partial \boldsymbol{r}_m}.\end{aligned} \tag{5.6.8}$$

The first contribution in (5.6.8) is exactly what we obtained in (3.6.3) in the linear case. That is,

$$\left|\left[\mathscr{R}_z \frac{\partial \mathcal{H}^{\mathrm{L}}}{\partial \boldsymbol{r}_m}\mathscr{R}_z\right]_{\ell\ell}\right| \lesssim \mathfrak{d}_O^{-2} e^{-\min\{\gamma_{\mathrm{CT}}(\mathfrak{d}_O),\gamma_1\}r_{\ell m}}. \tag{5.6.9}$$

It remains to consider the non-linear contribution in (5.6.8), which includes derivatives of the electron density:

Lemma 5.11. *For $1 \leqslant j \leqslant \nu$, there exists $\gamma_\rho > 0$ such that*

$$\left|\frac{\partial^j \rho_\ell}{\partial \boldsymbol{r}_{m_1}\ldots\partial \boldsymbol{r}_{m_j}}\right| \lesssim e^{-\gamma_\rho \sum_{l=1}^j r_{\ell m_l}},$$

where $\gamma_\rho = c\min\{1, \gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}}), \gamma_{\mathrm{CT}}(\mathfrak{d}_{F^\beta})\}$ and $c > 0$ is independent of $\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}})$ and $\gamma_{\mathrm{CT}}(\mathfrak{d}_{F^\beta})$.

We return to the proof of Lemma 5.11 after the conclusion of the proof of Theorem 5.1.

Therefore, applying Lemma 5.11, we may bound the second term in (5.6.8):

$$\begin{aligned}\sum_{k,n}\left|[\mathscr{R}_{z,\ell k}]^{\mathrm{T}}\mathscr{R}_{z,\ell k}\nabla v(\rho)_{kn}\frac{\partial \rho_n}{\partial \boldsymbol{r}_m}\right| &\lesssim \sum_{kn}\mathfrak{d}_O^{-2}e^{-2\gamma_{\mathrm{CT}}(\mathfrak{d}_O)r_{\ell k}}\cdot e^{-\gamma_v r_{kn}}\cdot e^{-\gamma_\rho r_{\ell m}} \\ &\lesssim e^{-\frac{1}{4}\min\{\gamma_v,\gamma_{\mathrm{CT}}(\mathfrak{d}_O),\gamma_\rho\}}.\end{aligned} \tag{5.6.10}$$

Combining (5.6.9) and (5.6.10) together with (3.6.1), we conclude the proof for $j = 1$.

Higher derivatives can be treated by taking derivatives of (5.6.8). For

example, for $j = 2$, we have

$$\begin{aligned}\frac{\partial^2 \mathscr{R}_{z,\ell\ell}}{\partial \boldsymbol{r}_{m_2} \partial \boldsymbol{r}_{m_1}} &= -\frac{\partial}{\partial \boldsymbol{r}_{m_2}} \left[\mathscr{R}_z \frac{\partial \mathcal{H}}{\partial \boldsymbol{r}_{m_1}} \mathscr{R}_z \right]_{\ell\ell} \\ &\quad - \sum_{kn} \Big(\frac{\partial [\mathscr{R}_{z,\ell k}]^{\mathrm{T}}}{\partial \boldsymbol{r}_{m_2}} \mathscr{R}_{z,\ell k} + [\mathscr{R}_{z,\ell k}]^{\mathrm{T}} \frac{\partial \mathscr{R}_{z,\ell k}}{\partial \boldsymbol{r}_{m_2}} \Big) \nabla v(\rho)_{kn} \frac{\partial \rho_n}{\partial \boldsymbol{r}_{m_1}} \\ &\quad - \sum_{k} [\mathscr{R}_{z,\ell k}]^{\mathrm{T}} \mathscr{R}_{z,\ell k} v_0''(\rho_k) \frac{\partial \rho_k}{\partial \boldsymbol{r}_{m_2}} \frac{\partial \rho_k}{\partial \boldsymbol{r}_{m_1}} \\ &\quad - \sum_{kn} [\mathscr{R}_{z,\ell k}]^{\mathrm{T}} \mathscr{R}_{z,\ell k} \nabla v(\rho)_{kn} \frac{\partial^2 \rho_n}{\partial \boldsymbol{r}_{m_2} \partial \boldsymbol{r}_{m_1}}. \end{aligned} \tag{5.6.11}$$

Now, using the off-diagonal decay of the resolvent operators and their first derivatives ((5.6.8), (5.6.9) and (5.6.10)), the off-diagonal decay of $\nabla v(\rho)$, and the locality of the electron density (Lemma 5.11), we may conclude the proof of Theorem 5.1.

Proof of Lemma 5.11. We first consider $j = 1$. Taking derivatives in the self-consistency equation for ρ, we obtain the following identity,

$$\begin{aligned}\frac{\partial \rho_\ell}{\partial \boldsymbol{r}_m} &= -\mathrm{tr} \oint_{\mathscr{C}} F^\beta(z) \frac{\partial \mathscr{R}_{z,\ell\ell}}{\partial \boldsymbol{r}_m} \frac{\mathrm{d}z}{2\pi i} \\ &= \mathrm{tr} \oint_{\mathscr{C}} F^\beta(z) \left[\mathscr{R}_z \frac{\partial \mathcal{H}^{\mathrm{L}}}{\partial \boldsymbol{r}_m} \mathscr{R}_z \right]_{\ell\ell} \frac{\mathrm{d}z}{2\pi i} + \left[\mathscr{L}(\rho) \frac{\partial \rho}{\partial \boldsymbol{r}_m} \right]_\ell. \end{aligned}$$

That is,

$$\frac{\partial \rho_\ell}{\partial \boldsymbol{r}_m} = \big[(I - \mathscr{L}(\rho))^{-1} \phi^m \big]_\ell, \qquad \text{where} \tag{5.6.12}$$

$$\phi_\ell^m \coloneqq \mathrm{tr} \oint_{\mathscr{C}} F^\beta(z) \left[\mathscr{R}_z \frac{\partial \mathcal{H}^{\mathrm{L}}}{\partial \boldsymbol{r}_m} \mathscr{R}_z \right]_{\ell\ell} \frac{\mathrm{d}z}{2\pi i}. \tag{5.6.13}$$

Applying (5.6.5) and (5.6.9) (but for z in an admissible contour for F^β instead of O), we obtain

$$\begin{aligned}\left| \frac{\partial \rho_\ell}{\partial \boldsymbol{r}_m} \right| &\lesssim \sum_k 2\mathsf{d}_{\mathscr{L}}^{-1} e^{-\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}}) r_{\ell k}} \cdot \|F^\beta\|_{\mathscr{C}} \mathfrak{d}_{F^\beta}^{-2} e^{-\min\{\gamma_{\mathrm{CT}}(\mathfrak{d}_{F^\beta}), \gamma_1\} r_{km}} \\ &\lesssim e^{-\frac{1}{2}\min\{\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}}), \gamma_{\mathrm{CT}}(\mathfrak{d}_{F^\beta}), \gamma_1\} r_{\ell m}}. \end{aligned} \tag{5.6.14}$$

Now take $j = 2$. We have

$$\frac{\partial^2 \rho_\ell}{\partial \boldsymbol{r}_{m_2} \partial \boldsymbol{r}_{m_1}} = \Big[\big(I - \mathscr{L}(\rho)\big)^{-1} \Big\{ \frac{\partial \mathscr{L}(\rho)}{\partial \boldsymbol{r}_{m_2}} \big(I - \mathscr{L}(\rho)\big)^{-1} \phi^{m_1} + \frac{\partial \phi^{m_1}}{\partial \boldsymbol{r}_{m_2}} \Big\} \Big]_\ell, \tag{5.6.15}$$

where

$$\begin{aligned} \frac{\partial \mathscr{L}(\rho)_{\ell k}}{\partial \boldsymbol{r}_{m_2}} &= \operatorname{tr} \oint_{\mathscr{C}} F^\beta(z) \Big[[\mathscr{R}_{z,\ell k}]^{\mathrm{T}} \mathscr{R}_{z,\ell k} v_0''(\rho_k) \frac{\partial \rho_k}{\partial \boldsymbol{r}_{m_2}} \\ &\qquad + \sum_m \Big(\frac{\partial [\mathscr{R}_{z,\ell m}]^{\mathrm{T}}}{\partial \boldsymbol{r}_{m_2}} \mathscr{R}_{z,\ell m} + [\mathscr{R}_{z,\ell m}]^{\mathrm{T}} \frac{\partial \mathscr{R}_{z,\ell m}}{\partial \boldsymbol{r}_{m_2}} \Big) \nabla v(\rho)_{mk} \Big] \frac{\mathrm{d}z}{2\pi i}, \\ \frac{\partial \phi_\ell^{m_1}}{\partial \boldsymbol{r}_{m_2}} &= \operatorname{tr} \oint_{\mathscr{C}} F^\beta(z) \frac{\partial}{\partial \boldsymbol{r}_{m_2}} \Big[\mathscr{R}_z \frac{\partial \mathcal{H}^{\mathrm{L}}}{\partial \boldsymbol{r}_{m_1}} \mathscr{R}_z \Big]_{\ell\ell} \frac{\mathrm{d}z}{2\pi i}. \end{aligned} \tag{5.6.16}$$

In particular, since each term in (5.6.16) has off-diagonal decay, it can be shown that $\big|\frac{\partial \mathscr{L}(\rho)_{\ell k}}{\partial \boldsymbol{r}_{m_2}}\big| \lesssim e^{-\gamma(r_{\ell m_2} + r_{m_2 k})}$ and $\big|\frac{\partial \phi_\ell^{m_1}}{\partial \boldsymbol{r}_{m_2}}\big| \lesssim e^{\gamma'[r_{\ell m_1} + r_{\ell m_2}]}$ for some $\gamma, \gamma' > 0$ depending on $\mathfrak{d}_{F^\beta}, \mathsf{d}_{\mathscr{L}}$. Therefore, using the off-diagonal decay of $(I - \mathscr{L})^{-1}$ from (5.6.5), (5.6.15) may be bounded appropriately.

Higher derivatives may be treated similarly by taking derivatives of (5.6.15).

□

5.6.2 Point Defects: Proof of Theorem 5.3

Throughout this section, we will denote by $\mathscr{L}$ and $\mathscr{L}^{\mathrm{d}}$, the stability operators for $\boldsymbol{X}(\boldsymbol{r})$ and $\boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})$, respectively, and, to simplify notation further, we write $\mathcal{H} \coloneqq \mathcal{H}\big(\boldsymbol{X}(\boldsymbol{r})\big)$, $\mathcal{H}^{\mathrm{d}} \coloneqq \mathcal{H}\big(\boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})\big)$, and $\mathscr{R}_z \coloneqq \big(\mathcal{H} - z\big)^{-1}, \mathscr{R}_z^{\mathrm{d}} \coloneqq \big(\mathcal{H}^{\mathrm{d}} - z\big)^{-1}$.

For the moment, we suppose Proposition 5.2 holds and prove Theorem 5.3. Applying Lemma 3.4 to $\mathcal{H} + P_\varepsilon - z$ with $P \coloneqq P_{\mathrm{FR}}$ and $I - \mathscr{L} - Q_\varepsilon$ with $Q \coloneqq -Q_{\mathrm{F}R}$ (where $P_\varepsilon, P_{\mathrm{FR}}$ and $Q_\varepsilon, Q_{\mathrm{FR}}$ are the operators from Propositions 2.3 and 5.2, respectively), we obtain

$$\big|\mathscr{R}^{\mathrm{d}}_{z,\ell k}\big| \leqslant 2\mathfrak{d}^{-1} e^{-\gamma_{\mathrm{CT}}(\mathfrak{d}) r_{\ell k}} + c_P e^{-\gamma_{\mathrm{CT}}(\mathfrak{d})[|\boldsymbol{r}_\ell| + |\boldsymbol{r}_k|]} \tag{5.6.17}$$

$$\big|[(I - \mathscr{L}^{\mathrm{d}})^{-1}]_{\ell k}\big| \leqslant 2\mathsf{d}_{\mathscr{L}}^{-1} e^{-\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}}) r_{\ell k}} + c_Q e^{-\gamma_{\mathrm{CT}}(\mathsf{d}_{\mathscr{L}})[|\boldsymbol{r}_\ell| + |\boldsymbol{r}_k|]}. \tag{5.6.18}$$

Therefore, similarly to the improved locality estimates in the linear tight

binding model, we are able to replace the both the standard resolvent estimate from Lemma 3.3 and the estimate (5.6.5) with the improved estimates of (5.6.17) and (5.6.18), respectively. Therefore, whenever we apply these estimates, we obtain the exact same bound as in the defect-free case together with additional terms with larger prefactors but with exponential decay as (ℓ, k) move away from the defect core together. In particular, these additional terms vanish as the subsystem of interest moves away from the defect core together. See (3.6.11) for the analogous argument in the linear tight binding model.

Proof of Proposition 5.2. Recall that, since $\boldsymbol{X}(\boldsymbol{r})$ and $\boldsymbol{X}^{\mathrm{d}}(\boldsymbol{r}^{\mathrm{d}})$ satisfy Definition 2.2, after shifting the spectra of the Hamiltonians (as well as the chemical potential and integration contour) away from $\{0\}$, and extending the Hamiltonians to bounded linear operators on $\ell^2(\Lambda \cup \Lambda^{\mathrm{d}})$ as in (2.5.6), we have

$$\mathcal{H}^{\mathrm{d}} = \mathcal{H} + P_{\mathrm{FR}} + P_{\varepsilon}$$

where $[P_{\mathrm{FR}}]_{\ell k} = 0$ unless $(\boldsymbol{r}_\ell, \boldsymbol{r}_k) \in (B_R)^2$ for some R and $\|P_\varepsilon\|_{\ell^2 \to \ell^2} < \varepsilon$.

In order to apply the improved Combes–Thomas estimates on $I - \mathscr{L}^{\mathrm{d}}$, we must prove an analogous low rank decomposition result for the stability operator. First, we note that $\mathscr{R}_z^{\mathrm{d}} = \mathscr{R}_z - \mathscr{R}_z\big(I + (P_{\mathrm{FR}} + P_\varepsilon)\mathscr{R}_z\big)^{-1} P_{\mathrm{FR}}\mathscr{R}_z - \mathscr{R}_z^{\mathrm{d}} P_\varepsilon \mathscr{R}_z$. and so we may apply an argument identical to the proof of Proposition 2.3 to conclude

$$\mathscr{R}_z^{\mathrm{d}} = \mathscr{R}_z + Q_{z,\mathrm{FR}} + Q_{z,\varepsilon} \tag{5.6.19}$$

where

$$[Q_{z,\mathrm{FR}}]_{\ell k} \coloneqq \begin{cases} -\big[\mathscr{R}_z\big(I + (P_{\mathrm{FR}} + P_\varepsilon)\mathscr{R}_z\big)^{-1} P_{\mathrm{FR}}\mathscr{R}_z\big]_{\ell k} & \text{if } (\boldsymbol{r}_\ell, \boldsymbol{r}_k) \in B_{R_0}^2, \\ 0 & \text{otherwise} \end{cases}$$

for $R_0 > 0$ sufficiently large such that $\|Q_{z,\varepsilon}\|_{\ell^2 \to \ell^2} \leqslant C\varepsilon$ for some constant $C > 0$ depending on $\mathfrak{d}$ and $\mathfrak{d}^{\mathrm{d}}$. This in turn implies that the operator $\mathscr{F}(\rho^{\mathrm{d}})$

from (5.6.2) may be approximated by a finite rank update of $\mathscr{F}(\rho)$: on defining

$$S_{\mathrm{FR},\ell k} \coloneqq \begin{cases} \big[\mathscr{F}(\rho^{\mathrm{d}}) - \mathscr{F}(\rho)\big]_{\ell k} & \text{if } (\boldsymbol{r}_\ell, \boldsymbol{r}_k) \in B^2_{R_0}, \\ 0 & \text{otherwise,} \end{cases}$$

we have $[\mathscr{F}(\rho^{\mathrm{d}}) - \mathscr{F}(\rho) - S_{\mathrm{FR}}]_{\ell k} = \operatorname{tr} \oint_{\mathscr{C}} F^\beta(z)[(Q_{z,\varepsilon})_{\ell k}]^{\mathrm{T}} \big(\mathscr{R}_z + \mathscr{R}_z^{\mathrm{d}}\big)_{\ell k} \frac{\mathrm{d}z}{2\pi i}$ and so $\big\|\mathscr{F}(\rho^{\mathrm{d}}) - \mathscr{F}(\rho) - S_{\mathrm{FR}}\big\|_{\ell^2 \to \ell^2} \leqslant C\varepsilon$ for some constant C depending on $\|F^\beta\|_{\mathscr{C}}$, $\mathfrak{d}^{-1}$, and $(\mathfrak{d}^{\mathrm{d}})^{-1}$.

Therefore, we may apply (5.4.1) and

$$\mathscr{L}(\rho^{\mathrm{d}}) - \mathscr{L}(\rho) = \big(\mathscr{F}(\rho^{\mathrm{d}}) - \mathscr{F}(\rho)\big)\nabla v(\rho^{\mathrm{d}}) + \mathscr{F}(\rho)\big(\nabla v(\rho^{\mathrm{d}}) - \nabla v(\rho)\big)$$

to conclude. □

5.6.3 Body-ordered approximation

Throughout the following proofs, we denote by $B_r(\rho)$ the open ball of radius r about ρ with respect to the ℓ^∞-norm. Recall that the stability operator can be written as the product $\mathscr{L}(\rho) \coloneqq \mathscr{F}(\rho)\nabla v(\rho)$ where $\mathscr{F}(\rho)$ is given by (5.6.2).

Proof of Theorem 5.4. Since $\rho \mapsto F^\beta(\boldsymbol{X}(\rho))$ is C^2, and $\big(I - \mathscr{L}(\rho^\star)\big)^{-1}$ is a bounded linear operator, we necessarily have that $\big(I - \mathscr{L}(\rho)\big)^{-1}$ is a bounded linear operator for all $\rho \in B_r(\rho^\star)$ for some $r > 0$.

By applying Theorem 4.2, together with (5.2.1), we obtain

$$\begin{aligned} \big|\big[\mathscr{L}(\rho) - \mathscr{L}_N(\rho)\big]_{\ell k}\big| &\leqslant \sum_m \left| \left[\frac{\partial F^\beta_\ell(\boldsymbol{X})}{\partial v_m} - \frac{\partial I_N F^\beta_\ell(\boldsymbol{X})}{\partial v_m} \right] \frac{\partial v(\rho)_m}{\partial \rho_k} \right| && (5.6.20) \\ &\leqslant C \Big[\sum_m e^{-\eta\, r_{\ell m}} e^{-\gamma_v\, r_{mk}} \Big] e^{-\frac{1}{2}\gamma_N N} && (5.6.21) \\ &\leqslant C e^{-\frac{1}{2}\min\{\eta,\gamma_v\} r_{\ell k}} e^{-\frac{1}{2}\gamma_N N} && (5.6.22) \end{aligned}$$

for all $\rho \in B_r(\rho^\star)$. As a consequence, $\|\mathscr{L}(\rho) - \mathscr{L}_N(\rho)\|_{\ell^2 \to \ell^2} \leqslant C e^{-\frac{1}{2}\gamma_N N}$ and thus we may choose N such that $\|\mathscr{L}(\rho) - \mathscr{L}_N(\rho)\|_{\ell^2 \to \ell^2} < \|(I - \mathscr{L}(\rho))^{-1}\|^{-1}_{\ell^2 \to \ell^2}$. In particular, for such N, the operator $I - \mathscr{L}_N(\rho) \colon \ell^2 \to \ell^2$ is invertible with

inverse bounded above in operator norm independently of N.

We now show that $I - \mathscr{L}_N(\rho)$ satisfies the assumptions of Lemma 5.8. Using (5.6.2) and (5.2.1), together with the Combes–Thomas estimate (Lemma 3.3), we conclude

$$\big|\mathscr{L}_N(\rho)_{\ell k}\big| \leqslant C \sup_{z\in\mathscr{C}} |I_N F^\beta(z)| \sum_{m\in\Lambda} e^{-2\gamma_{\mathrm{CT}} r_{\ell m}} e^{-\gamma_v r_{mk}} \leqslant C e^{-\frac{1}{2}\min\{2\gamma_{\mathrm{CT}},\gamma_v\} r_{\ell k}}$$

for all $\rho \in B_r(\rho^\star)$. In particular, $I - \mathscr{L}_N(\rho)$ extends to a invertible bounded linear operator $\ell^\infty \to \ell^\infty$ and thus its inverse $\big(I - \mathscr{L}_N(\rho)\big)^{-1} \colon \ell^\infty \to \ell^\infty$ is bounded.

Now, the mapping $\rho \mapsto \rho - I_N F^\beta\big(\boldsymbol{X}(\rho)\big)$ between $\ell^\infty \to \ell^\infty$ is continuously differentiable on $B_r(\rho^\star)$ and the derivative at $\rho^\star$ is invertible (i.e. $\big(I - \mathscr{L}_N(\rho^\star)\big)^{-1} \colon \ell^\infty \to \ell^\infty$ is a well defined bounded linear operator). Since the map $\rho \mapsto I_N F^\beta\big(\boldsymbol{X}(\rho)\big)$ is C^2, its derivative $\mathscr{L}_N$ is locally Lipschitz about $\rho^\star$ and so there exists $L > 0$ such that

$$\big\|\big(I - \mathscr{L}_N(\rho^\star)\big)^{-1}\big(\mathscr{L}_N(\rho_1) - \mathscr{L}_N(\rho_2)\big)\big\|_{\ell^\infty\to\ell^\infty} \leqslant L\|\rho_1 - \rho_2\|_{\ell^\infty}$$

for $\rho_1, \rho_2 \in B_r(\rho^\star)$. Moreover, by Theorem 4.2, we have

$$\begin{aligned}&\big\|\big(I - \mathscr{L}_N(\rho^\star)\big)^{-1}\big(\rho^\star - I_N F^\beta(\boldsymbol{X}(\rho^\star))\big)\big\|_{\ell^\infty} \\ &\qquad \leqslant C\big\|F^\beta(\boldsymbol{X}(\rho^\star)) - I_N F^\beta(\boldsymbol{X}(\rho^\star))\big\|_{\ell^\infty} =: b_N,\end{aligned}$$

where $b_N \lesssim e^{-\gamma_N N}$. In particular, we may choose N sufficiently large such that $2b_N L < 1$ and $t_N^\star := \frac{1}{L}(1 - \sqrt{1 - 2b_N L}) < r$.

Thus, the Newton iteration with initial point $\rho^0 := \rho^\star$, defined by

$$\rho^{i+1} = \rho^i - \big(I - \mathscr{L}_N(\rho^i)\big)^{-1}\big(\rho^i - I_N F^\beta(\boldsymbol{X}(\rho^i))\big),$$

converges to a unique fixed point $\rho_N = I_N F^\beta(\boldsymbol{X}(\rho_N))$ in $B_{t_N^\star}(\rho^\star)$ [131, 133]. That is, $\|\rho_N - \rho^\star\|_{\ell^\infty} \leqslant t_N^\star \leqslant 2b_N$. Here, we have used the fact that $1 - \sqrt{1-x} \leqslant x$ for all $0 \leqslant x \leqslant 1$.

Since $\rho_N \in B_r(\rho^\star)$, we have $I - \mathscr{L}_N(\rho_N)\colon \ell^2 \to \ell^2$ is invertible and thus Lemma 5.6 also holds. □

Proof of Proposition 5.7. We proceed in the same way as in the proof of Theorem 5.4. In particular, since ρ_N is stable, if $\|\rho^0 - \rho_N\|_{\ell^\infty}$ is sufficiently small, $(I - \mathscr{L}_N(\rho^0))^{-1}$ is a bounded linear operator on ℓ^2. Moreover, by the exact same argument as in the proof of Theorem 5.4, $I - \mathscr{L}_N(\rho^0)\colon \ell^\infty \to \ell^\infty$ defines an invertible bounded linear operator. Also, $I - \mathscr{L}_N(\rho)$ is Lipschitz in a neighbourhood about ρ^0 and

$$\begin{aligned}
&\big\| \big(I - \mathscr{L}_N(\rho^0)\big)^{-1} \big(\rho^0 - I_N F^\beta(\boldsymbol{X}(\rho^0))\big) \big\|_{\ell^\infty} \\
&\qquad \leqslant C \big\| \rho^0 - \rho_N - \big(I_N F^\beta(\boldsymbol{X}(\rho^0)) - I_N F^\beta(\boldsymbol{X}(\rho_N))\big) \big\|_{\ell^\infty} \\
&\qquad \leqslant C \|\rho^0 - \rho_N\|_{\ell^\infty}.
\end{aligned}$$

Here, we have used:

$$\begin{aligned}
&\big| I_N F_\ell^\beta(\boldsymbol{X}(\rho^0)) - I_N F_\ell^\beta(\boldsymbol{X}(\rho_N)) \big| \\
&\qquad = \frac{1}{2\pi} \Big| \oint_{\mathscr{C}} I_N F^\beta(z) \big[\mathscr{R}_z(\rho^0) - \mathscr{R}_z(\rho_N) \big]_{\ell\ell} \Big| \\
&\qquad \leqslant C \sum_{k \in \Lambda} e^{-2\gamma_{\mathrm{CT}} r_{\ell k}} |v(\rho^0)_k - v(\rho_N)_k| \\
&\qquad \leqslant C \sum_{k \in \Lambda} e^{-2\gamma_{\mathrm{CT}} r_{\ell k}} \Big| \int_0^1 \sum_{m \in \Lambda} \frac{\partial v(t\rho^0 + (1-t)\rho_N)_k}{\partial \rho_m} \big[\rho^0 - \rho_N\big]_m \mathrm{d}t \Big| \\
&\qquad \leqslant C \sum_{m \in \Lambda} e^{-\frac{1}{2}\min\{2\gamma_{\mathrm{CT}}, \gamma_v\} r_{\ell m}} \big| \big[\rho^0 - \rho_N\big]_m \big| \\
&\qquad \leqslant C \|\rho^0 - \rho_N\|_{\ell^\infty}. \qquad (5.6.23)
\end{aligned}$$

Therefore, as long as $\|\rho^0 - \rho_N\|_{\ell^\infty}$ is sufficiently small, we may apply the Newton iteration starting from ρ^0 to conclude. □

Proof of Corollary 5.5. As a direct consequence of (5.6.23), we have

$$\begin{aligned}
&\big|O_\ell^{\mathrm{sc}}(\boldsymbol{X}) - I_N O_\ell\big(\boldsymbol{X}(\rho_N)\big)\big| \\
&\qquad \leqslant \big|O_\ell\big(\boldsymbol{X}(\rho^\star)\big) - I_N O_\ell\big(\boldsymbol{X}(\rho^\star)\big)\big| + \big|I_N O_\ell\big(\boldsymbol{X}(\rho^\star)\big) - I_N O_\ell\big(\boldsymbol{X}(\rho_N)\big)\big| \\
&\qquad \leqslant C\big[e^{-\gamma_N N} + \|\rho_N - \rho^\star\|_{\ell^\infty}\big] \\
&\qquad \leqslant C e^{-\gamma_N N}. \qquad (5.6.24)
\end{aligned}$$

Here, we have applied the standard convergence result (Theorem 4.2) with fixed effective potential. □

CHAPTER 6

An Application: Geometry Optimisation

This chapter is based on the article [95] "Point defects in tight binding models for insulators" published in Mathematical Models and Methods in Applied Sciences, 30(14): 2753–2797 (2020). This paper is co-authored by Christoph Ortner.

6.1 Introduction

In this chapter, we consider atomistic geometry relaxation in the context of linear tight binding models for point defects and formulate the limiting model as Fermi-temperature tends to zero. Further, we consider the thermodynamic limit at zero Fermi-temperature and explore the extent to which these two limits commute.

The simulation of local defects in solids remains a major issue in materials science and solid state physics [102, 115]. For a mathematical review of some works related to the modelling of point defects in materials science see [21]. Progress on local defects in the context of Thomas-Fermi-von-Weizsäcker

(TFW) and reduced Hartree-Fock (rHF) models has been made in [15, 18, 85] and [17, 60], respectively.

Thermodynamic limit (or bulk limit) problems have been widely studied in the literature. The case of a perfect crystalline lattice has been studied in [85] for the Thomas-Fermi (TF) model, [23] for the TFW model and in [25] and [24] for Hartree and Hartree-Fock type models, respectively. In these papers, the limit of the ground state energy per unit volume and minimising electronic density as domain size tends to infinity are identified in the cases where the energy functionals are convex (that is, for the TF, TFW, restricted Hartree and rHF models). For more general Hartree and Hartree-Fock type models, periodic models have been proposed and shown to be well-posed. In the setting of the rHF model, an exponential rate of convergence for the supercell energy per unit cell is obtained in the case of insulators [59].

It is important to note that in all of the papers mentioned above the nuclei degrees of freedom are fixed on a periodic lattice or with a given defect. Preliminary results concerning the simultaneous relaxation of the electronic structure together with geometry equilibriation (of the nuclei positions) can be found in [92] for the TFW model and [26, 29] for tight binding models.

This chapter is motivated by [26] which establishes the following two results: *(i)* under a mild condition on the prescribed number of electrons in the sequence of finite domain approximations, the Fermi level is shown to converge in the thermodynamic limit to that of a perfect crystal and is thus independent of the electron numbers and the defect. This result enables, *(ii)* the formulation of a unique limiting model in the grand-canonical ensemble for the electrons with chemical potential fixed at the perfect crystal level. The purpose of the present work is to explore the extent to which these results can be extended to the zero Fermi-temperature case, as well as consider the zero Fermi-temperature limit of the model described in [26].

Summary of Results

The main convergence results of [26] and the present work are summarised in Figure 6.1.

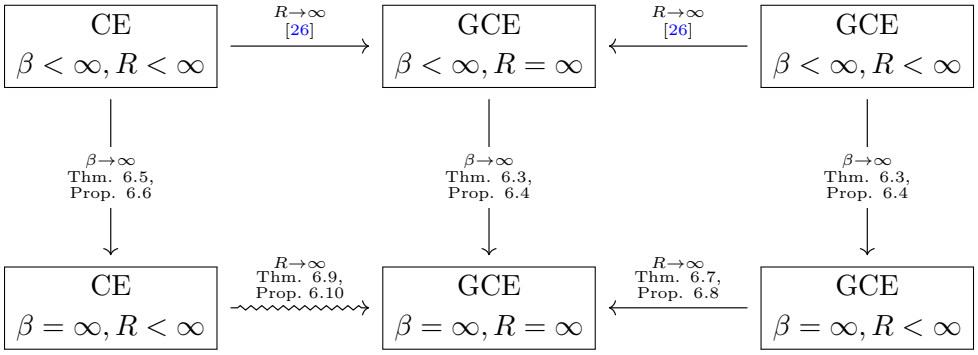


Figure 6.1: Diagram to illustrate the main results of [26] and Chapter 6 of the present work. Here, "GCE" denotes the grand canonical ensemble and "CE" the canonical ensemble. The top two thermodynamic limits represent the results of [26] and the results of this paper are indicated on the remaining arrows. The squiggly arrow in the bottom left of this diagram signifies the fact that the chemical potential used in the limiting grand canonical ensemble model is given as the limit of the sequence of the finite Fermi levels and is thus defect-dependent. This is in contrast to the finite Fermi-temperature case (top left arrow) in which the limiting chemical potential is fixed and equal to the Fermi-level for the homogeneous crystal.

Thermodynamic Limit

Since we are interested in the bulk properties of a material with local defects, it is convenient to consider an extended system of infinitely many nuclei. However, to simulate such a system, we must of course restrict ourselves to finite computational domains and impose an artificial boundary condition. Throughout this chapter we shall consider periodic boundary conditions for the nuclei (that is, a supercell model) in the form of a torus tight binding model and show that the thermodynamic limit is well defined under some appropriate choice of electron numbers in the sequence of finite domain approximations.

More precisely, we consider linear tight binding models with electrons in the canonical ensemble and at zero Fermi-temperature. We show that, because the zero temperature Fermi levels depend globally on each eigenvalue (and not just on the limiting density of states as in the case of finite Fermi-temperature),

the zero temperature Fermi levels only converge in the thermodynamic limit under strict conditions on the number of electrons imposed in the sequence of finite domain approximations. Moreover, the limiting Fermi level depends upon the polluted band structure and consequently also on the defect. Using this, the thermodynamic limit model is shown to be a grand canonical model with chemical potential fixed (but defect-dependent) and given by the limit of the sequence of finite domain Fermi levels. That is, the number of electrons imposed in the sequence of finite domain approximations is critical in identifying a limiting model. This analysis clarifies questions left open in [26] about the effect of Fermi-temperature on the convergence.

Zero Temperature Limit.

A key feature of zero temperature electronic structure models is the sharp cut-off between unoccupied and occupied electronic states. In practice (e.g. [30] for density functional theory), a low but positive Fermi-temperature may be chosen in order to approximate the sharp cut-off with a smooth Fermi-Dirac distribution (alternatively, artificial smearing methods may be used). One can then show that the error committed does not drastically affect the simulation; see [19] for an in-depth error analysis for typical observables (including the Fermi level, total energy and the density). Choosing a finite Fermi-temperature has the additional benefit that there is a unique Fermi level (see (6.3.3)) solving the electron number constraint which is advantageous in numerical simulations [30, 132].

In the present work, we give a comprehensive justification of this approach; assuming the electrons are in finite Fermi-temperature and the nuclei degrees of freedom are determined by minimising the grand potential associated with the electrons, we uniquely identify the limiting model as Fermi-temperature tends to zero by a grand canonical model for the electrons at zero Fermi-temperature. We obtain an exponential rate of convergence for the nuclei configuration.

Strong Energy Locality.

A key tool in [26] and the present work is the strong energy locality of the tight binding model (Chapter 3). This locality allows for a straightforward definition of a renormalised energy functional on the infinite lattice with embedded point defect and thus allows for the formulation of a limiting model [27].

6.2 Point Defect Reference Configurations

In this chapter, we restrict our attention to point defects embedded in multilattice reference configurations.

6.2.1 Multilattice Reference Configurations

For an invertible matrix $\mathsf{A} \in \mathbb{R}^{d\times d}$ and a *unit cell* $\Gamma \subseteq \mathbb{R}^d$ such that Γ is finite and contains the origin, we set $\Lambda^{\mathrm{ref}} = \bigcup_{\gamma\in\mathbb{Z}^d} \big(\Gamma + \mathsf{A}\gamma\big)$ and $\boldsymbol{X}^{\mathrm{ref}}_{\ell+\mathsf{A}\gamma} \coloneqq (\ell + \mathsf{A}\gamma, v^{\mathrm{ref}}_\ell, Z^{\mathrm{ref}}_\ell)$ for all $\ell \in \Gamma$ and $\gamma \in \mathbb{Z}^d$.

By exploiting the translational symmetry of the reference configuration, we may apply the Bloch transform [53] to conclude that the spectrum of the reference Hamiltonian is the union of finitely many spectral bands:

$$\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{ref}})\big) = \bigcup_j \varepsilon_j(\mathrm{BZ}),$$

where $\varepsilon_j \colon \mathrm{BZ} \to \mathbb{R}$ are continuous on the (first) Brillouin zone BZ, a compact and connected subset of $\mathbb{R}^d$. See Appendix B.2 for the full details.

For the remainder of this chapter, we will suppose that the system is an insulator:

(Gap). *There is a gap in the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{ref}})\big)$ and the chemical potential μ lies within the gap (i.e. $\mu \notin \sigma\big(\mathcal{H}(\boldsymbol{X}^{\mathrm{ref}})\big)$).*

6.2.2 Point Defects

Now, we consider *point defect domains* Λ with respect to the reference domain Λ^{ref} as in Chapter 2. That is, we suppose there exists $R_{\mathrm{d}} > 0$ such that

$\Lambda \setminus B_{R_\mathrm{d}} = \Lambda^\mathrm{ref} \setminus B_{R_\mathrm{d}}$ and $\Lambda \cap B_{R_\mathrm{d}}$ is finite. Then, for displacements $u\colon \Lambda \to \mathbb{R}^d$, we consider configurations $\boldsymbol{X}(u)$ with $\boldsymbol{X}_\ell(u) \coloneqq (\ell + u(\ell), v_\ell, Z_\ell)$ for $\ell \in \Lambda$ and $(v_\ell, Z_\ell) = (v_\ell^\mathrm{ref}, Z_\ell^\mathrm{ref})$ for all $\ell \in \Lambda \setminus B_{R_\mathrm{d}}$. In particular, $\big(\boldsymbol{X}^\mathrm{ref}, \boldsymbol{X}(\mathbf{0})\big)$ satisfies $\mathbf{(P}_0\mathbf{)}$ with $\Lambda^\mathrm{ff} = \Lambda \setminus B_{R_\mathrm{d}}$.

Following [26,27,29,98], we introduce a space of finite energy displacements which restricts the class of admissible configurations: Given $\ell \in \Lambda$ and $\rho \in \Lambda - \ell$, we define the finite difference $D_\rho u(\ell) \coloneqq u(\ell + \rho) - u(\ell)$. The full (infinite) finite difference stencil is then defined to be $Du(\ell) \coloneqq \big(D_\rho u(\ell)\big)_{\rho \in \Lambda - \ell}$ and for $\Upsilon > 0$, we define the ℓ^2_Υ semi-norm by

$$\|Du\|_{\ell^2_\Upsilon} \coloneqq \bigg(\sum_{\ell \in \Lambda} \sum_{\rho \in \Lambda - \ell} e^{-2\Upsilon|\rho|} |D_\rho u(\ell)|^2 \bigg)^{1/2}.$$

Since all of the semi-norms $\|D \cdot\|_{\ell^2_\Upsilon}$, for $\Upsilon > 0$, are equivalent [27], we will fix $\Upsilon > 0$ for the remainder of this chapter and define the following function space of finite energy displacements:

$$\dot{\mathscr{W}}^{1,2}(\Lambda) \coloneqq \big\{ u\colon \Lambda \to \mathbb{R}^d \colon \|Du\|_{\ell^2_\Upsilon} < \infty \big\}$$

with semi-norm $\|D \cdot\|_{\ell^2_\Upsilon}$. Recall also that $\boldsymbol{r}_{\ell k}(u) \coloneqq \ell + u(\ell) - k - u(k)$ and $r_{\ell k}(u) = |\boldsymbol{r}_{\ell k}(u)|$ and suppose that the following non-interpenetration condition is satisfied:

(L). *There exists* $\mathfrak{m} > 0$ *such that* $r_{\ell k}(u) \geqslant \mathfrak{m}\, r_{\ell k}(\mathbf{0})$ *for all* $\ell, k \in \Lambda$.

Configurations arising in this way satisfy $\mathbf{(P}_\delta\mathbf{)}$:

Lemma 6.1 (Decomposition of the Spectrum)**.** *Suppose* $u \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ *such that* **(L)** *is satisfied. Then,* $\big(\boldsymbol{X}^\mathrm{ref}, \boldsymbol{X}(u)\big)$ *satisfies* $\mathbf{(P}_\delta\mathbf{)}$ *for all* $\delta > 0$.

To simplify notation in the following, we will write $\mathcal{H}(u) \coloneqq \mathcal{H}\big(\boldsymbol{X}(u)\big)$.

6.3 Torus Tight Binding Model

We follow the notation of §6.2 and take a reference $\boldsymbol{X}^\mathrm{ref}$ and corresponding point defect configuration $\boldsymbol{X}(u)$ for displacements $u \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ such that $\boldsymbol{X}(u)$

satisfies **(L)**.

In order to simulate the model described in §2.2, we must restrict ourselves to finite computational domains and impose artificial boundary conditions. A popular choice for simulating the far-field behaviour of point defects is periodic boundary conditions which we now introduce.

For $R > 0$, we consider a sequence, Λ_R, of computational cells given by:

(Ref$_R$). *For $R > 0$, we suppose $\Omega_R \subseteq \mathbb{R}^d$ is a bounded connected domain with $B_R \subseteq \Omega_R$. Further, we take an invertible matrix $\mathsf{M}_R = (\mathsf{m}_1, \dots, \mathsf{m}_d) \in \mathbb{R}^{d\times d}$ such that $\mathsf{m}_j \in \Lambda^{\rm ref}$ and $\mathbb{R}^d$ is the disjoint union of the shifted domains $\Omega_R + \mathsf{M}_R\alpha$ for $\alpha \in \mathbb{Z}^d$. The computational cell is defined to be $\Lambda_R \coloneqq \Omega_R \cap \Lambda$.*

When employing periodic boundary conditions, we consider displacements $u\colon \Lambda \to \mathbb{R}^d$ or $u\colon \Lambda_R \to \mathbb{R}^d$ and the corresponding configuration $\boldsymbol{X}^R(u)$ with index set $\bigcup_{\alpha\in\mathbb{Z}^d}(\Lambda_R + \mathsf{M}_R\alpha)$ and atomic positions $\boldsymbol{r}_{\ell+\mathsf{M}_R\alpha}(u) \coloneqq \ell + u(\ell) + \mathsf{M}_R\alpha$ for $\ell \in \Lambda_R$ and $\alpha \in \mathbb{Z}^d$.

To simplify notation, we define $r^{\#}_{\ell k}(u) \coloneqq \min_{\alpha\in\mathbb{Z}^d} |\boldsymbol{r}_{\ell k}(u) + \mathsf{M}_R\alpha|$ to be the torus distance between atomic positions $\ell + u(\ell)$ and $k + u(k)$. If it is clear from context, we shall drop the argument (u).

The torus tight binding Hamiltonian is defined as follows: for $\ell, k \in \Lambda_R$, the torus model is given by considering the interactions between atomic sites ℓ and k and all periodic images:

$$\mathcal{H}^R(u)_{\ell k} \coloneqq \sum_{\alpha\in\mathbb{Z}^d} \mathcal{H}\big(\boldsymbol{X}^R(u)\big)_{\ell,k+\mathsf{M}_R\alpha}. \tag{6.3.1}$$

Remark 6.1. *We consider periodic boundary conditions in order to avoid spectral pollution that is known to occur when using clamped boundary conditions, see for example [22]. Indeed, in Lemma 6.14 we prove that spectral pollution does not occur in our setting.*

6.3.1 Potential Energy at Finite Fermi-Temperature

Canonical Ensemble. We consider a particle system containing $N_{e,R}$ electrons and nuclei described by some admissible displacement $u\colon \Lambda_R \to \mathbb{R}^d$. We first suppose that the electrons are in a canonical ensemble. That is, we fix the number of particles in the system, the volume and Fermi-temperature.

The particle number functional is then given by summing the electronic occupation numbers according to the Fermi-Dirac distribution:

$$\mathcal{N}^{\beta,R}(u;\tau) \coloneqq 2\sum_s F^\beta(\lambda_s;\tau) \quad \text{and} \quad F^\beta(\varepsilon;\tau) \coloneqq \frac{1}{1+e^{\beta(\varepsilon-\tau)}}, \tag{6.3.2}$$

where $\{\lambda_s\}_s$ is some enumeration of $\sigma(\mathcal{H}^R(u))$. Here, the factor of two accounts for the spin.

Since $\tau \mapsto \mathcal{N}^{\beta,R}(u;\tau)$ is strictly increasing, for any electron number $N_{e,R} \in (0, 2N_\mathrm{b}\cdot|\Lambda_R|)$, the Fermi level, $\varepsilon_\mathrm{F}^{\beta,R} = \varepsilon_\mathrm{F}^{\beta,R}(u)$, at finite Fermi-temperature, solving

$$\mathcal{N}^{\beta,R}(u;\varepsilon_\mathrm{F}^{\beta,R}) = N_{e,R} \tag{6.3.3}$$

is well-defined.

The Helmholtz free energy is then given by

$$\begin{aligned} \mathcal{E}^{\beta,R}(u) &\coloneqq \sum_s E^\beta(\lambda_s;\varepsilon_\mathrm{F}^{\beta,R}) \quad \text{where} \\ E^\beta(\lambda;\tau) &\coloneqq 2\lambda F^\beta(\lambda;\tau) + \frac{2}{\beta}S\big(F^\beta(\lambda;\tau)\big) \\ &= 2\tau F^\beta(\lambda;\tau) + \frac{2}{\beta}\log\Big(1-F^\beta(\lambda;\tau)\Big) \end{aligned} \tag{6.3.4}$$

where $S(f) \coloneqq f\log(f) + (1-f)\log(1-f)$ is the Fermi-Dirac entropy. More details regarding the derivation can be found in [26] or [96, Appendix C].

In the following, it will be useful to consider the Helmholtz free energy as a function of both the configuration and Fermi level. That is, we define $\mathcal{E}^{\beta,R}(u;\tau) \coloneqq \sum_s E^\beta(\lambda_s;\tau)$. In this notation, we have $\mathcal{E}^{\beta,R}(u) \equiv \mathcal{E}^{\beta,R}(u,\varepsilon_\mathrm{F}^{\beta,R}(u))$.

Grand Canonical Ensemble. For a many-particle system that is free to exchange particles with a reservoir, it is useful to also consider the grand canonical ensemble. This framework will also allow us to formulate the limiting models as $R \to \infty$. In this case, the Fermi-temperature, volume and chemical potential, μ, are fixed model parameters ($TV\mu$) and, instead of the Helmholtz free energy, we subtract the contribution resulting from varying the particle number and consider the grand potential:

$$\begin{aligned} \mathcal{G}^{\beta,R}(u;\mu) &\coloneqq \mathcal{E}^{\beta,R}(u;\mu) - \mu\mathcal{N}^{\beta,R}(u;\mu) = \sum_s G^\beta(\lambda_s;\mu) \quad \text{where} \\ G^\beta(\lambda;\tau) &\coloneqq E^\beta(\lambda;\tau) - 2\tau F^\beta(\lambda;\tau) = \frac{2}{\beta}\log\Big(1 - F^\beta(\lambda;\tau)\Big). \end{aligned} \tag{6.3.5}$$

When it is clear from the context, we will drop μ in the argument for the particle number functional and grand potential: that is, $\mathcal{N}^{\beta,R}(u;\mu) = \mathcal{N}^{\beta,R}(u)$ and $\mathcal{G}^{\beta,R}(u;\mu) = \mathcal{G}^{\beta,R}(u)$.

6.3.2 Potential Energy at Zero Fermi-Temperature

We now consider the Helmholtz free energy and grand potential at zero Fermi-temperature. We simply take the pointwise limit of (6.3.5) as $\beta \to \infty$ to obtain

$$\begin{aligned} \mathcal{G}^{\infty,R}(u;\mu) &\coloneqq \sum_s G^\infty(\lambda_s;\mu) \quad \text{where} \\ G^\infty(\lambda;\tau) &= 2(\lambda - \tau)\chi_{(-\infty,\tau)}(\lambda). \end{aligned} \tag{6.3.6}$$

See Lemma 6.15 for justification of this limit. Moreover, we define the zero temperature particle number in the limit as $\beta \to \infty$:

$$\begin{aligned} \mathcal{N}^{\infty,R}(u;\tau) &\coloneqq 2\sum_s F^\infty(\lambda_s;\tau) \\ &= 2\#\{\lambda \in \sigma(\mathcal{H}^R(u))\colon \lambda < \tau\} + \#\{\lambda \in \sigma(\mathcal{H}^R(u))\colon \lambda = \tau\}, \end{aligned}$$

where the Fermi-Dirac distribution at zero Fermi-temperature $F^\infty(\,\cdot\,;\tau)$ is given by (2.4.4) with chemical potential τ.

For the Helmholtz free energy, we must also consider the Fermi level constraint. However, taking the $\beta \to \infty$ limit of the particle number functional yields a step function. This means that there may not be a unique solution to the particle number constraint (6.3.3) at zero Fermi-temperature. We define the zero temperature Fermi level as the zero temperature limit of the finite temperature Fermi levels:

Lemma 6.2 (Fermi Level at Zero Fermi-Temperature)**.** *Suppose* $u\colon \Lambda_R \to \mathbb{R}^d$ *satisfies* **(L)** *and that* $\varepsilon_{\mathrm{F}}^{\beta,R}$ *is the corresponding Fermi level solving* (6.3.3)*. Then, on defining* $\underline{\varepsilon} \coloneqq \arg\max\left\{\lambda \in \sigma(\mathcal{H}^R(u))\colon \mathcal{N}^{\infty,R}(u;\lambda) \leqslant N_{e,R}\right\}$ *and* $\overline{\varepsilon} \coloneqq \arg\min\left\{\lambda \in \sigma(\mathcal{H}^R(u))\colon \mathcal{N}^{\infty,R}(u;\lambda) \geqslant N_{e,R}\right\}$*, we have*

$$\lim_{\beta\to\infty} \varepsilon_{\mathrm{F}}^{\beta,R} = \varepsilon_{\mathrm{F}}^{\infty,R} \coloneqq \begin{cases} \underline{\varepsilon} & \text{if } \mathcal{N}^{\infty,R}(u;\tfrac{1}{2}(\underline{\varepsilon}+\overline{\varepsilon})) > N_{e,R}, \\ \tfrac{1}{2}(\underline{\varepsilon}+\overline{\varepsilon}) & \text{if } \mathcal{N}^{\infty,R}(u;\tfrac{1}{2}(\underline{\varepsilon}+\overline{\varepsilon})) = N_{e,R}, \\ \overline{\varepsilon} & \text{if } \mathcal{N}^{\infty,R}(u;\tfrac{1}{2}(\underline{\varepsilon}+\overline{\varepsilon})) < N_{e,R}. \end{cases}$$

Proof. See [97, Appendix D]. □

This result suggests that we may formally define the zero Fermi-temperature Helmholtz free energy by considering the pointwise limit as $\beta \to \infty$ and fixing the Fermi level as in Lemma 6.2. That is, we define

$$\begin{gathered} \mathcal{E}^{\infty,R}(u) \equiv \mathcal{E}^{\infty,R}(u;\varepsilon_{\mathrm{F}}^{\infty,R}(u)) \coloneqq \sum_s E^{\infty}(\lambda_s;\varepsilon_{\mathrm{F}}^{\infty,R}), \\ \text{where} \quad E^{\infty}(\lambda;\tau) \coloneqq 2\lambda\chi_{(-\infty,\tau)}(\lambda) + \lambda\chi_{\{\tau\}}(\lambda). \end{gathered} \tag{6.3.7}$$

6.4 Thermodynamic Limit

In this section, we apply the locality results of Chapter 3 to renormalise the total energy in order to define a *grand potential difference functional* for infinite systems.

Firstly we note that, if $\boldsymbol{X}$ is a finite system, we may diagonalise the

Hamiltonian, $\mathcal{H}(\boldsymbol{X})\psi_s = \lambda_s\psi_s$, and write

$$\sum_s G^\beta(\lambda_s;\mu) = \operatorname{Tr} G^\beta\big(\mathcal{H}(\boldsymbol{X});\mu\big) = \operatorname{tr}\sum_\ell G^\beta\big(\mathcal{H}(\boldsymbol{X});\mu\big)_{\ell\ell} = \sum_\ell G^\beta_\ell(\boldsymbol{X};\mu) \tag{6.4.1}$$

where $G^\beta_\ell(\boldsymbol{X};\mu)$ are defined in (2.4.1).

While the site energies G^β_ℓ are well-defined for infinite systems (Chapter 3), the total energy (6.4.1) is of course ill-defined. However, we may renormalise the total energy and, formally at first, define the following grand potential difference functional: for $\beta \in (0,\infty]$,

$$\mathcal{G}^\beta(u;\mu) \coloneqq \sum_{\ell\in\Lambda}\Big[G^\beta_\ell\big(\boldsymbol{X}(u);\mu\big) - G^\beta_\ell\big(\boldsymbol{X}(\mathbf{0});\mu\big)\Big]. \tag{6.4.2}$$

The strong locality estimates for the site energies from Chapter 3 allow us to conclude that the grand potential difference functional is well defined on the space of compact displacements [27, Theorem 3.1]. Therefore, by a density argument, we may extend the definition to the following space of admissible displacements by continuity [27, Theorem 2.1]:

$$\operatorname{Adm}(\Lambda) \coloneqq \{u \in \dot{\mathscr{W}}^{1,2}(\Lambda) \text{ satisfying } \mathbf{(L)} \colon \mu \notin \sigma(\mathcal{H}(u))\}. \tag{6.4.3}$$

The restriction $\mu \notin \sigma\big(\mathcal{H}(\boldsymbol{X}(u))\big)$ ensures the grand potential difference functional is differentiable for $\beta = \infty$. We also impose this condition for $\beta < \infty$ since we are interested in taking the zero Fermi-temperature limit.

When it is clear from the context, we will drop μ in the argument for the site energies and grand potential difference functional.

6.5 Equilibiration of Nuclei Positions

For a point defect configuration Λ, finite computational cells Λ_R, $\beta \in (0,\infty]$, and fixed chemical potential, μ, we consider the following geometry optimisation

problems

$$\overline{u} \in \arg\min\Big\{\mathcal{E}^{\beta,R}(u)\colon u \text{ satisfies } \mathbf{(L)}\Big\}, \tag{$\mathrm{CE}^{\beta,R}_{N_{e,R}}$}$$

$$\overline{u} \in \arg\min\Big\{\mathcal{G}^{\beta,R}(u;\mu)\colon u \text{ satisfies } \mathbf{(L)}\Big\}, \qquad \text{and} \tag{$\mathrm{GCE}^{\beta,R}_{\mu}$}$$

$$\overline{u} \in \arg\min\Big\{\mathcal{G}^{\beta}(u;\mu)\colon u \in \mathrm{Adm}(\Lambda)\Big\}. \tag{$\mathrm{GCE}^{\beta,\infty}_{\mu}$}$$

Here and throughout, "arg min" denotes the set of local minimisers. We denote these problems by $(\mathrm{CE}^{\beta,R}_{N_{e,R}})$ and $(\mathrm{GCE}^{\beta,R}_{\mu})$ so that we can reference the problem and associated parameters using a single compact notation.

6.5.1 Stability Conditions

In the main results of this chapter, we will assume that solutions $\overline{u}_R$ to $(\mathrm{CE}^{\beta,R}_{N_{e,R}})$ or to $(\mathrm{GCE}^{\beta,R}_{\mu})$ and $\overline{u}$ to $(\mathrm{GCE}^{\beta,\infty}_{\mu})$ are *strongly stable* in the following sense:

$$\Big\langle \delta^2\mathcal{E}^{\beta,R}(\overline{u}_R)v, v\Big\rangle \geqslant c_0\|Dv\|^2_{\ell^2_\Upsilon} \tag{6.5.1}$$

$$\Big\langle \delta^2\mathcal{G}^{\beta,R}(\overline{u}_R;\mu)v, v\Big\rangle \geqslant c_0\|Dv\|^2_{\ell^2_\Upsilon} \tag{6.5.2}$$

$$\Big\langle \delta^2\mathcal{G}^{\beta}(\overline{u};\mu)v, v\Big\rangle \geqslant c_0\|Dv\|^2_{\ell^2_\Upsilon} \tag{6.5.3}$$

for some positive constant $c_0 > 0$. Here, we have fixed the chemical potential μ and are considering the second variation of $\mathcal{G}^{\beta,R}(\,\cdot\,;\mu)$ and $\mathcal{G}^{\beta}(\,\cdot\,;\mu)$ at $\overline{u}_R$ and $\overline{u}$, respectively.

For $\beta \in (0,\infty]$, we denote by $\mathcal{G}^{\beta}_{\mathrm{ref}}$ the reference grand potential which is given by (6.4.2) but with Λ replaced with Λ^{ref}. We assume that the reference configuration is an equilibrium state and stable in the sense that: there exists $c_{\mathrm{stab}} > 0$ such that

$$\delta\mathcal{G}^{\beta}_{\mathrm{ref}}(\mathbf{0}) = 0 \quad \text{and} \quad \Big\langle \delta^2\mathcal{G}^{\beta}_{\mathrm{ref}}(\mathbf{0})v, v\Big\rangle \geqslant c_{\mathrm{stab}}\|Dv\|^2_{\ell^2_\Upsilon} \quad \forall\, v \in \dot{\mathscr{W}}^{1,2}(\Lambda). \tag{6.5.4}$$

We will often drop the superscript in the site energy and grand potential difference functional in the case of zero Fermi-temperature (e.g. $\mathcal{G} = \mathcal{G}^{\infty}$).

6.6 Main Results

The results of this work can be summarised in Figure 6.1. Each arrow represents the following mathematical statements: *(i) Strong limit:* for any strongly stable solution to the limit problem, there exists a sequence of solutions to the finite domain or finite temperature problem that converges to the solution to the limit problem; *(ii) Weak limit:* for any bounded sequence of solutions to the finite domain or finite temperature problem, there is a weak limit along a subsequence that is a critical point of the limiting energy functional.

This work generalises the results of [26] to the zero temperature case but also to the case where Λ is not necessarily a Bravais lattice.

When we say that the limiting model is given by a grand-canonical model, we have to be careful in specifying the limiting chemical potential. For example, the limit of $(\mathrm{CE}^{\beta,R}_{N_{e,R}})$ as $R \to \infty$ for $\beta < \infty$ is given by $(\mathrm{GCE}^{\beta,\infty}_{\mu_\#})$ where $\mu_\#$ is the Fermi level for the homogeneous crystal [26, Theorems A.2 and A.3]. This subtlety means that Figure 6.1 *cannot* be seen as a commutative diagram.

We also stress that these results only hold in the case where $\mu \notin \sigma(\mathcal{H}(\overline{u}))$. This is simply because the site energies and hence the grand potential difference functional are not differentiable if the chemical potential is an eigenvalue. In this case the main techniques used in this chapter cannot be applied.

6.6.1 Zero Temperature Limit

First, we state the zero Fermi-temperature limit result for the grand canonical ensemble model

Theorem 6.3 (Strong Zero Temperature Limit, $(\mathrm{GCE}^{\beta,\infty}_{\mu}) \to (\mathrm{GCE}^{\infty,\infty}_{\mu})$)**.** *Suppose that μ satisfies* **(Gap)** *and $\overline{u}$ is a solution to $(\mathrm{GCE}^{\infty,\infty}_{\mu})$ that is strongly stable* (6.5.3)*. Then, there exist solutions $\overline{u}_\beta$ to $(\mathrm{GCE}^{\beta,\infty}_{\mu})$ such that*

$$\|D\overline{u}_\beta - D\overline{u}\|_{\ell^2_\Upsilon} \leqslant Ce^{-\frac{1}{12}\mathsf{d}\beta} \quad \text{and} \quad |\mathcal{G}^\beta(\overline{u}_\beta) - \mathcal{G}(\overline{u})| \leqslant Ce^{-\frac{1}{12}\mathsf{d}\beta}$$

where $\mathsf{d} := \mathrm{dist}(\mu, \sigma(\mathcal{H}(\overline{u})))$.

Proposition 6.4 (Weak Zero Temperature Limit, $(\mathrm{GCE}_{\mu}^{\beta,\infty}) \to (\mathrm{GCE}_{\mu}^{\infty,\infty})$)**.** *Suppose that $\overline{u}_{\beta_j}$ is a bounded sequence (with $\beta_j \to \infty$) of solutions to $(\mathrm{GCE}_{\mu}^{\beta_j,\infty})$ each satisfying* **(L)** *with an accumulation parameter uniformly bounded below by $\mathfrak{m} > 0$ and such that μ is (eventually) uniformly bounded away from $\sigma(\mathcal{H}(\overline{u}_{\beta_j}))$. Then, there exists $\overline{u} \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ such that along a subsequence*

$$D_{\rho}\overline{u}_{\beta_j}(\ell) \to D_{\rho}\overline{u}(\ell) \quad \forall \ell \in \Lambda,\, \rho \in \Lambda - \ell. \tag{6.6.1}$$

Moreover, $\overline{u}$ is a critical point of $\mathcal{G}$.

The exact same arguments can be made in the finite domain case. That is, every strongly stable solution to $(\mathrm{GCE}_{\mu}^{\infty,R})$ is an accumulation point of a sequence of solutions to $(\mathrm{GCE}_{\mu}^{\beta,R})$. Moreover, for every bounded sequence of solutions to $(\mathrm{GCE}_{\mu}^{\beta,R})$, with spectrum uniformly bounded away from the chemical potential, up to a subsequence, there exists a weak limit. The limit is a critical point of the limiting functional.

Further, we have an analogous result in the canonical ensemble. Here we only consider $R < \infty$ since $(\mathrm{CE}^{\infty,\infty})$ is not well defined.

Theorem 6.5 (Strong Zero Temperature Limit, $(\mathrm{CE}_{N_{e,R}}^{\beta,R}) \to (\mathrm{CE}_{N_{e,R}}^{\infty,R})$)**.** *Suppose $\overline{u}_R$ is a solution to $(\mathrm{CE}_{N_{e,R}}^{\infty,R})$ with $\varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R) \notin \sigma(\mathcal{H}^R(\overline{u}_R))$ and such that* (6.5.1) *is satisfied. Then, there exist solutions $\overline{u}_{R,\beta}$ to $(\mathrm{CE}_{N_{e,R}}^{\beta,R})$ such that*

$$\|D\overline{u}_{R,\beta} - D\overline{u}_R\|_{\ell^2_{\Upsilon}} + \left|\varepsilon_{\mathrm{F}}^{\beta,R}(\overline{u}_{R,\beta}) - \varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R)\right| \leqslant Ce^{-\frac{1}{12}\mathsf{d}\beta}$$

where $\mathsf{d} = \operatorname{dist}(\mu, \sigma(\mathcal{H}^R(\overline{u}_R)))$.

Proposition 6.6 (Weak Zero Temperature Limit, $(\mathrm{CE}_{N_{e,R}}^{\beta,R}) \to (\mathrm{CE}_{N_{e,R}}^{\infty,R})$)**.** *Suppose that $\overline{u}_{R,\beta_j}$ is a bounded sequence (with $\beta_j \to \infty$) of solutions to $(\mathrm{CE}_{N_{e,R}}^{\beta_j,R})$ each satisfying* **(L)** *with an accumulation parameter uniformly bounded below by $\mathfrak{m} > 0$. Then, there exists $\overline{u}_R \colon \Lambda_R \to \mathbb{R}^d$ such that along a subsequence $\overline{u}_{R,\beta_j} \to \overline{u}_R$ and $\varepsilon_{\mathrm{F}}^{\beta_j,R}(\overline{u}_{R,\beta_j}) \to \varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R)$ as $j \to \infty$.*

Moreover, if $\varepsilon_{\mathrm{F}}^{\beta_j,R}(\overline{u}_{R,\beta_j})$ is (eventually) uniformly bounded away from $\sigma(\mathcal{H}^R(\overline{u}_{R,\beta_j}))$, then $\overline{u}_R$ is a critical point of $\mathcal{G}^{\infty,R}(\,\cdot\,;\mu)$ with $\mu \coloneqq \varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R)$.

Remark 6.2 (Convergence Rates)**.** *The convergence rates in Theorems 6.3 and 6.5 are obtained by a suitable consistency estimate and application of the inverse function theorem. For example, in the $R < \infty$ case, we may use the fact that $\overline{u}$ is an equilibrium state for $\beta = \infty$ to conclude that,*

$$\left|\frac{\partial G^{R,\beta}(\overline{u})}{\partial u(\ell)}\right| \leqslant \sum_{s\colon \lambda_s<\mu} 2(1 - f_\beta(\lambda_s - \mu))\left|\frac{\partial \lambda_s(\overline{u})}{\partial \overline{u}(\ell)}\right| + \sum_{s\colon \lambda_s>\mu} 2f_\beta(\lambda_s - \mu)\left|\frac{\partial \lambda_s(\overline{u})}{\partial \overline{u}(\ell)}\right| \tag{6.6.2}$$

where $\lambda_s = \lambda_s(\overline{u})$ is some enumeration of $\sigma(\mathcal{H}(\overline{u}))$. The dominant contribution in (6.6.2) *is exponentially small in the distance from the closest eigenvalue to the chemical potential. Unless there is significant cancellation in this summation (which we have no reason to expect), this simple calculation suggests that the convergence rates obtained in Theorems 6.3 and 6.5 depend on the defect states within the band gap and can be no better than a constant multiple of* $\operatorname{dist}(\mu, \sigma(\mathcal{H}(\overline{u})))$.

6.6.2 Thermodynamic Limit

Now we move on to consider the thermodynamic limit results.

Theorem 6.7 (Strong Thermodynamic Limit, $(\mathrm{GCE}_\mu^{\infty,R}) \to (\mathrm{GCE}_\mu^{\infty,\infty})$)**.** *Suppose that μ is fixed such that* **(Gap)** *is satisfied and $\overline{u}$ is a solution to* $(\mathrm{GCE}_\mu^{\infty,\infty})$ *that is strongly stable* (6.5.3)*. Then, there exist solutions $\overline{u}_R$ to* $(\mathrm{GCE}_\mu^{\infty,R})$ *such that $\overline{u}_R \to \overline{u}$ in $\dot{\mathscr{W}}^{1,2}(\Lambda)$.*

Proposition 6.8 (Weak Thermodynamic Limit, $(\mathrm{GCE}_\mu^{\infty,R}) \to (\mathrm{GCE}_\mu^{\infty,\infty})$)**.** *Suppose that $\overline{u}_{R_j}$ is a bounded sequence (with $R_j \to \infty$) of solutions to* $(\mathrm{GCE}_\mu^{\infty,R_j})$ *each satisfying* **(L)** *with an accumulation parameter uniformly bounded below by $\mathfrak{m} > 0$ and such that μ is uniformly bounded away from $\sigma(\mathcal{H}^{R_j}(\overline{u}_{R_j}))$. Then, there exists $\overline{u} \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ such that along a subsequence*

$$D_\rho \overline{u}_{R_j}(\ell) \to D_\rho \overline{u}(\ell) \quad \forall \ell \in \Lambda,\, \rho \in \Lambda - \ell. \tag{6.6.3}$$

Moreover, $\overline{u}$ is a critical point of $\mathcal{G}(\,\cdot\,;\mu)$.

We now turn our attention to the thermodynamic limit of the canonical model. Here, we see that the prescribed number of particles in the sequence of finite domain approximations is vital in identifying a limiting model.

Theorem 6.9 (Strong Thermodynamic Limit, $(\mathrm{CE}^{\infty,R}_{N_{e,R}}) \to (\mathrm{GCE}^{\infty,\infty}_{\mu})$)**.** *Suppose that μ is fixed such that* **(Gap)** *is satisfied and $\overline{u}$ is a solution to $(\mathrm{GCE}^{\infty,\infty}_{\mu})$ that is strongly stable* (6.5.3)*. Then, there exists a sequence $N_{e,R}$ and solutions $\overline{u}_R$ to $(\mathrm{CE}^{\infty,R}_{N_{e,R}})$ such that $\overline{u}_R \to \overline{u}$ in $\dot{\mathscr{W}}^{1,2}(\Lambda)$.*

Moreover, $\varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R) \to \nu$ as $R \to \infty$ for some $\nu \in \mathbb{R}$ and $\overline{u}$ is also a strongly stable solution to $(\mathrm{GCE}^{\infty,\infty}_{\nu})$.

Proposition 6.10 (Weak Thermodynamic Limit, $(\mathrm{CE}^{\infty,R_j}_{N_{e,R}}) \to (\mathrm{GCE}^{\infty,\infty}_{\mu})$)**.** *Suppose that $\overline{u}_{R_j}$ is a bounded sequence of solutions to $(\mathrm{CE}^{\infty,R_j}_{N_{e,R_j}})$ each satisfying* **(L)** *with an accumulation parameter uniformly bounded below by $\mathfrak{m} > 0$. Then, there exists $\overline{u} \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ and $\mu \in \mathbb{R}$ such that along a subsequence*

$$D_\rho \overline{u}_{R_j}(\ell) \to D_\rho \overline{u}(\ell) \quad \forall\, \ell \in \Lambda, \rho \in \Lambda - \ell \quad \text{and} \quad \varepsilon_{\mathrm{F}}^{\infty,R_j}(\overline{u}_{R_j}) \to \mu.$$

Moreover, if $\varepsilon_{\mathrm{F}}^{\infty,R_j}(\overline{u}_{R_j})$ is (eventually) uniformly bounded away from $\sigma(\mathcal{H}^{R_j}(\overline{u}_{R_j}))$, then $\overline{u}$ is a critical point of $\mathcal{G}(\,\cdot\,;\mu)$.

Remark 6.3. *Every strongly stable solution $\overline{u}$ to $(\mathrm{GCE}^{\infty,\infty}_{\mu})$ also solves $(\mathrm{GCE}^{\infty,\infty}_{\nu})$ for all ν in some maximal interval $(\underline{\nu}, \overline{\nu})$, displayed in Figure 6.2. In particular, $\overline{u}$ is a strongly stable solution to $(\mathrm{GCE}^{\infty,\infty}_{\nu})$ with $\nu := \frac{1}{2}(\underline{\nu} + \overline{\nu})$. Theorem 6.9 states that, under some appropriate choice of particle number, there exist solutions $\overline{u}_R$ solving $(\mathrm{CE}^{\infty,R}_{N_{e,R}})$ such that $\overline{u}_R \to \overline{u}$ and $\varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R) \to \nu$ as $R \to \infty$.*

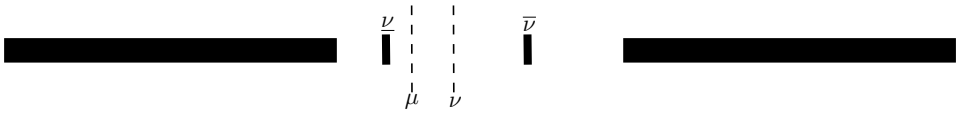


Figure 6.2: Cartoon depicting an approximation of $\sigma(\mathcal{H}(\overline{u}))$ together with the limiting chemical potential, ν, from Theorem 6.9.

We are not implying that any of the problems $(\mathrm{GCE}^{\infty,\infty}_{\nu})$ are equivalent for $\nu \in (\underline{\nu}, \overline{\nu})$, only that they are locally equivalent around the fixed displacement $\overline{u}$.

This is simply because there are no eigenvalues between $\underline{\nu}$ and $\overline{\nu}$, as depicted in Figure 6.2, and we are considering the case of zero Fermi-temperature.

Remark 6.4 (Convergence Rates)**.** *Since we are considering the case where Λ^{ref} is more general than a Bravais lattice $\mathrm{A}\mathbb{Z}^d$, we do not prove any convergence rates for $R \to \infty$. In the case where $\Lambda^{\mathrm{ref}} = \mathsf{A}\mathbb{Z}^d$, strongly stable solutions $\overline{u}$ to $(\mathrm{GCE}_{\mu}^{\infty,\infty})$ satisfy the following far field decay estimate [27]:*

$$\Big(\sum_{\rho \in \Lambda - \ell} e^{-2\Upsilon|\rho|} |D_\rho \overline{u}(\ell)|^2 \Big)^{1/2} \lesssim (1 + |\ell|)^{-d} \quad \text{for all } \ell \in \Lambda. \tag{6.6.4}$$

If the estimate (6.6.4) *holds in the case where $\Lambda^{\mathrm{ref}} \neq \mathsf{A}\mathbb{Z}^d$, we can simply repeat the proofs of Theorem 6.7 and 6.9 verbatim and obtain the following convergence rate:*

$$\|D\overline{u}_R - D\overline{u}\|_{\ell^2_\Upsilon} \lesssim R^{-d/2}.$$

For finite interaction range models and in the case of multilattices, far-field decay estimates of the form (6.6.4) *are satisfied [94]. In light of [27], which extends [48] to infinite interaction range models, it is safe to assume that* (6.6.4) *can be extended to our setting.*

Remark 6.5. *In the weak convergence results (Propositions 6.4, 6.6, 6.8 and 6.10) we assume that the chemical potential (or Fermi level) is uniformly bounded away from the spectrum. By the spectral pollution results (Lemma 6.14, below), this implies that the chemical potential (or the limit of the Fermi level) is not in the limiting spectrum. However, we prefer to make the assumption on the sequence of solutions rather than imposing a condition on the (*a priori *unknown) weak limit.*

6.7 Conclusions

In this chapter, we have formulated the zero Fermi-temperature limit models for geometry relaxation problems in the context of linear tight binding models for point defects and quantified an exponential rate of convergence for the

nuclei positions.

Further, we have extended the results of [26] to the case of zero Fermi-temperature under the assumption that the chemical potential is not an eigenvalue of the Hamiltonian. That is, we have formulated zero Fermi-temperature models in the grand canonical ensemble for the electrons for general point defects. We have shown that, under an assumption on the number of electrons imposed in the sequence of finite domain approximations, this is a limiting model as domain size is sent to infinity in a tight binding model in the canonical ensemble for the electrons and at zero Fermi-temperature. In contrast to the finite Fermi-temperature results of [26], we have shown that a specific choice of electron number in the sequence of finite domain approximations is crucial in identifying the limiting model.

A consequence of these results is that, in general, the zero Fermi-temperature and thermodynamic limits of the geometry optimisation problem do not commute. In particular, taking the thermodynamic limit first, we obtain a limiting model with fixed chemical potential at the reference domain level. On the other hand, if we take the zero Fermi-temperature limit first, the limit model is a grand canonical model but the fixed chemical potential depends on the sequence of solutions to the finite domain problems. The limit of the Fermi levels depends on the polluted band structure and so there is no reason why the limiting Fermi level agrees with the reference Fermi level.

We stress again here that the weak convergence results of Propositions 6.4, 6.6, 6.8, and 6.10 are weaker than the analogous results in the finite Fermi-temperature case [26]. Indeed, by assuming the chemical potential (or sequence of Fermi levels) is bounded away from the spectrum, we are ensuring that the limiting Fermi level is not an eigenvalue of the Hamiltonian, an assumption that we cannot justify in general. We do this to ensure differentiability of the limiting site energies which is required to define the zero Fermi-temperature grand potential difference functional. Exploring the consequences of lifting this technical assumption is beyond the scope of this work.

Thus, we have completed the diagram in Figure 6.1 however, we must

reiterate here that some care is needed in order to interpret this diagram correctly.

6.8 Proofs of the Main Results

It will be convenient to rewrite the site energies as a function of the full interaction stencil, $Du(\ell)$. This can be done since the site energies inherit the translational invariance from the Hamiltonian operators (as in [26, 29]). Therefore, in the following, we shall abuse notation slightly and write

$$\mathcal{G}_\ell^{\beta,R}(Du(\ell);\mu) \coloneqq \mathcal{G}_\ell^{\beta,R}(u;\mu) \tag{6.8.1}$$

for each $\beta \in (0,\infty]$ and $R \in (0,\infty]$. In the case where $R = \infty$, we simply write $\mathcal{G}_\ell^{\beta} \coloneqq \mathcal{G}_\ell^{\beta,\infty}$.

Moreover, we will use the following notation: for $\ell \in \Lambda$, $\boldsymbol{m} = (m_1,\dots,m_j) \in \Lambda^j$ and $\boldsymbol{\rho} = (\rho_1,\dots,\rho_j) \in (\Lambda-\ell)^j$, we write

$$\begin{aligned}\mathcal{H}_{,\boldsymbol{m}}(u) &\coloneqq \frac{\partial^j \mathcal{H}(u)}{\partial u(m_1)\dots\partial u(m_j)}, \quad \text{and}\\ \mathcal{G}_{\ell,\boldsymbol{\rho}}^{\beta,R}(Du(\ell)) &\coloneqq \frac{\partial^j \mathcal{G}_\ell^{\beta,R}(Du(\ell))}{\partial D_{\rho_1}u(\ell)\dots\partial D_{\rho_j}u(\ell)} = \frac{\partial^j \mathcal{G}_\ell^{\beta,R}(u)}{\partial u(\ell+\rho_1)\dots\partial u(\ell+\rho_j)}\end{aligned}$$

and similarly for $\mathcal{H}_{,\boldsymbol{m}}^R(u)$ (with appropriate $\boldsymbol{m}$ and u).

6.8.1 Spectrum of the Hamiltonian

First, we show that the error in the Hamiltonian operators may be bounded above by the errors in the displacements:

Lemma 6.11. *Suppose $u_1, u_2 \colon \Lambda_R \to \mathbb{R}^d$ satisfy* **(L)** *with some $\mathfrak{m} > 0$. Then, for $\ell, k \in \Lambda_R$ with $|D_{k-\ell}(u_1-u_2)(\ell)| \leqslant \mathfrak{m}|\ell-k|$, we have*

$$\left|\left[\mathcal{H}^R(u_1) - \mathcal{H}^R(u_2)\right]_{\ell k}^{ab}\right| \leqslant Ce^{-c\gamma_0 \min_{\alpha\in\mathbb{Z}^d}|\ell-k+\mathsf{M}_R\alpha|}|D_{k-\ell}(u_1-u_2)(\ell)|, \tag{6.8.2}$$

where $c = \frac{\mathfrak{m}\sqrt{3}}{4}$.

Moreover, if $\|D(u_1-u_2)\|_{\ell^2_\Upsilon}$ is sufficiently small, then

$$\begin{aligned}\operatorname{dist}\big(\sigma(\mathcal{H}^R(u_1)),\sigma(\mathcal{H}^R(u_2))\big) &\leqslant \|\mathcal{H}^R(u_1)-\mathcal{H}^R(u_2)\|_{\mathrm{F}}\\ &\leqslant C\|D(u_1-u_2)\|_{\ell^2_\Upsilon}. \end{aligned}\tag{6.8.3}$$

Proof. After extending $\mathcal{H}^R$ by periodicity, we may assume $|\ell-k+\mathsf{M}_R\alpha|\geqslant|\ell-k|$ for all $\alpha\in\mathbb{Z}^d$. Applying Taylor's theorem we can conclude that there exists $\xi^\alpha=(1-\theta)(\boldsymbol{r}_{\ell k}(u_1)+\mathsf{M}_R\alpha)+\theta(\boldsymbol{r}_{\ell k}(u_2)+\mathsf{M}_R\alpha)$ for some $\theta=\theta(\alpha,\ell,k)\in[0,1]$ such that

$$\begin{aligned}\Big|\big[\mathcal{H}^R(u_1)-\mathcal{H}^R(u_2)\big]^{ab}_{\ell k}\Big| &= \Big|\sum_{\alpha\in\mathbb{Z}^d}\nabla h\big((\xi^\alpha,Z_\ell,Z_k)\big)\cdot D_{k-\ell}(u_1-u_2)(\ell)\Big|\\ &\leqslant h_0\sum_{\alpha\in\mathbb{Z}^d}e^{-\gamma_0|\xi^\alpha|}|D_{k-\ell}(u_1-u_2)(\ell)|.\end{aligned}$$

Since $|\boldsymbol{r}_{\ell k}(u_l)+\mathsf{M}_R\alpha|\geqslant\mathfrak{m}|\ell-k|$ for $l=1,2$ and $|D_{k-\ell}(u_1-u_2)(\ell)|\leqslant\mathfrak{m}|\ell-k|$ we can conclude that $|\xi^\alpha|\geqslant\frac{\mathfrak{m}\sqrt{3}}{2}|\ell-k|$ (here, we have used the following: if $x,y\in\mathbb{R}^d$ with $|x|,|y|\geqslant r$ and $|x-y|\leqslant r$, then $|tx+(1-t)y|\geqslant\sqrt{r^2-(\frac{r}{2})^2}=\frac{\sqrt{3}}{2}r$ for all $t\in[0,1]$). Therefore, after summing over $\alpha\in\mathbb{Z}^d$, we obtain (6.8.2).

In the following, we suppose that $\|D(u_1-u_2)\|_{\ell^2_\Upsilon}$ is sufficiently small such that $|D_\rho(u_1-u_2)(\ell)|\leqslant\mathfrak{m}|\rho|$ for all $\ell\in\Lambda$ and $\rho\in\Lambda-\ell$. This can be done as the semi-norm defined by $\sup_{\ell,\rho}|D_\rho v(\ell)|/|\rho|$ is equivalent to $\|D\cdot\|_{\ell^2_\Upsilon}$ [27].

We extend $\mathcal{H}^R$ and u_1,u_2 by periodicity and so, for each $\ell\in\Lambda_R$, we can sum over the set $\Lambda_R(\ell)$ of all $k\in\bigcup_\alpha(\Lambda_R+\mathsf{M}_R\alpha)$ for which $|\ell-k|=\min_\alpha|\ell-k+\mathsf{M}_R\alpha|$:

$$\begin{aligned}\|\mathcal{H}^R(u_1)-\mathcal{H}^R(u_2)\|_{\mathrm{F}}^2 &\leqslant C\sum_{\ell\in\Lambda_R}\sum_{k\in\Lambda_R(\ell)}e^{-2c\gamma_0|\ell-k|}|D_{k-\ell}(u_1-u_2)(\ell)|^2\\ &\leqslant C\sum_{\ell\in\widetilde{\Lambda}_R}\sum_{k\in\widetilde{\Lambda}_R}e^{-2c\gamma_0|\ell-k|}|D_{k-\ell}(u_1-u_2)(\ell)|^2\\ &\leqslant C\|D(u_1-u_2)\|^2_{\ell^2_\Upsilon(\widetilde{\Lambda}_R)}\leqslant C_d\|D(u_1-u_2)\|^2_{\ell^2_\Upsilon(\Lambda_R)}\end{aligned}\tag{6.8.4}$$

where $\widetilde{\Lambda}_R\coloneqq\bigcup_{\ell\in\Lambda_R}\Lambda_R(\ell)$.

The perturbation in the spectrum (6.8.3) follows directly from (6.8.2) since small perturbations in the Frobenius norm give rise to small perturbations in the spectrum [76]. □

We now consider the $R = \infty$ case:

Lemma 6.12. *Suppose $u_1, u_2 \in \mathrm{Adm}(\Lambda)$ satisfying* **(L)** *for both $l = 1, 2$ and some $\mathfrak{m} > 0$. Then, for $\ell, k, m \in \Lambda$, if $|D_{k-\ell}(u_1 - u_2)(\ell)| \leqslant \mathfrak{m}|\ell - k|$, we have*

$$\begin{aligned} \left|[\mathcal{H}(u_1) - \mathcal{H}(u_2)]^{ab}_{\ell k}\right| &\leqslant Ce^{-c\gamma_0|\ell-k|}|D_{k-\ell}(u_1 - u_2)(\ell)|, \quad \textit{and} \\ \left|[\mathcal{H}_{,m}(u_1) - \mathcal{H}_{,m}(u_2)]^{ab}_{\ell k}\right| &\leqslant Ce^{-c\gamma_0(|\ell-m|+|m-k|)}|D_{k-\ell}(u_1 - u_2)(\ell)|. \end{aligned} \tag{6.8.5}$$

where $c = \frac{\mathfrak{m}\sqrt{3}}{2}$.

In particular, if $\|D(u_1 - u_2)\|_{\ell^2_\Upsilon}$ is sufficiently small, we have

$$\begin{aligned} \mathrm{dist}(\sigma(\mathcal{H}(u_1)), \sigma(\mathcal{H}(u_2))) &\leqslant \|\mathcal{H}(u_1) - \mathcal{H}(u_2)\|_{\mathrm{F}} \\ &\leqslant C\|D(u_1 - u_2)\|_{\ell^2_\Upsilon}. \end{aligned} \tag{6.8.6}$$

Proof. Using the same idea as in Lemma 6.11, we have

$$\begin{aligned} \left|[\mathcal{H}(u_1) - \mathcal{H}(u_2)]^{ab}_{\ell k}\right| &\leqslant h_0 e^{-\gamma_0|\xi_0|}|D_{k-\ell}(u_1 - u_2)(\ell)| \quad \text{and} \\ \left|[\mathcal{H}_{,m}(u_1) - \mathcal{H}_{,m}(u_2)]^{ab}_{\ell k}\right| &\leqslant h_0 e^{-\gamma_0|\xi_1|}|D_{k-\ell}(u_1 - u_2)(\ell)| \end{aligned}$$

where $\xi_j = (1 - \theta_j)\boldsymbol{r}_{\ell k}(u_1) + \theta_j \boldsymbol{r}_{\ell k}(u_2)$ for some $\theta_j = \theta_j(a, b, \ell, k) \in [0, 1]$ and both $j = 1, 2$. Now, since $r_{\ell k}(u_l) \geqslant \mathfrak{m}|\ell - k|$ for both $l = 1, 2$ and $|D_{k-\ell}(u_1 - u_2)(\ell)| \leqslant \mathfrak{m}|\ell - k|$, we necessarily have that $|\xi_l| \geqslant \frac{\sqrt{3}}{2}\mathfrak{m}|\ell - k|$. Therefore, we obtain (6.8.5) and thus (6.8.6) as in the proof of Lemma 6.11. □

In particular, we have shown Lemma 6.1 holds and we also immediately obtain the decomposition from Proposition 2.3:

$$\widetilde{\mathcal{H}}(u) = \widetilde{\mathcal{H}}^{\mathrm{ref}} + P_{\mathrm{FR}}(u) + P_\varepsilon(u) \tag{6.8.7}$$

where $\|P_\varepsilon(u)\|_{\mathrm{F}} \leqslant \varepsilon$ and $P_{\mathrm{FR}}(u)_{\ell k} = 0$ for all $(\ell, k) \notin B_{R_\varepsilon} \times B_{R_\varepsilon}$. Here, in an

argument identical to (2.5.6), we have shifted the spectra away from zero and added artificial zero rows and columns to the Hamiltonian operators to ensure $\widetilde{\mathcal{H}}(u)$ and $\widetilde{\mathcal{H}}^{\mathrm{ref}}$ are defined on the same spatial domains.

We now discuss the corresponding $R < \infty$ case which allows us to describe $\sigma(\mathcal{H}^R(u_R))$ and the limiting spectrum as $R \to \infty$ (in Lemma 6.14, below):

Lemma 6.13 (Decomposition of the Hamiltonian, $R < \infty$)**.** *For each R, suppose that $u_R \colon \Lambda_R \to \mathbb{R}^d$ satisfies* **(L)** *with some constant uniformly bounded below by $\mathfrak{m} > 0$ and $\sup_R \|Du_R\|_{\ell^2_\Upsilon} < \infty$. Then, for $\varepsilon > 0$,*

- *There exists an R independent constant, $R_\varepsilon > 0$, a constant $R_\infty = R_\infty(R)$ with $R_\infty(R) \to \infty$ as $R \to \infty$ and operators $P^R_\varepsilon, P^R_{\mathrm{loc}}, P^R_\infty$ such that*

$$\widetilde{\mathcal{H}}^R(u_R) = \widetilde{\mathcal{H}}^{\mathrm{ref},R} + P^R_\varepsilon + P^R_{\mathrm{loc}} + P^R_\infty \tag{6.8.8}$$

  where $\|P^R_\varepsilon\|_{\mathrm{F}} \leqslant \varepsilon$ and $P^R_{\mathrm{loc}}, P^R_\infty$ are finite rank operators with rank independent of R, and matrix entries non-zero only on $B_{R_\varepsilon} \times B_{R_\varepsilon}$ and $(\Lambda_R \setminus B_{R_\infty}) \times (\Lambda_R \setminus B_{R_\infty})$, respectively,

- *Moreover, if $u_R \rightharpoonup u$, then $P^R_{\mathrm{loc}} \to P^\infty_{\mathrm{loc}}$ where $[P^\infty_{\mathrm{loc}}]^{ab}_{\ell k} \coloneqq [\widetilde{\mathcal{H}}(u) - \widetilde{\mathcal{H}}^{\mathrm{ref}}]^{ab}_{\ell k}$ as $R \to \infty$ for all $\ell, k \in B_{R_\varepsilon}$,*

- *In particular,*

$$\sup_R \#\Big(\sigma(\mathcal{H}^R(u_R)) \setminus B_\varepsilon(\sigma(\mathcal{H}^{\mathrm{ref}}))\Big) < \infty. \tag{6.8.9}$$

Proof. The construction of (6.8.8) is similar to that of Proposition 2.3. For a complete proof, see [96, Appendix F].

(6.8.9) follows in the same way as in the proof of Proposition 2.3 after noting that $\sigma(\mathcal{H}^{\mathrm{ref},R}) \subseteq \sigma(\mathcal{H}^{\mathrm{ref}})$. The latter statement can be shown by writing $\sigma(\mathcal{H}^{\mathrm{ref}})$ as the union of energy bands defined on the Brillouin zone and noting that $\sigma(\mathcal{H}^{\mathrm{ref},R})$ can then be written as a union of these energy bands over a discretised Brillouin zone (see [96, Appendix E] for the details). □

Resolvent Calculus

For fixed $u \in \mathrm{Adm}(\Lambda)$, we suppose that $\mathscr{C}^-$ and $\mathscr{C}^+$ are simple closed contours encircling $\sigma(\mathcal{H}(u)) \cap (-\infty, \mu)$ and $\sigma(\mathcal{H}(u)) \cap (\mu, \infty)$, respectively, and avoiding the line $\mu + i\mathbb{R}$, see Figure 6.3. Further, we may suppose that for all $z \in \mathscr{C}^- \cup \mathscr{C}^+$, we have

$$\begin{aligned} \operatorname{dist}(z, \sigma(\mathcal{H}(u))) &\geqslant \frac{1}{2}\mathsf{d}(u) \quad \text{and} \\ |\operatorname{Re}(z) - \mu| &\geqslant \frac{1}{2}\mathsf{d}(u), \end{aligned} \tag{6.8.10}$$

where $\mathsf{d}(u) \coloneqq \operatorname{dist}(\mu, \sigma(\mathcal{H}(u)))$ and $\mathsf{d}^{\mathrm{ref}} \coloneqq \operatorname{dist}(\mu, \sigma(\mathcal{H}^{\mathrm{ref}}))$.

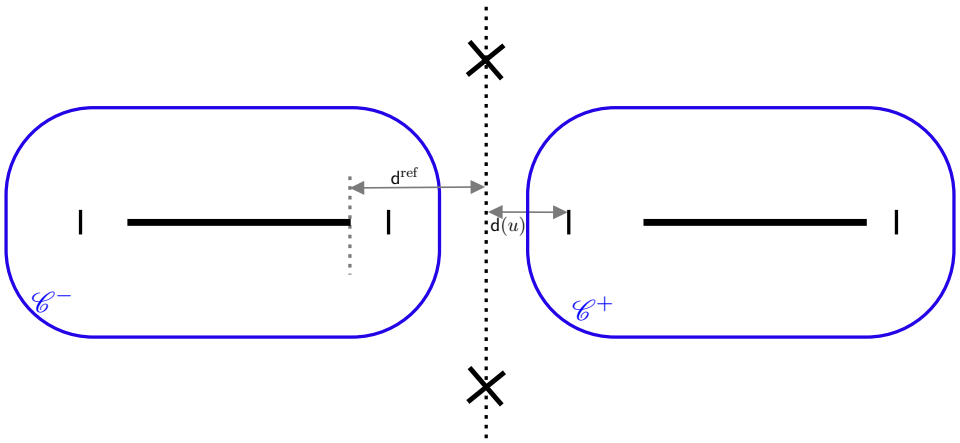


Figure 6.3: Cartoon depicting an approximation of $\sigma(\mathcal{H}(u))$ for $u \in \mathrm{Adm}(\Lambda)$ (on the real axis) and the contours $\mathscr{C}^-$ and $\mathscr{C}^+$. The positive constants $\mathsf{d}(u)$ and $\mathsf{d}^{\mathrm{ref}}$ are also displayed.

Therefore, $\mathscr{C}^- \cup \mathscr{C}^+$ is an admissible system of contours to define $\mathcal{G}_\ell^\beta$ as in (2.4.1): for $\beta \in (0, \infty]$,

$$\mathcal{G}_\ell^\beta(Du(\ell)) = \operatorname{tr}\left[\oint_{\mathscr{C}^- \cup \mathscr{C}^+} G^\beta(z;\mu)\big(z - \mathcal{H}(u)\big)^{-1} \frac{\mathrm{d}z}{2\pi i}\right]_{\ell\ell} \tag{6.8.11}$$

We shall often simplify notation and write $\mathcal{G}_\ell \coloneqq \mathcal{G}_\ell^\infty$. We may define $G_\ell^{\beta,R}$ similarly.

From now on, we denote the resolvent operators by $\mathscr{R}_z(u) \coloneqq (\mathcal{H}(u) - z)^{-1}$ and $\mathscr{R}_z^R(u) \coloneqq (\mathcal{H}^R(u) - z)^{-1}$.

Remark 6.6. *We briefly note here that the Combes–Thomas resolvent estimate*

(Lemma 3.3) applies in the periodic setting by replacing $r_{\ell k}(u)$ with the torus distance $r^{\#}_{\ell k}(u)$. The proof of this result follows in the exact same way as in the corresponding $R = \infty$ result.

Spectral Pollution

It is well known (see [35, 84] and references therein) that, in general, when approximating the spectrum of an operator with a sequence of finite dimensional spaces, spurious eigenvalues may be present in the limit. That is, accumulation points of eigenvalues along the sequence are not necessarily contained in the spectrum of the limit operator. In this section, we discuss the extent to which spectral pollution occurs when approximating $\sigma(\mathcal{H}(u))$ with $\sigma(\mathcal{H}^R(u_R))$.

More specifically, we are able to show that, if $u_R \to u$ strongly, then spectral pollution does not occur and, in the case that $u_R \rightharpoonup u$, we show that the spectral pollution is very mild. That is, we may use Lemma 6.13 to conclude that there are at most finitely many additional eigenstates in the band gap which arise due to finitely many $O(1)$ distortions of the lattice. These distortions are sent to infinity as $R \to \infty$ and so the additional eigenstates are not present in the limit.

We remark here that the use of periodic boundary conditions prevents spectral pollution that is known to occur in the case of clamped boundary conditions, for example. See [22] for a proof in the case of local defects in a crystalline material in a PDE setting.

Lemma 6.14. *Suppose $u_R \colon \Lambda_R \to \mathbb{R}^d$ is a bounded sequence satisfying* **(L)** *with some uniform constant $\mathfrak{m} > 0$ and $u_R \rightharpoonup u$ for some $u \in \dot{\mathscr{W}}^{1,2}(\Lambda)$. Let $P^R_\infty(u_R)$ be the finite rank operator from Lemma 6.13 with the constant $\varepsilon > 0$. Then,*

(i) $\sigma(\mathcal{H}(u)) \subseteq \liminf_{R\to\infty} \sigma\big(\mathcal{H}^R(u_R) - P^R_\infty(u_R)\big)$,

(ii) $\sigma(\mathcal{H}(u)) \subseteq \liminf_{R\to\infty} \sigma\big(\mathcal{H}^R(u_R)\big)$,

(iii) $\sigma(\mathcal{H}(u)) \supseteq \limsup_{R\to\infty} \big[\sigma\big(\mathcal{H}^R(u_R) - P^R_\infty(u_R)\big) \setminus B_{2\varepsilon}(\sigma(\mathcal{H}^{\mathrm{ref}}))\big]$,

(iv) If $u_R \to u$ strongly, then $\sigma(\mathcal{H}(u)) = \lim_{R\to\infty} \sigma(\mathcal{H}^R(u_R))$.

Remark 6.7. *Following the proof of Lemma 6.14, one can easily see that if* $u_\beta, u \in \dot{\mathscr{W}}^{1,2}(\Lambda)$*, satisfying* **(L)** *with a uniform constant* $\mathfrak{m}$*, and* $u_\beta \rightharpoonup u$ *as* $\beta \to \infty$*, then* $\sigma(\mathcal{H}(u)) \subseteq \liminf_{\beta\to\infty} \sigma(\mathcal{H}(u_\beta))$.

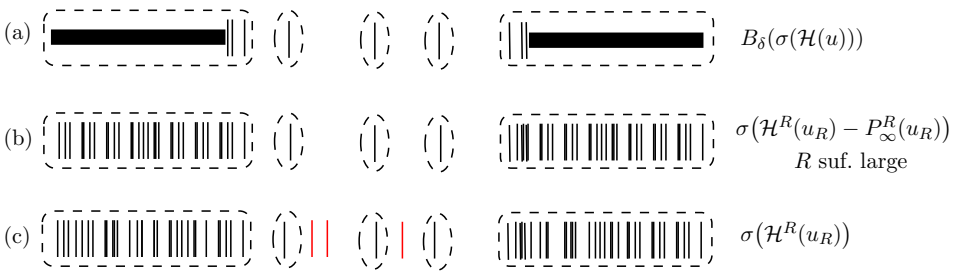


Figure 6.4: Cartoon illustrating Lemma 6.14. (a) is qualitatively similar to $\sigma(\mathcal{H}(u))$ for $u \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ as asserted in Lemma 6.1. (b) illustrates Lemma 6.14 *(i)* and *(iii)*: eigenvalues of $\mathcal{H}(u)$ lying in the band gap can be approximated by eigenvalues of $\mathcal{H}^R(u_R) - P^R_\infty(u_R)$ and every accumulation point of $\sigma\big(\mathcal{H}^R(u_R) - P^R_\infty(u_R)\big)$ is contained in $\sigma(\mathcal{H}(u))$. (c) illustrates Lemma 6.14 *(ii)* where the finitely many eigenvalues outside $B_\delta(\sigma(\mathcal{H}(u)))$ are the "defect states" that arise when including the far-field contribution $P^R_\infty(u_R)$. These defect states vanish in the weak limit.

Proof. The first part of this proof loosely follows the first part of [22, Proof of Thm. 3.1].

(i). Take $\lambda \in \sigma(\mathcal{H}(u))$. For every $\tau > 0$, we may choose ψ of compact support such that $\|\psi\|_{\ell^2} = 1$, $\operatorname{supp}(\psi) \subseteq B_{R_0}$ for some $R_0 > 0$, and

$$\|(\mathcal{H}(u) - \lambda)\psi\|_{\ell^2} \leqslant \tau.$$

For $R \geqslant R_0$, we let $\psi_R \coloneqq \psi|_{\Lambda_R}$ and calculate: for $\ell \in \Lambda_R$,

$$\begin{aligned}\big[\big(\mathcal{H}^R(u_R) - P^R_\infty(u_R)\big)\psi_R\big]_\ell = [\mathcal{H}(u)\psi]_\ell &- \sum_{k\in\Lambda_R\cap B_{R_0}} P^R_\infty(u_R)_{\ell k}[\psi_R]_k \\ &+ \sum_{k\in\Lambda_R\cap B_{R_0}} (\mathcal{H}(u_R)_{\ell k} - \mathcal{H}(u)_{\ell k})\psi_k \\ &+ \sum_{k\in\Lambda_R\cap B_{R_0}} \sum_{\substack{\alpha\in\mathbb{Z}^d\\ \alpha\neq 0}} \mathcal{H}(u_R)_{\ell,k+\mathsf{M}_R\alpha}[\psi_R]_k. \quad (6.8.12)\end{aligned}$$

Therefore, after choosing R sufficiently large such that $P^R_\infty(u_R)_{\ell k} = 0$ for all $k \in \Lambda_R \cap B_{R_0}$, squaring, summing over $\ell \in \Lambda_R$ and applying Lemma 6.12, we

have: for sufficiently large R,

$$\begin{aligned}
&\big\|\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - \lambda\big)\psi_R\big\|_{\ell^2(\Lambda_R)} \\
&\quad\leqslant \big\|\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R)\big)\psi_R - \mathcal{H}(u)\psi\big\|_{\ell^2(\Lambda_R)} + \|(\mathcal{H}(u) - \lambda)\psi\|_{\ell^2(\Lambda_R)} \\
&\quad\leqslant C\|D(u_R - u)\|_{\ell^2_\Upsilon(\Lambda_R \cap B_{2R_0})} + Ce^{-\gamma_0 \mathfrak{m} R_0} + Ce^{-\frac{1}{2}\gamma_0 \mathfrak{m}(R - R_0)} + \tau.
\end{aligned} \tag{6.8.13}$$

Here, we have used the fact that for $\ell \in \Lambda_R$ and $k \in B_{R_0}$, we have $|\ell - k + \mathsf{M}_R\alpha| \geqslant R - R_0$ for all $\alpha \in \mathbb{Z}^d \setminus \{0\}$.

Therefore, by choosing R_0 and then R sufficiently large, we have either $\lambda \in \sigma\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R)\big)$ or

$$\begin{aligned}
1 &= \|\psi_R\|_{\ell^2(\Lambda_R)} \\
&\leqslant \|(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - \lambda)^{-1}\|_{\ell^2 \to \ell^2} \|(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - \lambda)\psi_R\|_{\ell^2(\Lambda_R)} \\
&\leqslant \|(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - \lambda)^{-1}\|_{\ell^2 \to \ell^2} \cdot 2\tau.
\end{aligned}$$

That is, if $\lambda \notin \sigma\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R)\big)$, then $(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - \lambda)^{-1}$ defines a bounded linear operator and so

$$\operatorname{dist}\big(\lambda, \sigma\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R)\big)\big) = \frac{1}{\|(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - \lambda)^{-1}\|_{\ell^2 \to \ell^2}} \leqslant 2\tau.$$

Here, we have used the fact that, for a bounded normal operator, the operator norm equals the spectral radius.

(ii). The exact same arguments may be made for the operator $\mathcal{H}^R(u_R)$. In this case, the second term in (6.8.12) is omitted and $\|(\mathcal{H}^R(u_R) - \lambda)\psi_R\|_{\ell^2} \leqslant 2\tau$ for all R sufficiently large as in the proof of *(i)*.

(iii). We suppose that $\lambda \in \limsup_{R\to\infty} \sigma\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R)\big)$ with $\lambda \notin B_{2\varepsilon}(\sigma(\mathcal{H}^{\mathrm{ref}}))$. By Lemma 6.13, there exists $S_\varepsilon > 0$ such that

$$\sigma\big(\mathcal{H}^{\mathrm{ref},R} + P_\varepsilon^R(u_R)\big) \cap B_\varepsilon(\lambda) = \emptyset \tag{6.8.14}$$

$$\#\big(\sigma\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R)\big) \cap B_\varepsilon(\lambda)\big) \leqslant S_\varepsilon \quad \forall\, R \tag{6.8.15}$$

where $P_\varepsilon^R(u_R)$ is the perturbation arising in Lemma 6.13 with $\|P_\varepsilon^R(u_R)\|_{\mathrm{F}} \leqslant \varepsilon$.

By (6.8.14) and (6.8.15), we may let $\mathscr{C} = \partial B_\varepsilon(\lambda)$ be the positively oriented circle of radius ε centred at λ, and obtain

$$\begin{aligned}
&\sum_j \lambda_R^{(j)} \psi_R^{(j)} \otimes \psi_R^{(j)} \\
&= -\oint_{\mathscr{C}} (\mathcal{H}^R(u_R) - P_\infty^R(u_R) - z)^{-1} \frac{\mathrm{d}z}{2\pi i} \\
&= -\oint_{\mathscr{C}} \Big[(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - z)^{-1} - (\mathcal{H}^{\mathrm{ref},R} + P_\varepsilon^R(u_R) - z)^{-1} \Big] \frac{\mathrm{d}z}{2\pi i}
\end{aligned} \tag{6.8.16}$$

where $\operatorname{span}\{\psi_R^{(j)}\}_j$ is the eigenspace corresponding to the eigenvalues $\lambda_R^{(j)} \in \sigma\big(\mathcal{H}^R(u_R) - P_\infty^R(u_R)\big)$ with $\lambda_R^{(j)} \in B_\varepsilon(\lambda)$ and $\|\psi_R^{(j)}\|_{\ell^2} = 1$. By Lemma 6.13, for sufficiently large R, we have

$$\begin{aligned}
&\Big| \Big[(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - z)^{-1} - (\mathcal{H}^{\mathrm{ref},R} + P_\varepsilon^R(u_R) - z)^{-1} \Big]_{\ell k} \Big| \\
&\quad = \Big| \Big[(\mathcal{H}^R(u_R) - P_\infty^R(u_R) - z)^{-1} P_{\mathrm{loc}}^R(u_R) (\mathcal{H}^{\mathrm{ref},R} + P_\varepsilon^R(u_R) - z)^{-1} \Big]_{\ell k} \Big| \\
&\quad \leqslant C \sum_{\ell_1, \ell_2 \in \Lambda_R \cap B_{R_\varepsilon}} e^{-\gamma_{\mathrm{CT}}(r_{\ell\ell_1}^{\#} + r_{\ell_2 k}^{\#})} \leqslant C e^{-\gamma_{\mathrm{CT}}(|\ell| + |k|)}.
\end{aligned} \tag{6.8.17}$$

Equation (6.8.17) is analogous to the $R = \infty$ result shown in [98, Eq. (4.19)]. Therefore, by applying (6.8.16), we have

$$|\psi_R^{(j)}(\ell)| \leqslant C e^{-\gamma_{\mathrm{CT}}|\ell|} \quad \text{for all } \ell \in \Lambda_R. \tag{6.8.18}$$

Now, after defining $\widetilde{\psi}_R^{(j)}$ to be equal to $\psi_R^{(j)}$ on Λ_R and extending by zero to Λ, we have: for sufficiently large R,

$$\begin{aligned}
&\|(\mathcal{H}(u) - \lambda_R^{(j)}) \widetilde{\psi}_R^{(j)}\|_{\ell^2} \\
&\qquad \leqslant C \|D(u_R - u)\|_{\ell^2_\Upsilon(\Lambda \cap B_{R_0})} + C\big(e^{-\eta_1 R_0} + e^{-\eta_2(R - R_0)} + e^{-\eta_3 R_\infty}\big)
\end{aligned}$$

where $\eta_j > 0$ for each $j \in \{1, 2, 3\}$ and R_∞ is the constant from Lemma 6.13 (that is, $P_\infty^R(u_R)$ zero on $(\Lambda_R \setminus B_{R_\infty})^2$ with $R_\infty \to \infty$ as $R \to \infty$). This

calculation is analogous to (6.8.13) where, instead of exploiting the fact the (approximate) eigenvectors are of compact support, we now use the exponential decay of the eigenvectors (6.8.18).

For a strictly increasing sequence $(R_n)_n \subseteq \mathbb{N}$ and sequence of indices $(j_n)_n$, we define the subsequence $(\lambda_n, \psi_n) \coloneqq (\lambda_{R_n}^{(j_n)}, \widetilde{\psi}_{R_n}^{(j_n)})$. We can conclude that if $\lambda_n \to \lambda$ as $n \to \infty$, we have

$$\big\|(\mathcal{H}(u) - \lambda)\psi_n\big\|_{\ell^2} \leqslant \big\|(\mathcal{H}(u) - \lambda_n)\psi_n\big\|_{\ell^2} + |\lambda - \lambda_n| \to 0 \quad \text{as } n \to \infty.$$

Therefore, by applying Weyl's criterion [71, Ch. 7], we can conclude that $\lambda \in \sigma(\mathcal{H}(u))$.

(iv). In the case that $u_R \to u$ strongly as $R \to \infty$, we have: for all $\varepsilon > 0$, there exists $R_\varepsilon > 0$ such that $\|Du_R\|_{\ell^2_\Upsilon(\Lambda_R \setminus B_{R_\varepsilon})} \leqslant \varepsilon$ for all R sufficiently large. Following the proof of Lemma 6.13, we can conclude that $P_\infty^R(u_R) = 0$. □

Limits of the Site Energies

We now state that $G^\beta(\,\cdot\,;\mu)$ converges exponentially as $\beta \to \infty$ which is used in the convergence of the site energies in the zero temperature limit.

Lemma 6.15. *Fix $z \in \mathbb{C}$ such that $\mathsf{d} \coloneqq \frac{1}{2}|\mathrm{Re}(z) - \mu| > 0$. Then, for all $\beta_0 > 0$, there exists a positive constant $C_{\beta_0 \mathsf{d}}$ such that*

$$|G^\beta(z;\mu) - G^\infty(z;\mu)| \leqslant C_{\beta_0 \mathsf{d}} \beta^{-1} e^{-\frac{1}{3}\beta|\,\mathrm{Re}(z) - \mu|} \quad \forall\, \beta > \beta_0.$$

Proof. A proof of this fact is elementary and can be found in [96, Appendix G]. □

We now apply Lemma 6.15 together with the Combes–Thomas estimate (Lemma 3.3) to show that the site energies and their derivatives converge in the zero temperature limit:

Lemma 6.16 (Zero Temperature Limit of the Site Energies)**.** *Let $u \in \mathrm{Adm}(\Lambda)$. Then, for each $\beta_0 > 0$, $0 \leqslant j \leqslant \nu$, $\ell \in \Lambda$, $\boldsymbol{m} = (m_1, \ldots, m_j) \in \Lambda^j$ and*

$1 \leqslant i_1, \dots, i_j \leqslant d$, *there exists a constant* C *depending on* $\beta_0, N_{\mathrm{b}}, \mathsf{d}(u), d$ *such that, for all* $\beta > \beta_0$, *we have*

$$\left| \frac{\partial^j \mathcal{G}_\ell^\beta(Du(\ell))}{\partial[u(m_1)]_{i_1} \dots \partial[u(m_j)]_{i_j}} - \frac{\partial^j \mathcal{G}_\ell(Du(\ell))}{\partial[u(m_1)]_{i_1} \dots \partial[u(m_j)]_{i_j}} \right| \leqslant C\beta^{-1} e^{-\frac{1}{6}\mathsf{d}(u)\beta} e^{-\gamma_{\mathrm{CT}} \sum_{l=1}^j r_{\ell m_l}}.$$

Proof. The proof follows from the resolvent estimates of Lemma 3.3 and the convergence of the integrand G^β shown in Lemma 6.15. □

The corresponding $R \to \infty$ result is as follows:

Lemma 6.17 (Thermodynamic Limit of the Site Energies)**.** *Let* $u \in \mathrm{Adm}(\Lambda)$ *be of compact support and fix* $\beta \in (0, \infty]$. *Then, for sufficiently large* R *and each* $0 \leqslant j \leqslant \nu$, $\ell \in \Lambda_R$, $\boldsymbol{m} = (m_1, \dots, m_j) \in \Lambda_R^j$ *and* $1 \leqslant i_1, \dots, i_j \leqslant d$, *we have*

$$\left| \frac{\partial^j \mathcal{G}_\ell^{\beta,R}(u)}{\partial[u(m_1)]_{i_1} \dots \partial[u(m_j)]_{i_j}} - \frac{\partial^j \mathcal{G}_\ell^\beta(u)}{\partial[u(m_1)]_{i_1} \dots \partial[u(m_j)]_{i_j}} \right| \leqslant C e^{-\eta\left(\mathrm{dist}(\ell, \mathbb{R}^d \setminus \Omega_R) + \sum_{l=1}^j r_{\ell m_l}^{\#}(u)\right)}$$

where $\eta := \frac{1}{2}\mathfrak{m} \min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\}$.

Proof. Similar to the calculations in the proof of Lemma 6.16, we write the site energies using resolvent calculus. Using the fact $G^\beta(z;\mu)$ is uniformly bounded along the contour $\mathscr{C}^- \cup \mathscr{C}^+$, it is sufficient to prove that the derivatives of the resolvent operators converge in the thermodynamic limit. A full proof is given in [96, Appendix H]. □

6.8.2 Zero Temperature Limit

We are now in a position to prove the first main convergence results:

Proof of Theorem 6.3: $\beta \to \infty$ **in the Grand Canonical Ensemble**

We may choose $r > 0$ such that $B_r(\overline{u}; \|D \cdot\|_{\ell^2_\Upsilon}) \subseteq \mathrm{Adm}(\Lambda)$. Now, since $\mathcal{G}^\beta \in C^3(B_r(\overline{u}; \|D \cdot\|_{\ell^2_\Upsilon}))$, we know that $\delta^2 \mathcal{G}^\beta$ is Lipschitz in a neighbourhood

of $\overline{u}$.

For the remainder of the proof, we fix $\beta_0 > 0$. By Lemma 6.16, for all $v, w \in \dot{\mathscr{W}}^{1,2}(\Lambda)$, we have,

$$\begin{aligned}
&\left\langle \left(\delta^2\mathcal{G}^\beta(\overline{u}) - \delta^2\mathcal{G}(\overline{u})\right)v, w\right\rangle \\
&\quad = \sum_{\ell\in\Lambda}\sum_{\rho_1,\rho_2\in\Lambda-\ell} D_{\rho_1}v(\ell)^T\left(\mathcal{G}^\beta_{\ell,\rho_1\rho_2}(D\overline{u}(\ell)) - \mathcal{G}_{\ell,\rho_1\rho_2}(D\overline{u}(\ell))\right)D_{\rho_2}w(\ell) \\
&\quad \leqslant CC_{\beta_0\mathsf{d}}\beta^{-1}e^{-\frac{1}{6}\beta\mathsf{d}(\overline{u})}\cdot C_2\sum_{\ell\in\Lambda}\sum_{\rho_1,\rho_2\in\Lambda-\ell} e^{-\gamma_{\mathrm{CT}}(|\rho_1|+|\rho_2|)}|D_{\rho_1}v(\ell)||D_{\rho_2}w(\ell)| \\
&\quad \leqslant C\beta^{-1}e^{-\frac{1}{6}\beta\mathsf{d}(\overline{u})}\|Dv\|_{\ell^2_\Upsilon}\|Dw\|_{\ell^2_\Upsilon}
\end{aligned} \tag{6.8.19}$$

for all $\beta > \beta_0$. The constant C in the final line depends on $\mathsf{d} \coloneqq \mathsf{d}(\overline{u})$. By the assumed strong stability (6.5.3) and (6.8.19), we immediately obtain the following stability estimate,

$$\begin{aligned}
\left\langle \delta^2\mathcal{G}^\beta(\overline{u})v, v\right\rangle &= \left\langle \delta^2\mathcal{G}(\overline{u})v, v\right\rangle + \left\langle \left(\delta^2\mathcal{G}^\beta(\overline{u}) - \delta^2\mathcal{G}(\overline{u})\right)v, v\right\rangle \\
&\geqslant \left(c_0 - C\beta^{-1}e^{-\frac{1}{6}\beta\mathsf{d}(\overline{u})}\right)\|Dv\|^2_{\ell^2_\Upsilon}.
\end{aligned} \tag{6.8.20}$$

We now move on to consider consistency. It will be useful to consider the following truncation operator to split a given displacement into core and far field contributions [47, Lemma 7.3]:

Lemma 6.18 (Truncation Operator)**.** *For $R > 0$, there exist truncation operators $T_R\colon \left(\mathbb{R}^d\right)^\Lambda \to \dot{\mathscr{W}}^c(\Lambda)$ such that T_Ru has compact support in B_R and, for all R sufficiently large, $DT_Ru(\ell) = Du(\ell)$ for all $\ell \in \Lambda \cap B_{R/2}$ and*

$$\begin{aligned}
\|DT_Ru - Du\|_{\ell^2_\Upsilon} &\leqslant C\|Du\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R/2})}, \quad \textit{and} \\
\|DT_Ru\|_{\ell^2_\Upsilon} &\leqslant C\|Du\|_{\ell^2_\Upsilon(\Lambda\cap B_R)},
\end{aligned}$$

where C is independent of R and u.

We use the notation of Lemma 6.18 and let $v^{\mathrm{co}} \coloneqq T_Rv$ and $v^{\mathrm{ff}} = v - v^{\mathrm{co}}$ for some $R > 0$ to be chosen later. In the following, we use the fact that $\delta\mathcal{G}(\overline{u}) = 0$

and estimate each of the terms in the following expression:

$$\left\langle \delta\mathcal{G}^{\beta}(\overline{u}), v \right\rangle = \left\langle \delta\mathcal{G}^{\beta}(\overline{u}) - \delta\mathcal{G}(\overline{u}), v^{\mathrm{co}} \right\rangle + \left\langle \delta\mathcal{G}^{\beta}(\overline{u}) - \delta\mathcal{G}(\overline{u}), v^{\mathrm{ff}} \right\rangle \tag{6.8.21}$$

Core. Since the core region is finite, the first term of (6.8.21) is straightforward to deal with. Here, we simply apply the convergence of the site energies directly to obtain

$$\begin{aligned} &\left| \left\langle \delta\mathcal{G}^{\beta}(\overline{u}) - \delta\mathcal{G}(\overline{u}), v^{\mathrm{co}} \right\rangle \right| \\ &\qquad \leqslant \sum_{\substack{\ell\in\Lambda,\rho\in\Lambda-\ell:\\ |\ell|\leqslant R \text{ or } |\ell+\rho|\leqslant R}} \left| \left(\mathcal{G}^{\beta}_{\ell,\rho}(D\overline{u}(\ell)) - \mathcal{G}_{\ell,\rho}(D\overline{u}(\ell))\right) \cdot D_{\rho} v^{\mathrm{co}}(\ell) \right| \\ &\qquad \leqslant C\beta^{-1} e^{-\frac{1}{6}\mathsf{d}(\overline{u})\beta} \sum_{\substack{\ell\in\Lambda,\rho\in\Lambda-\ell:\\ |\ell|\leqslant R \text{ or } |\ell+\rho|\leqslant R}} e^{-\gamma_{\mathrm{CT}}|\rho|} \left| D_{\rho} v^{\mathrm{co}}(\ell) \right|. \end{aligned} \tag{6.8.22}$$

Now we may use the fact that v^{co} has compact support inside B_R, to conclude:

$$\begin{aligned} \sum_{\substack{\ell\in\Lambda\\ |\ell|\geqslant R}} \sum_{\substack{\rho\in\Lambda-\ell\\ |\ell+\rho|\leqslant R}} e^{-\eta|\rho|} \left| D_{\rho} v^{\mathrm{co}}(\ell) \right| &\leqslant CR^{d/2} \Bigg(\sum_{|\ell|\geqslant R} e^{-\eta(|\ell|-R)} \Bigg)^{1/2} \|Dv^{\mathrm{co}}\|_{\ell^2_{\Upsilon}} \\ &\leqslant CR^{d/2} R^{(d-1)/2} \|Dv^{\mathrm{co}}\|_{\ell^2_{\Upsilon}}. \end{aligned} \tag{6.8.23}$$

In the exact same way,

$$\sum_{\substack{\ell\in\Lambda\\ |\ell|< R}} \sum_{\rho\in\Lambda-\ell} e^{-\eta|\rho|} \left| D_{\rho} v^{\mathrm{co}}(\ell) \right| \leqslant CR^{d/2} R^{(d-1)/2} \|Dv^{\mathrm{co}}\|_{\ell^2_{\Upsilon}}. \tag{6.8.24}$$

Combining (6.8.22), (6.8.23), (6.8.24) and Lemma 6.18 we have

$$\left| \left\langle \delta\mathcal{G}^{\beta}(\overline{u}) - \delta\mathcal{G}(\overline{u}), v^{\mathrm{co}} \right\rangle \right| \leqslant C\beta^{-1} e^{-\frac{1}{6}\mathsf{d}(\overline{u})\beta} R^{d/2} R^{(d-1)/2} \|Dv\|_{\ell^2_{\Upsilon}(\Lambda\cap B_R)}. \tag{6.8.25}$$

Far-field. We now turn our attention to the far field contribution in (6.8.21). We will replace $\overline{u}$ with some compactly supported approximation $\widetilde{u}$ and show that the error in this approximation can be bounded appropriately. We then use the fact that $\widetilde{u}$ has compact support to bound the far field contribution to

(6.8.21).

We define $\widetilde{u} \coloneqq T_{\widetilde{R}}\overline{u}$ for some $0 < \widetilde{R} < R$ to be chosen later and note that, by Lemma 6.18, we have $\|D\widetilde{u} - D\overline{u}\|_{\ell^2_\Upsilon} \leqslant C\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{\widetilde{R}/2})}$. Therefore, by Lemma 6.12, for $\widetilde{R}$ sufficiently large, we have

$$\operatorname{dist}(\mu, \sigma(\mathcal{H}(u))) \geqslant \frac{1}{4}\mathsf{d}(\overline{u}) \tag{6.8.26}$$

for all $u \coloneqq t\overline{u} + (1-t)\widetilde{u}$ and $t \in [0,1]$. The inequality in (6.8.26) implies that, for every displacement along the linear path between $\overline{u}$ and $\widetilde{u}$, we have uniform convergence rates in the site energies as $\beta \to \infty$ (as in Lemma 6.16). Since we have perturbed the displacement, the exponent in the convergence estimates are reduced (in this case by a factor of 2, but this factor is arbitrary).

We will now estimate the error committed by replacing $\overline{u}$ with the compactly supported displacement $\widetilde{u}$. By (6.8.19) and (6.8.26), we have

$$\begin{aligned}
&\Big\langle \delta\mathcal{G}^\beta(\overline{u}) - \delta\mathcal{G}(\overline{u}), v^{\mathrm{ff}} \Big\rangle - \Big\langle \delta\mathcal{G}^\beta(\widetilde{u}) - \delta\mathcal{G}(\widetilde{u}), v^{\mathrm{ff}} \Big\rangle \\
&\quad = \int_0^1 \Big\langle \Big(\delta^2\mathcal{G}^\beta(t\overline{u} + (1-t)\widetilde{u}) - \delta^2\mathcal{G}(t\overline{u} + (1-t)\widetilde{u}) \Big)(\overline{u} - \widetilde{u}), v^{\mathrm{ff}} \Big\rangle \mathrm{d}t \\
&\quad \leqslant C\beta^{-1} e^{-\frac{1}{12}\mathsf{d}(\overline{u})\beta} \|D(\overline{u} - \widetilde{u})\|_{\ell^2_\Upsilon} \|Dv^{\mathrm{ff}}\|_{\ell^2_\Upsilon} \\
&\quad \leqslant C\beta^{-1} e^{-\frac{1}{12}\mathsf{d}(\overline{u})\beta} \|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{\widetilde{R}/2})} \|Dv\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R/2})}.
\end{aligned} \tag{6.8.27}$$

Now, since we are only considering the far field behaviour of v and $\widetilde{u}$ is of compact support, we are able to show that $\big\langle \delta\mathcal{G}^\beta(\widetilde{u}) - \delta\mathcal{G}(\widetilde{u}), v^{\mathrm{ff}} \big\rangle$ decays exponentially in the buffer region $B_R \setminus B_{\widetilde{R}}$:

$$\left| \Big\langle \delta\mathcal{G}^\beta(\widetilde{u}) - \delta\mathcal{G}(\widetilde{u}), v^{\mathrm{ff}} \Big\rangle \right| \leqslant C\beta^{-1} e^{-\frac{1}{12}\mathsf{d}(\overline{u})\beta} \widetilde{R}^{d/2} e^{-\eta(R-\widetilde{R})} \|Dv^{\mathrm{ff}}\|_{\ell^2_\Upsilon} \tag{6.8.28}$$

where $\eta \coloneqq \frac{1}{2}\mathfrak{m}\min\{\gamma_{\mathrm{CT}}, \gamma_0\}$. A full proof of (6.8.28) is given after the conclusion of the current proof.

Therefore, by applying (6.8.21), the estimate for the core region (6.8.25) and (6.8.27) and choosing $\widetilde{R}$ and R sufficiently large (independently of β) we

obtain

$$\begin{aligned}&\left|\left\langle \delta\mathcal{G}^\beta(\overline{u}), v\right\rangle\right| \\ &\leqslant C\beta^{-1}e^{-\frac{1}{12}\mathsf{d}(\overline{u})\beta}\Big(R^{d/2}R^{(d-1)/2} + \|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{\widetilde{R}/2})} + \widetilde{R}^{d/2}e^{-\eta(R-\widetilde{R})}\Big)\|Dv\|_{\ell^2_\Upsilon}.\end{aligned}$$

We may choose $R, \widetilde{R}$ in such a way as to obtain an exponential rate of convergence as $\beta \to \infty$.

Applying the inverse function theorem [88, Lemma B.1], we can conclude that, for sufficiently large β, there exist $\overline{u}_\beta \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ and $c_1 > 0$ such that

$$\begin{gathered}\|D\overline{u}_\beta - D\overline{u}\|_{\ell^2_\Upsilon} \leqslant Ce^{-\frac{1}{12}\mathsf{d}(\overline{u})\beta}, \quad \delta\mathcal{G}^\beta(\overline{u}_\beta) = 0 \\ \left\langle \delta^2\mathcal{G}^\beta(\overline{u}_\beta)v, v\right\rangle \geqslant c_1\|Dv\|^2_{\ell^2_\Upsilon}\end{gathered}$$

for all $v \in \dot{\mathscr{W}}^{1,2}(\Lambda)$.

Finally we consider the error in the energy. Using an analogous argument to that of [29, Eq. (78)], we obtain

$$|\mathcal{G}^\beta(\overline{u}_\beta) - \mathcal{G}^\beta(\overline{u})| \leqslant C\|D\overline{u}_\beta - D\overline{u}\|^2_{\ell^2_\Upsilon}. \tag{6.8.29}$$

In order to deal with the model error, we consider a compactly supported displacement $T_R\overline{u}$:

$$\big(\mathcal{G}^\beta(\overline{u}) - \mathcal{G}^\beta(T_R\overline{u})\big) - \big(\mathcal{G}(\overline{u}) - \mathcal{G}(T_R\overline{u})\big) = \int_0^1 \left\langle \delta\mathcal{G}^\beta(u_t) - \delta\mathcal{G}(u_t), T_R\overline{u} - \overline{u}\right\rangle \mathrm{d}t$$

where $u_t \coloneqq (1-t)\overline{u} + tT_R\overline{u}$. Therefore, choosing R sufficiently large such that $\operatorname{dist}(\mu, \sigma(\mathcal{H}(u_t))) \geqslant \frac{1}{4}\mathsf{d}(\overline{u})$ for all $t \in [0,1]$, we may replace u_t with a compactly supported displacement $\widetilde{u}$ as in (6.8.27) and (6.8.28) and obtain

$$\left|\big(\mathcal{G}^\beta(\overline{u}) - \mathcal{G}^\beta(T_R\overline{u})\big) - \big(\mathcal{G}(\overline{u}) - \mathcal{G}(T_R\overline{u})\big)\right| \leqslant Ce^{-\frac{1}{12}\mathsf{d}(\overline{u})\beta}\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R/2})}. \tag{6.8.30}$$

Finally, by applying Lemma 6.12, we obtain

$$
\begin{aligned}
&|\mathcal{G}^{\beta}(T_R\overline{u}) - \mathcal{G}(T_R\overline{u})| \\
&\leqslant C\sum_{\ell\in\Lambda} \|G^{\beta}(\,\cdot\,;\mu) - G(\,\cdot\,;\mu)\|_{C^-\cup\mathscr{C}^+} \big|\big[\mathscr{R}_z(T_R\overline{u})[\mathcal{H}(T_R\overline{u}) - \mathcal{H}(x)]\mathscr{R}_z(x)\big]_{\ell\ell}\big| \\
&\leqslant C\beta^{-1}e^{-\frac{1}{12}\mathtt{d}\beta} \sum_{\substack{\ell_1\in\Lambda \\ \ell_2\in\Lambda\cap B_R}} \big|\big[\mathcal{H}(T_R\overline{u}) - \mathcal{H}(x)\big]_{\ell_1\ell_2}\big| \\
&\leqslant CR^{d/2}\|D\overline{u}\|_{\ell^2_{\Upsilon}}\beta^{-1}e^{-\frac{1}{12}\mathtt{d}(\overline{u})\beta} \qquad (6.8.31)
\end{aligned}
$$

where η is some positive constant and $x\colon \Lambda\to\Lambda$ denotes the identity configuration.

Combining (6.8.29), (6.8.30) and (6.8.31), we obtain $|\mathcal{G}^{\beta}(\overline{u}_{\beta}) - \mathcal{G}(\overline{u})| \leqslant Ce^{-\frac{1}{12}\mathtt{d}(\overline{u})\beta}$ as required.

Proof of (6.8.28). We will argue that site energies are close to the corresponding reference site energies. We again define $\widetilde{\mathcal{H}}(\widetilde{u})$ and $\widetilde{\mathcal{H}}^{\mathrm{ref}}$ as in (2.5.6) so that we can compare these quantities.

If $\ell\in(\Lambda^{\mathrm{ref}}\cup\Lambda)\cap B_{\widetilde{R}}$ or $k\in(\Lambda^{\mathrm{ref}}\cup\Lambda)\cap B_{\widetilde{R}}$, then $|\ell-k|\geqslant \mathrm{dist}(\ell,B_{\widetilde{R}}) + \mathrm{dist}(k,B_{\widetilde{R}})$ and so we have

$$
\Big|\Big[\widetilde{\mathcal{H}}(\widetilde{u}) - \widetilde{\mathcal{H}}^{\mathrm{ref}}\Big]_{\ell k}\Big| \leqslant Ce^{-\gamma_0\mathfrak{m}\left(|\ell|+|k|-2\widetilde{R}\right)} \qquad (6.8.32)
$$

Similarly, for $m\in\Lambda$,

$$
\Big|\Big[\widetilde{\mathcal{H}}(\widetilde{u})_{,m} - \widetilde{\mathcal{H}}^{\mathrm{ref}}_{,m}\Big]_{\ell k}\Big| \leqslant Ce^{-\frac{1}{2}\gamma_0\mathfrak{m}\left(|\ell|+|k|-2\widetilde{R}\right)}e^{-\frac{1}{2}\gamma_0(r_{\ell m}(\widetilde{u})+r_{km}(\widetilde{u}))}. \qquad (6.8.33)
$$

In the following, we use the notation $\mathscr{R}_z(\widetilde{u}) \coloneqq (\widetilde{\mathcal{H}}(\widetilde{u}) - z)^{-1}$, and extend v^{ff}

by zero to $\Lambda \cup \Lambda^{\mathrm{ref}}$. Since $\delta\mathcal{G}^{\beta}_{\mathrm{ref}}(\mathbf{0}) = 0$, we have

$$
\begin{aligned}
&\Big\langle \delta\mathcal{G}^{\beta}(\widetilde{u}) - \delta\mathcal{G}(\widetilde{u}), v^{\mathrm{ff}} \Big\rangle \\
&= \Big\langle \delta\mathcal{G}^{\beta}(\widetilde{u}) - \delta\mathcal{G}^{\beta}_{\mathrm{ref}} - \big(\delta\mathcal{G}(\widetilde{u}) - \delta\mathcal{G}_{\mathrm{ref}}\big), v^{\mathrm{ff}} \Big\rangle \\
&= \oint_{\mathscr{C}^- \cup \mathscr{C}^+} \Big[G^{\beta}(z) - G(z)\Big] \sum_{\substack{\ell \in \Lambda \cup \Lambda^{\mathrm{ref}}, \rho \in \Lambda \cup \Lambda^{\mathrm{ref}} - \ell \\ |\ell| \geqslant R \text{ or } |\ell+\rho| \geqslant R}} \frac{\partial[\mathscr{R}_z(\widetilde{u}) - \mathscr{R}^{\mathrm{ref}}_z]^{aa}_{\ell\ell}}{\partial u(\ell+\rho)} \cdot D_{\rho} v^{\mathrm{ff}}(\ell) \frac{\mathrm{d}z}{2\pi i} \\
&\leqslant C\beta^{-1} e^{-\frac{1}{12}\mathfrak{d}(\overline{u})\beta} \sum_{\substack{\ell, k \in \Lambda \cup \Lambda^{\mathrm{ref}} \\ |\ell| \geqslant R \text{ or } |k| \geqslant R}} \max_{z \in \mathscr{C}^- \cup \mathscr{C}^+} \bigg| \frac{\partial[\mathscr{R}_z(\widetilde{u}) - \mathscr{R}^{\mathrm{ref}}_z]_{\ell\ell}}{\partial u(k)} \cdot D_{k-\ell} v^{\mathrm{ff}}(\ell) \bigg|.
\end{aligned}
\tag{6.8.34}
$$

We have therefore reduced the problem to considering the derivatives of the difference of two resolvent operators:

$$
\begin{aligned}
\frac{\partial[\mathscr{R}_z(\widetilde{u}) - \mathscr{R}^{\mathrm{ref}}_z]_{\ell\ell}}{\partial u(k)} &= \Big[-\mathscr{R}_z(\widetilde{u}) \mathcal{H}(\widetilde{u})_{,k} \mathscr{R}_z(\widetilde{u}) + \mathscr{R}^{\mathrm{ref}}_z \widetilde{\mathcal{H}}^{\mathrm{ref}}_{,k} \mathscr{R}^{\mathrm{ref}}_z \Big]_{\ell\ell} \\
&= \Big[(\mathscr{R}^{\mathrm{ref}}_z - \mathscr{R}_z(\widetilde{u})) \widetilde{\mathcal{H}}^{\mathrm{ref}}_{,k} \mathscr{R}^{\mathrm{ref}}_z + \mathscr{R}_z(\widetilde{u}) (\widetilde{\mathcal{H}}^{\mathrm{ref}}_{,k} - \widetilde{\mathcal{H}}(\widetilde{u})_{,k}) \mathscr{R}^{\mathrm{ref}}_z \\
&\qquad + \mathscr{R}_z(\widetilde{u}) \widetilde{\mathcal{H}}(\widetilde{u})_{,k} (\mathscr{R}^{\mathrm{ref}}_z - \mathscr{R}_z(\widetilde{u})) \Big]_{\ell\ell}.
\end{aligned}
\tag{6.8.35}
$$

In the following, we shall drop the argument $(\widetilde{u})$. Now, since $\mathscr{R}_z - \mathscr{R}^{\mathrm{ref}}_z = \mathscr{R}_z(\widetilde{\mathcal{H}}^{\mathrm{ref}} - \widetilde{\mathcal{H}})\mathscr{R}^{\mathrm{ref}}_z$, we have: for $z \in \mathscr{C}^- \cup \mathscr{C}^+$,

$$
\begin{aligned}
&\sum_{\substack{\ell, k \in \Lambda \cup \Lambda^{\mathrm{ref}} \\ |\ell| \geqslant R \text{ or } |k| \geqslant R}} \Big| \Big[(\mathscr{R}_z - \mathscr{R}^{\mathrm{ref}}_z) \widetilde{\mathcal{H}}_{,k} \mathscr{R}_z \Big]_{\ell\ell} \cdot D_{k-\ell} v^{\mathrm{ff}}(\ell) \Big| \\
&\leqslant \sum_{\substack{\ell, k \in \Lambda \cup \Lambda^{\mathrm{ref}} \\ |\ell| \geqslant R \text{ or } |k| \geqslant R}} \sum_{\ell_1, \ell_2, \ell_3, \ell_4} \Big| [\mathscr{R}_z]_{\ell\ell_3} (\widetilde{\mathcal{H}}^{\mathrm{ref}} - \widetilde{\mathcal{H}})_{\ell_3\ell_4} [\mathscr{R}^{\mathrm{ref}}_z]_{\ell_4\ell_1} [\widetilde{\mathcal{H}}_{,k}]_{\ell_1\ell_2} [\mathscr{R}_z]_{\ell_2\ell} \Big| \big| D_{k-\ell} v^{\mathrm{ff}}(\ell) \big| \\
&\lesssim \sum_{\substack{\ell, k, \ell_1, \ell_2, \ell_3, \ell_4 \\ |\ell| \geqslant R \text{ or } |k| \geqslant R}} e^{-\gamma_{\mathrm{CT}} \left(r_{\ell\ell_3} + r_{\ell_4\ell_1} + r_{\ell_2\ell} \right)} e^{-\frac{1}{2}\gamma_0 \mathfrak{m} \left(|\ell_3| + |\ell_4| - 2\widetilde{R} \right)} e^{-\gamma_0 \left(r_{\ell_1 k} + r_{\ell_2 k} \right)} \big| D_{k-\ell} v^{\mathrm{ff}}(\ell) \big| \\
&\lesssim \Bigg(\sum_{\substack{\ell, k \in \Lambda \cup \Lambda^{\mathrm{ref}} \\ |\ell| \geqslant R \text{ or } |k| \geqslant R}} \Bigg(\sum_{\ell_1, \ell_3, \ell_4} e^{-\eta \left(r_{\ell\ell_3} + r_{\ell_4\ell_1} + |\ell_3| - \widetilde{R} + |\ell_4| - \widetilde{R} + r_{\ell_1 k} \right)} \Bigg)^2 \Bigg)^{1/2} \| Dv^{\mathrm{ff}} \|_{\ell^2_{\Upsilon}}
\end{aligned}
\tag{6.8.36}
$$

where $\eta \coloneqq \frac{1}{2}\mathfrak{m} \min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\}$.

We now bound the first term in the product (6.8.36). Here we only consider

the summation over $\ell, k \in \Lambda \cup \Lambda^{\mathrm{ref}}$ and $|\ell| \geqslant R$ (the case where $|\ell| \leqslant R$ and $|k| \geqslant R$ can be treated in a similar way):

$$\begin{aligned}
&\sum_{\substack{\ell,k,\ell_1,\ell_3,\ell_4 \\ |\ell|\geqslant R}} e^{-\eta\left(r_{\ell\ell_3}+r_{\ell_4\ell_1}+|\ell_3|+|\ell_4|-2\widetilde{R}+r_{\ell_1 k}\right)} \\
&\qquad \leqslant C\Bigg(\sum_{\substack{\ell,\ell_3 \\ |\ell|\geqslant R}} e^{-\eta\left(r_{\ell\ell_3}+|\ell_3|-\widetilde{R}\right)}\Bigg)\Bigg(\sum_{k,\ell_4} e^{-\eta\left(r_{k\ell_4}+|\ell_4|-\widetilde{R}\right)}\Bigg) \\
&\qquad \leqslant C\widetilde{R}^d e^{-\frac{1}{2}\eta(R-\widetilde{R})}. \qquad (6.8.37)
\end{aligned}$$

Here, the $\widetilde{R}^d$ comes from the second factor in the line above. The exact same argument can be used to bound the third term in (6.8.35) similarly.

We now consider the second term in (6.8.35): for $z \in \mathscr{C}^- \cup \mathscr{C}^+$,

$$\begin{aligned}
&\sum_{\substack{\ell,k\in\Lambda\cup\Lambda^{\mathrm{ref}} \\ |\ell|\geqslant R \text{ or } |k|\geqslant R}} \Big|\Big[\mathscr{R}_z^{\mathrm{ref}}(\widetilde{\mathcal{H}}_{,k}-\widetilde{\mathcal{H}}_{,k}^{\mathrm{ref}})\mathscr{R}_z\Big]_{\ell\ell}\cdot D_{k-\ell}v^{\mathrm{ff}}(\ell)\Big| \\
&\leqslant \sum_{\substack{\ell,k\in\Lambda\cup\Lambda^{\mathrm{ref}} \\ |\ell|\geqslant R \text{ or } |k|\geqslant R}} \sum_{\ell_1,\ell_2\in\Lambda\cup\Lambda^{\mathrm{ref}}} \Big|[\mathscr{R}_z^{\mathrm{ref}}]_{\ell\ell_1}[\widetilde{\mathcal{H}}_{,k}-\widetilde{\mathcal{H}}_{,k}^{\mathrm{ref}}]_{\ell_1\ell_2}[\mathscr{R}_z^{\mathrm{ref}}]_{\ell_2\ell}\Big|\Big|D_{k-\ell}v^{\mathrm{ff}}(\ell)\Big| \\
&\leqslant C \sum_{\substack{\ell,k,\ell_1,\ell_2\in\Lambda\cup\Lambda^{\mathrm{ref}} \\ |\ell|\geqslant R \text{ or } |k|\geqslant R}} e^{-\gamma_{\mathrm{CT}}(r_{\ell\ell_1}+r_{\ell_2\ell})}e^{-\frac{1}{2}\gamma_0\mathfrak{m}(|\ell_1|+|\ell_2|-2\widetilde{R})}e^{-\gamma_0(r_{\ell_1 k}+r_{\ell_2 k})}\big|D_{k-\ell}v^{\mathrm{ff}}(\ell)\big| \\
&\leqslant C \sum_{\substack{\ell,k\in\Lambda\cup\Lambda^{\mathrm{ref}} \\ |\ell|\geqslant R \text{ or } |k|\geqslant R}} \Bigg(\sum_{\ell_1} e^{-\eta(r_{\ell\ell_1}+|\ell_1|-\widetilde{R}+r_{\ell_1 k})}\Bigg)e^{-\frac{1}{2}\eta r_{\ell k}}\big|D_{k-\ell}v^{\mathrm{ff}}(\ell)\big| \\
&\leqslant C\Bigg(\sum_{\substack{\ell,k,\ell_1\in\Lambda\cup\Lambda^{\mathrm{ref}} \\ |\ell|\geqslant R \text{ or } |k|\geqslant R}} e^{-\eta(r_{\ell\ell_1}+|\ell_1|-\widetilde{R}+r_{\ell_1 k})}\Bigg)^{1/2}\|Dv^{\mathrm{ff}}\|_{\ell^2_\Upsilon}. \qquad (6.8.38)
\end{aligned}$$

We again show that the prefactor in this expression is bounded: by summing over k, ℓ_1 and ℓ (in that order) we have,

$$\sum_{\substack{\ell,k,\ell_1\in\Lambda\cup\Lambda^{\mathrm{ref}} \\ |\ell|\geqslant R \text{ or } |k|\geqslant R}} e^{-\eta(r_{\ell\ell_1}+|\ell_1|-\widetilde{R}+r_{\ell_1 k})} \leqslant Ce^{-\frac{1}{2}\eta(R-\widetilde{R})}. \qquad (6.8.39)$$

Therefore, after collecting (6.8.36)−(6.8.39) and applying (6.8.34) and (6.8.35), we obtain (6.8.28). □

Proof of Proposition 6.4: $\beta \to \infty$ in the Grand Canonical Ensemble

We consider a sequence, $\overline{u}_{\beta_j}$, of solutions to ($\mathrm{GCE}_\mu^{\beta_j,\infty}$) (with $\beta_j \to \infty$ as $j \to \infty$) such that $\sup_j \|D\overline{u}_{\beta_j}\|_{\ell^2_\Upsilon} < \infty$. Noting that, after factoring out a constant shift, $\dot{\mathscr{W}}^{1,2}(\Lambda)$ is a Hilbert space and so we may apply the Banach-Alaoglu theorem to conclude that there exists a $\overline{u} \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ such that

$$\overline{u}_{\beta_j} \rightharpoonup \overline{u} \quad \text{in } \dot{\mathscr{W}}^{1,2} \text{ as } j \to \infty$$

along a subsequence (which we do not relabel). Now, because $v \mapsto D_\rho v(\ell)$ is a linear functional for all $\ell \in \Lambda$ and $\rho \in \Lambda - \ell$, we have obtained (6.6.1).

To simplify notation, let us define the forces

$$\mathcal{F}_\ell^\beta(u) \coloneqq \frac{\partial \mathcal{G}^\beta(u)}{\partial u(\ell)} \quad \text{and} \quad \mathcal{F}_\ell(u) \coloneqq \frac{\partial \mathcal{G}(u)}{\partial u(\ell)}. \tag{6.8.40}$$

Since $\overline{u}_{\beta_j}$ solves ($\mathrm{GCE}_\mu^{\beta_j,\infty}$), we have

$$0 = \Big\langle \delta \mathcal{G}^{\beta_j}(\overline{u}_{\beta_j}), v \Big\rangle = \sum_{\ell \in \Lambda} \mathcal{F}_\ell^{\beta_j}(\overline{u}_{\beta_j}) \cdot v(\ell) \quad \text{for all } v \in \dot{\mathscr{W}}^{1,2}(\Lambda).$$

Let us fix $v \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ with compact support in B_{R_v} for some $R_v > 0$. Now, it is sufficient to show that

$$\mathcal{F}_\ell^{\beta_j}(\overline{u}_{\beta_j}) \to \mathcal{F}_\ell(\overline{u}) \quad \text{as } j \to \infty$$

for all $\ell \in \Lambda \cap B_{R_v}$. Here, we may apply Remark 6.7 and the fact that μ is uniformly bounded away from $\sigma(\mathcal{H}(\overline{u}_{\beta_j}))$ to conclude that $\mathcal{G}(\overline{u})$ is differentiable.

For sufficiently large j,

$$|\mathcal{F}_\ell^{\beta_j}(\overline{u}_{\beta_j}) - \mathcal{F}_\ell^{\beta_j}(\overline{u})| \leqslant C\Big(e^{-\gamma_{\mathrm{CT}} R_v} + \|D(\overline{u}_{\beta_j} - \overline{u})\|_{\ell^2_\Upsilon(\Lambda \cap B_{2R_v})}\Big). \tag{6.8.41}$$

The proof of this estimate is given below. By first choosing R_v and then j sufficiently large, (6.8.41) can be made arbitrarily small.

Applying Lemma 6.16, we obtain

$$|\mathcal{F}_\ell^{\beta_j}(\overline{u}) - \mathcal{F}_\ell(\overline{u})| \leqslant C\beta_j^{-1} e^{-\frac{1}{6}\mathsf{d}(\overline{u})\beta_j} \sum_{k\in\Lambda} e^{-\gamma_{\mathrm{CT}} r_{\ell k}} \leqslant C\beta_j^{-1} e^{-\frac{1}{6}\mathsf{d}(\overline{u})\beta_j}. \quad (6.8.42)$$

Combining (6.8.41) and (6.8.42), we obtain $\mathcal{F}_\ell^{\beta_j}(\overline{u}_{\beta_j}) \to \mathcal{F}_\ell(\overline{u})$ as $j \to \infty$ and so $\mathcal{F}_\ell(\overline{u}) = 0$.

Proof of (6.8.41). We will prove a more general statement: for $\beta \in (0, \infty]$ and $u_1, u_2 \in \dot{\mathscr{W}}^{1,2}(\Lambda)$, with $\|D(u_1 - u_2)\|_{\ell^2_\Upsilon(\Lambda\cap B_{2R_v})}$ sufficiently small, we have

$$|\mathcal{F}_\ell^{\beta}(u_1) - \mathcal{F}_\ell^{\beta}(u_2)| \leqslant C\Big(e^{-\gamma_{\mathrm{CT}} R_v} + \|D(u_1 - u_2)\|_{\ell^2_\Upsilon(\Lambda\cap B_{2R_v})}\Big). \quad (6.8.43)$$

This result is also true in the case of periodic displacements u_1, u_2 as will become clear in the proof.

Using the chain rule, we obtain the formula:

$$\mathcal{F}_\ell^{\beta}(u) = \sum_{\rho\in\ell-\Lambda} \mathcal{G}^{\beta}_{\ell-\rho,\rho}(Du(\ell-\rho)) - \sum_{\rho\in\Lambda-\ell} \mathcal{G}^{\beta}_{\ell,\rho}(Du(\ell)), \quad (6.8.44)$$

which is valid for both $\beta < \infty$ and $\beta = \infty$.

We first notice that

$$\mathcal{G}^{\beta}_{\ell,k-\ell}(Du_1(\ell)) - \mathcal{G}^{\beta}_{\ell,k-\ell}(Du_2(\ell)) = \\ \operatorname{tr} \oint_{\mathscr{C}^+\cup\mathscr{C}^-} G^\beta(z;\mu) \frac{\partial[\mathscr{R}_z(u_2) - \mathscr{R}_z(u_1)]_{\ell\ell}}{\partial u(k)} \frac{\mathrm{d}z}{2\pi i}. \quad (6.8.45)$$

We again consider the derivative of the difference of two resolvents as in (6.8.35), above. By Lemma 6.12, if $\|D(u_1 - u_2)\|_{\ell^2_\Upsilon(\Lambda\cap B_{2R_v})}$ is sufficiently small, we have:

for $m \in \Lambda$,

$$
\begin{aligned}
&[\mathscr{R}_z(u_2) - \mathscr{R}_z(u_1)]_{\ell m} = [\mathscr{R}_z(u_2)(\mathcal{H}(u_1) - \mathcal{H}(u_2))\mathscr{R}_z(u_1)]_{\ell m} \\
&\lesssim \sum_{\substack{\ell_1,\ell_2\in\Lambda \\ |\ell_1|>2R_v \text{ or } |\ell_2|>2R_v}} e^{-\gamma_{\mathrm{CT}}(r_{\ell\ell_1}+r_{\ell_2 m})} e^{-\gamma_0 r_{\ell_1\ell_2}} \\
&+ C\Big(\sum_{\ell_1,\ell_2\in\Lambda\cap B_{2R_v}} e^{-\gamma_{\mathrm{CT}}(r_{\ell\ell_1}+r_{\ell_2 m})}\Big)^{1/2} \Big(\sum_{\ell_1,\ell_2\in\Lambda\cap B_{2R_v}} \big|[\mathcal{H}(u_1) - \mathcal{H}(u_2)]_{\ell_1\ell_2}\big|^2\Big)^{1/2} \\
&\leqslant C\Big(e^{-\frac{1}{2}\min\{\gamma_{\mathrm{CT}},\gamma_0\}R_v} + \|D(u_1-u_2)\|_{\ell^2_{\Upsilon}(\Lambda\cap B_{2R_v})}\Big).
\end{aligned}
$$

Here, we have used the fact that $\ell \in B_{R_v}$ in the first term. Therefore, we have:

$$
\begin{aligned}
&\big[(\mathscr{R}_z(u_2) - \mathscr{R}_z(u_1))\mathcal{H}(u_2)_{,k}\mathscr{R}_z(u_2)\big]_{\ell\ell} \\
&\quad\leqslant C\Big(e^{-\gamma_{\mathrm{CT}}R_v} + \|D(u_1-u_2)\|_{\ell^2_{\Upsilon}(\Lambda\cap B_{2R_v})}\Big) \sum_{\ell_1,\ell_2\in\Lambda} e^{-\gamma_0(r_{\ell_1 k}+r_{\ell_2 k})} e^{-\gamma_{\mathrm{CT}} r_{\ell_2\ell}} \\
&\quad\leqslant C\Big(e^{-\gamma_{\mathrm{CT}}R_v} + \|D(u_1-u_2)\|_{\ell^2_{\Upsilon}(\Lambda\cap B_{2R_v})}\Big) e^{-\frac{1}{2}\min\{\gamma_{\mathrm{CT}},\gamma_0\}r_{\ell k}}.
\end{aligned}
\tag{6.8.46}
$$

Similarly, by Lemma 6.12, we have

$$
\begin{aligned}
&\big[\mathscr{R}_z(u_1)[\mathcal{H}(u_2)_{,k} - \mathcal{H}(u_1)_{,k}]\mathscr{R}_z(u_2)\big]_{\ell\ell} \\
&\quad\leqslant C\Big(e^{-\gamma_{\mathrm{CT}}R_v} + \|D(u_1-u_2)\|_{\ell^2_{\Upsilon}(\Lambda\cap B_{2R_v})}\Big) e^{-\frac{1}{2}\min\{\gamma_{\mathrm{CT}},c\gamma_0\}r_{\ell k}}
\end{aligned}
\tag{6.8.47}
$$

where $c = \frac{\mathfrak{m}\sqrt{3}}{2}$ is the constant from Lemma 6.12.

Therefore, by combining (6.8.46) and (6.8.47) and using the formula for the derivative of the difference between two resolvent operators (6.8.35) together with the chain rule formula (6.8.44), we have (6.8.43). □

Proofs of Theorem 6.5 and Proposition 6.6: $\beta \to \infty$ in the Canonical Ensemble

Before we proceed with the proofs of Theorem 6.5 and Proposition 6.6, we first recall that $\varepsilon_{\mathrm{F}}^{\beta,R}(u_R)$ denotes the Fermi level given by (6.3.3). For $\beta = \infty$, we define $\varepsilon_{\mathrm{F}}^{\infty,R}(u_R)$ via the zero Fermi-temperature limit (Lemma 6.2).

Proof of Theorem 6.5. We suppose that $\overline{u}_R$ is a strongly stable solution to $(\mathrm{CE}^{\infty,R}_{N_{e,R}})$. In particular, $\overline{u}_R$ is a strongly stable solution to $(\mathrm{GCE}^{\infty,R}_{\mu})$ for all $\mu \in I$ where I is a closed interval such that $I \cap B_\delta(\sigma(\mathcal{H}^R(\overline{u}_R))) = \emptyset$ for some $\delta > 0$ and $\varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R) \in I$. Therefore, by Theorem 6.3, for sufficiently large β (depending on δ and not on μ), there exists a unique solution $\overline{u}^{\mu}_{R,\beta}$ to $(\mathrm{GCE}^{\beta,R}_{\mu})$ satisfying

$$\|D\overline{u}^{\mu}_{R,\beta} - D\overline{u}_R\|_{\ell^2_\Upsilon} \leqslant Ce^{-\frac{1}{12}\mathsf{d}(\overline{u}_R)\beta} =: \tau_\beta. \tag{6.8.48}$$

Since $I \cap B_\delta(\sigma(\mathcal{H}(\overline{u}_R))) = \emptyset$, the pre-factor and exponent can be chosen to depend on δ but not on $\mu \in I$. Now by Lemma 6.11, for β sufficiently large, we have

$$|\lambda_s(\overline{u}^{\mu}_{R,\beta}) - \lambda_s(\overline{u}_R)| \leqslant Ce^{-\frac{1}{12}\mathsf{d}(\overline{u}_R)\beta} \tag{6.8.49}$$

where $\lambda_s(u)$ denotes the eigenvalues of $\mathcal{H}^R(u)$ in increasing order. In particular, $\varepsilon_{\mathrm{F}}^{\beta,R}(\overline{u}^{\mu}_{R,\beta}) \to \varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R)$ as $\beta \to \infty$ and so, for sufficiently large β, we have $\varepsilon_{\mathrm{F}}^{\beta,R}(\overline{u}^{\mu}_{R,\beta}) \in I$ for all $\mu \in I$.

For now, we assume that the mapping $I \to I$ given by $\mu \mapsto \varepsilon_{\mathrm{F}}^{\beta,R}(\overline{u}^{\mu}_{R,\beta})$ is continuous for all sufficiently large β. We will prove this fact after noting that this is sufficient to conclude. Since I is a compact and convex set, we can apply Brouwer's fixed point theorem to conclude that there exists $\mu^\star = \varepsilon_{\mathrm{F}}^{\beta,R}(\overline{u}^{\mu^\star}_{R,\beta}) \in I$. In particular, $\overline{u}^{\mu^\star}_{R,\beta}$ is a solution to $(\mathrm{GCE}^{\beta,R}_{\mu^\star})$ with Fermi level $\mu^\star$. That is, $\overline{u}^{\mu^\star}_{R,\beta}$ solves $(\mathrm{CE}^{\beta,R}_{N_{e,R}})$ and, by (6.8.48), we have $\|D\overline{u}^{\mu^\star}_{R,\beta} - D\overline{u}_R\|_{\ell^2_\Upsilon} \leqslant Ce^{-\frac{1}{12}\mathsf{d}(\overline{u}_R)\beta}$.

Continuity of $\mu \mapsto \varepsilon_{\mathrm{F}}^{\beta,R}(\overline{u}^{\mu}_{R,\beta})$: We now wish to show that $I \to I \colon \mu \mapsto \varepsilon_{\mathrm{F}}^{\beta,R}(\overline{u}^{\mu}_{R,\beta})$ is continuous for all sufficiently large β. To do so, we fix $\nu \in I$ and apply the inverse function theorem on $\delta\mathcal{G}^{\beta,R}(\,\cdot\,;\nu)$ around $\overline{u}^{\mu}_{R,\beta}$ for $\mu \in I$ close to ν.

Firstly, we remark that $\delta^2\mathcal{G}^{\beta,R}(\,\cdot\,;\nu)$ is Lipschitz continuous in a neighbourhood of $\overline{u}^{\mu}_{R,\beta}$ for all $\mu \in I$ with Lipschitz constant uniformly bounded below by a positive constant for all $\mu \in I$.

Since $G^\beta(\,\cdot\,;\nu)$ is analytic on $\mathbb{C} \setminus \{\nu + ir \colon r \in \mathbb{R}\}$, we know that $G^\beta(\,\cdot\,;\nu)$ is Lipschitz continuous on all compact sets $K \subseteq \mathbb{C} \setminus \{\nu + ir \colon r \in \mathbb{R}\}$. In particular,

if $\mu \in I$, then

$$|G^\beta(z;\mu) - G^\beta(z;\nu)| = |G^\beta(z+\nu-\mu;\nu) - G^\beta(z;\nu)| \leqslant L|\mu-\nu|$$

for all $z \in \mathscr{C}^- \cup \mathscr{C}^+$ for some appropriate choice of contours as in Figure 6.3 with $\operatorname{dist}(\operatorname{Re}(z), I) \geqslant \frac{1}{2}\delta$ for all $z \in \mathscr{C}^- \cup \mathscr{C}^+$. Since $G^\beta(z;\cdot) \to 2(z-\cdot)$ pointwise as $\beta \to \infty$, we can conclude that the Lipschitz constant can be chosen uniformly (for sufficiently large β). Using this, together with the stability of $\overline{u}^\mu_{R,\beta}$ (where the stability constant c_1 is independent of $\mu \in I$), we obtain

$$\begin{aligned}
\Big\langle \delta^2\mathcal{G}^{\beta,R}(\overline{u}^\mu_{R,\beta};\nu)v, v\Big\rangle &= \Big\langle \delta^2\mathcal{G}^{\beta,R}(\overline{u}^\mu_{R,\beta};\mu)v, v\Big\rangle \\
&\qquad - \Big\langle \Big(\delta^2\mathcal{G}^{\beta,R}(\overline{u}^\nu_{R,\beta};\nu) - \delta^2\mathcal{G}^{\beta,R}(\overline{u}^\nu_{R,\beta};\mu)\Big)v, v\Big\rangle \\
&\geqslant (c_1 - C|\mu-\nu|)\|Dv\|_{\ell^2_\Upsilon} \quad \text{and} \\
\Big\langle \delta\mathcal{G}^{\beta,R}(\overline{u}^\mu_{R,\beta};\nu), v\Big\rangle &= \Big\langle \delta\mathcal{G}^{\beta,R}(\overline{u}^\mu_{R,\beta};\nu) - \delta\mathcal{G}^{\beta,R}(\overline{u}^\mu_{R,\beta};\mu), v\Big\rangle \\
&\leqslant C|\mu-\nu|.
\end{aligned}$$

Therefore, if $|\mu-\nu|$ is sufficiently small, the inverse function theorem yields the existence of $\overline{u}^{\mu\nu}_{R,\beta}$ satisfying

$$\delta\mathcal{G}^{\beta,R}(\overline{u}^{\mu\nu}_{R,\beta};\nu) = 0 \quad \text{and} \quad \|D\overline{u}^{\mu\nu}_{R,\beta} - D\overline{u}^\mu_{R,\beta}\|_{\ell^2_\Upsilon} \leqslant C|\mu-\nu|. \tag{6.8.50}$$

In particular, $\overline{u}^{\mu\nu}_{R,\beta}$ solves $(\mathrm{GCE}^{\beta,R}_\nu)$. By (6.8.48), if $|\nu-\mu|$ is sufficiently small, we necessarily have $\overline{u}^{\mu\nu}_{R,\beta} \in B_{\tau_\beta}(\overline{u}_R; \|D\cdot\|_{\ell^2_\Upsilon})$ and thus, by uniqueness of the solution $\overline{u}^\nu_{R,\beta}$ to $(\mathrm{GCE}^{\beta,R}_\nu)$ on $B_{\tau_\beta}(\overline{u}_R; \|D\cdot\|_{\ell^2_\Upsilon})$, we have $\overline{u}^{\mu\nu}_{R,\beta} = \overline{u}^\nu_{R,\beta}$. Therefore, for all $\mu,\nu \in I$ with $|\mu-\nu|$ sufficiently small, $\|D\overline{u}^\nu_{R,\beta} - D\overline{u}^\mu_{R,\beta}\|_{\ell^2_\Upsilon} \leqslant C|\mu-\nu|$ and thus, by Lemma 6.11, $\operatorname{dist}\big(\sigma(\mathcal{H}^R(\overline{u}^\mu_{R,\beta})), \sigma(\mathcal{H}^R(\overline{u}^\nu_{R,\beta}))\big) \leqslant C|\mu-\nu|$. In particular, $\mu \mapsto \varepsilon^{\beta,R}_{\mathrm{F}}(\overline{u}^\mu_{R,\beta})$ is continuous on I. □

Proof of Proposition 6.6. Suppose that $\overline{u}_{\beta_j}$ is a bounded sequence (with $\beta_j \to \infty$) of solutions to $(\mathrm{CE}^{\beta_j,R}_{N_{e,R}})$. As before, along a subsequence, there exists a weak limit $\overline{u}_{\beta_j} \rightharpoonup \overline{u}$ as $j \to \infty$. By applying Lemma 6.11 and noting that weak convergence on a finite domain implies strong convergence, we can conclude

that

$$|\lambda_s(\overline{u}_{\beta_j}) - \lambda_s(\overline{u})| \to 0$$

as $j \to \infty$ for each $s = 1, \ldots, N_R$. Therefore $\varepsilon_{\mathrm{F}}^{\beta_j,R}(\overline{u}_{\beta_j}) \to \varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u})$ as $j \to \infty$.

Since we have assumed that $\varepsilon_{\mathrm{F}}^{\beta_j,R}(\overline{u}_{\beta_j})$ is uniformly bounded away from $\sigma(\mathcal{H}^R(\overline{u}_{\beta_j}))$, we can apply Remark 6.7 to conclude $\mu \coloneqq \varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}) \notin \sigma(\mathcal{H}^R(\overline{u}))$.

Since $\overline{u}_{\beta_j}$ solves $(\mathrm{CE}^{\beta_j,R}_{N_{e,R}})$,

$$\begin{aligned}\left|\frac{\partial \mathcal{G}^{\beta_j,R}(\overline{u}_{\beta_j};\mu)}{\partial \overline{u}_{\beta_j}(\ell)}\right| &= \left|\frac{\partial \mathcal{G}^{\beta_j,R}(\overline{u}_{\beta_j};\mu)}{\partial \overline{u}_{\beta_j}(\ell)} - \frac{\partial \mathcal{G}^{\beta_j,R}(\overline{u}_{\beta_j};\tau)}{\partial \overline{u}_{\beta_j}(\ell)}\bigg|_{\tau=\varepsilon_{\mathrm{F}}^{\beta_j,R}(\overline{u}_{\beta_j})}\right| \\ &\leqslant C\big|\varepsilon_{\mathrm{F}}^{\beta_j,R}(\overline{u}_{\beta_j}) - \mu\big| \to 0 \quad \text{as } j \to \infty.\end{aligned} \tag{6.8.51}$$

On the other hand, as in the proof of Proposition 6.4 (see, (6.8.40)−(6.8.42)), we have

$$\frac{\partial \mathcal{G}^{\beta_j,R}(\overline{u}_{\beta_j};\mu)}{\partial \overline{u}_{\beta_j}(\ell)} \to \frac{\partial \mathcal{G}^{\infty,R}(\overline{u};\mu)}{\partial \overline{u}(\ell)} \quad \text{as } j \to \infty. \tag{6.8.52}$$

Therefore, by combining (6.8.52) and (6.8.51), we can conclude that $\overline{u}$ is a critical point of $\mathcal{G}^{\infty,R}(\,\cdot\,;\mu)$. □

6.8.3 Thermodynamic Limit

The results of [26] are analogous to Theorem 6.9 and Proposition 6.10 but in the case of finite Fermi-temperature. Moreover, the authors of [26] only consider the case of a Bravais lattice $\Lambda^{\mathrm{ref}} = \mathsf{B}\mathbb{Z}^d$. In this section, we prove that these results can be extended to the case of zero Fermi-temperature for insulators in the more general case where Λ^{ref} need not be a Bravais lattice.

In principle, one may prove these thermodynamic limit results by using Theorem 6.3 and Proposition 6.4 to compare the zero Fermi-temperature problems with the analogous finite temperature problems and showing that the convergence rates in [26] are independent of Fermi-temperature. However, we opt for a more direct approach here because the case $\Lambda^{\mathrm{ref}} \neq \mathsf{B}\mathbb{Z}^d$ was not considered in [26] and thus a rigorous treatment would be lengthy.

Proof of Theorem 6.7: $R \to \infty$ in the Grand Canonical Ensemble

Throughout this proof $\beta \in (0, \infty]$ will be fixed and therefore we omit the index corresponding to Fermi-temperature on the grand potential and the site energies. Again, we will use the notation of Lemma 6.18 for the truncation operator $T_R \colon \dot{\mathscr{W}}^{1,2}(\Lambda) \to \dot{\mathscr{W}}^{\mathrm{c}}(\Lambda)$.

Step 1: Quasi-best approximation. For some $r > 0$ sufficiently small, we have $x + B_{2r}(\overline{u}) \subseteq \mathrm{Adm}(\Lambda)$. We may choose R sufficiently large such that $T_R\overline{u} \in B_r(\overline{u})$ and so $x + B_r(T_R\overline{u}) \subseteq \mathrm{Adm}(\Lambda)$. We know that $\mathcal{G} \in C^3(\mathrm{Adm}(\Lambda))$ and so $\delta\mathcal{G}$ and $\delta^2\mathcal{G}$ are Lipschitz continuous on $\mathrm{Adm}(\Lambda) \cap B_r(\overline{u})$. In particular,

$$\begin{aligned} \|\delta\mathcal{G}(\overline{u}) - \delta\mathcal{G}(T_R\overline{u})\| &\leqslant C\|D\overline{u} - DT_R\overline{u}\|_{\ell^2_\Upsilon} \leqslant C\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R/2})}, \quad \text{and} \\ \|\delta^2\mathcal{G}(\overline{u}) - \delta^2\mathcal{G}(T_R\overline{u})\| &\leqslant C\|D\overline{u} - DT_R\overline{u}\|_{\ell^2_\Upsilon} \leqslant C\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R/2})}. \end{aligned} \tag{6.8.53}$$

Step 2: Consistency. We fix $v \colon \Lambda_R \to \mathbb{R}^d$ satisfying **(L)**. Since v is periodic and not necessarily an admissible displacement on Λ, we consider the compactly supported displacement $T_{R^\star}v$ for some $R^\star < R$ and extend by zero to Λ. Rewriting $\langle \delta\mathcal{G}^R(T_R\overline{u}), v\rangle$, we have

$$\begin{aligned} \langle \delta\mathcal{G}^R(T_R\overline{u}), v\rangle &= \langle \delta\mathcal{G}^R(T_R\overline{u}), (I - T_{R^\star})v\rangle \\ &\quad + \langle \delta\mathcal{G}^R(T_R\overline{u}) - \delta\mathcal{G}(T_R\overline{u}), T_{R^\star}v\rangle \\ &\quad + \langle \delta\mathcal{G}(T_R\overline{u}) - \delta\mathcal{G}(\overline{u}), T_{R^\star}v\rangle \end{aligned} \tag{6.8.54}$$

We consider each of these contributions in turn.

Replacing $T_R\overline{u}$ with $T_{\tilde{R}}\overline{u}$ for some $\tilde{R} < R^\star < R$ in the first term of (6.8.54) gives an approximation error of $C\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\cap B_R\setminus B_{\tilde{R}/2})}$. Since $(I - T_{R^\star})v = 0$ on $\Lambda \cap B_{R^\star}$ and $T_{\tilde{R}}\overline{u} = 0$ on $\Lambda \setminus B_{\tilde{R}}$, we can bound $\langle \delta G^R(T_{\tilde{R}}\overline{u}), (I - T_{R^\star})v\rangle$

as follows:

$$
\begin{aligned}
&|\big\langle \delta\mathcal{G}^R(T_R\overline{u}), (I - T_{R^\star})v\big\rangle| \\
&\leqslant |\big\langle \delta\mathcal{G}^R(T_{\tilde{R}}\overline{u}), (I - T_{R^\star})v\big\rangle| + |\big\langle \delta\mathcal{G}^R(T_R\overline{u}) - \delta\mathcal{G}^R(T_{\tilde{R}}\overline{u}), (I - T_{R^\star})v\big\rangle| \\
&\leqslant C\tilde{R}^{d/2}e^{-\eta(R^\star - \tilde{R})}\|Dv\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R^\star/2})} + C\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\cap B_R\setminus B_{\tilde{R}/2})}\|Dv\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R^\star/2})}
\end{aligned}
\tag{6.8.55}
$$

where $\eta \coloneqq \frac{1}{2}\mathfrak{m}\min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\}$. The first term in (6.8.55) is bounded by comparing the first derivative of the grand potential with the corresponding reference grand potential and taking the derivatives inside the contour integration in an argument that is exactly the same as in (6.8.28). Bounding the second term in (6.8.55) is done by applying Taylor's theorem and using the locality of the second derivatives of the site energies (for an identical argument see (6.8.27)).

Next, we consider the second term of (6.8.54). We simply apply the convergence of the site energies as $R \to \infty$ (Lemma 6.17), together with the locality of the site energies (Theorem 3.1) and the fact that $T_{R^\star}v$ has compact support in $B_{R^\star}$ to conclude:

$$
\begin{aligned}
&\big\langle \delta\mathcal{G}^R(T_R\overline{u}) - \delta\mathcal{G}(T_R\overline{u}), T_{R^\star}v\big\rangle \\
&\quad= \sum_{\ell\in\Lambda_R}\sum_{\rho\in\Lambda_R-\ell}\big(\mathcal{G}^R_{\ell,\rho}(DT_R\overline{u}(\ell)) - \mathcal{G}_{\ell,\rho}(DT_R\overline{u}(\ell))\big)\cdot D_\rho T_{R^\star}v(\ell) \\
&\qquad\quad - \sum_{\substack{\ell\in\Lambda,\rho\in\Lambda-\ell \\ \ell\notin\Lambda_R \text{ or } \ell+\rho\notin\Lambda_R}} \mathcal{G}_{\ell,\rho}(DT_R\overline{u}(\ell))\cdot D_\rho T_{R^\star}v(\ell) \\
&\quad\leqslant C\sum_{\ell\in\Lambda_R}\sum_{\rho\in\Lambda_R-\ell} e^{-\eta(\mathrm{dist}(\ell,\Omega_R^c)+|\rho|)}|D_\rho T_{R^\star}v(\ell)| \\
&\qquad\quad + C\sum_{\substack{\ell\in\Lambda,\rho\in\Lambda-\ell \\ \ell\notin\Lambda_R \text{ or } \ell+\rho\notin\Lambda_R}} e^{-\gamma_{\mathrm{CT}}|\rho|}|D_\rho T_{R^\star}v(\ell)| \\
&\quad\leqslant C(R^\star)^{d/2}e^{-\frac{1}{2}\eta(R-R^\star)}\|DT_{R^\star}v\|_{\ell^2_\Upsilon}
\end{aligned}
\tag{6.8.56}
$$

where $\eta \coloneqq \frac{1}{2}\mathfrak{m}\min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\}$. In the final line, we have used the fact that $T_{R^\star}v$ has compact support in $B_{R^\star}$. More specifically, in the first term, we have used the fact that, if $\ell \in B_{R^\star}$ or $\ell + \rho \in B_{R^\star}$, then $\mathrm{dist}(\ell, \Omega_R^c) + |\rho| > R - R^\star$.

Moreover, in the second term, we have that, if $\ell \notin \Lambda_R$ then we must sum over $\ell + \rho \in B_{R^\star}$ and so $|\rho| > R - R^\star$ (and *vice versa*).

Finally, we consider the third contribution from (6.8.54): by (6.8.53), we have

$$|\langle \delta\mathcal{G}(T_R\overline{u}) - \delta\mathcal{G}(\overline{u}), T_{R^\star}v\rangle| \leqslant C\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R/2})}\|DT_{R^\star}v\|_{\ell^2_\Upsilon}. \tag{6.8.57}$$

Combining (6.8.54)−(6.8.57) we obtain the following consistency estimate:

$$\begin{aligned}&\big|\big\langle \delta G^R(T_R\overline{u}), v\big\rangle\big| \\ &\leqslant C\Big(\widetilde{R}^{d/2}e^{-\eta(R^\star-\tilde{R})} + \|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{\tilde{R}/2})} + (R^\star)^{d/2}e^{-\frac{1}{2}\eta(R-R^\star)}\Big)\|Dv\|_{\ell^2_\Upsilon}\end{aligned} \tag{6.8.58}$$

where $\eta \coloneqq \frac{1}{2}\mathfrak{m}\min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\}$. Here, we can see that if $\|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_R)} \lesssim R^{-d/2}$ (which would follow if (6.6.4) holds), then we obtain a convergence rate as discussed in Remark 6.4.

Step 3: Stability. We now show the following stability estimate: there exists $c_1 > 0$ such that

$$\big\langle \delta^2\mathcal{G}^R(T_R\overline{u})v, v\big\rangle \geqslant c_1\|Dv\|^2_{\ell^2_\Upsilon} \tag{6.8.59}$$

for all sufficiently large R.

We first take a sequence v_R of test functions with $\|Dv_R\|_{\ell^2_\Upsilon} = 1$ and note that $w_R \coloneqq T_Rv_R \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ and $\|Dw_R\|_{\ell^2_\Upsilon} \leqslant C\|Dv_R\|_{\ell^2_\Upsilon(\Lambda\cap B_R)} \leqslant C$ where C is independent of R. Therefore, along a subsequence (which we do not relabel) we have $w_R \rightharpoonup v$ in $\dot{\mathscr{W}}^{1,2}(\Lambda)$ as $R \to \infty$ for some $v \in \dot{\mathscr{W}}^{1,2}(\Lambda)$. By [47, Lemma 7.8], we may choose a sequence of radii $S(R)$ with $S(R) \to \infty$

as $R \to \infty$ "sufficiently slowly" such that

$$T_{S(R)} w_R \to v \quad \text{strongly in } \dot{\mathscr{W}}^{1,2}(\Lambda), \tag{6.8.60}$$

$$T_{S(R)} w_R - w_R \rightharpoonup 0 \quad \text{weakly in } \dot{\mathscr{W}}^{1,2}(\Lambda) \text{ and} \tag{6.8.61}$$

$$R - S(R) \to \infty \quad \text{as } R \to \infty. \tag{6.8.62}$$

We let $v_R^{\mathrm{co}} \coloneqq T_{S(R)} w_R$ and $v_R^{\mathrm{ff}} \coloneqq v_R - v_R^{\mathrm{co}}$ and expand $\langle \delta^2 \mathcal{G}^R(T_R \overline{u}) v_R, v_R \rangle$ as follows:

$$\begin{aligned}
&\langle \delta^2 \mathcal{G}^R(T_R \overline{u}) v_R, v_R \rangle \\
&\quad = \langle \delta^2 \mathcal{G}^R(T_R \overline{u}) v_R^{\mathrm{co}}, v_R^{\mathrm{co}} \rangle + 2 \Big\langle \delta^2 \mathcal{G}^R(T_R \overline{u}) v_R^{\mathrm{co}}, v_R^{\mathrm{ff}} \Big\rangle + \Big\langle \delta^2 \mathcal{G}^R(T_R \overline{u}) v_R^{\mathrm{ff}}, v_R^{\mathrm{ff}} \Big\rangle \\
&\quad =: \mathrm{T}_1 + 2\mathrm{T}_2 + \mathrm{T}_3.
\end{aligned} \tag{6.8.63}$$

We shall consider each of these terms separately.

Using the fact that v_R^{co} has compact support in $B_{S(R)}$, we obtain:

$$\begin{aligned}
&\big\langle \big(\delta^2 \mathcal{G}^R(T_R \overline{u}) - \delta^2 \mathcal{G}(\overline{u}) \big) v_R^{\mathrm{co}}, w \big\rangle \\
&\qquad \leqslant C \Big(e^{-\frac{1}{2}\eta(R - S(R))} + \|D\overline{u}\|_{\ell^2_\Upsilon(\Lambda \setminus B_{R/2})} \Big) \|D v_R^{\mathrm{co}}\|_{\ell^2_\Upsilon} \|Dw\|_{\ell^2_\Upsilon}
\end{aligned} \tag{6.8.64}$$

where $\eta \coloneqq \frac{1}{2}\mathfrak{m} \min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\}$. The proof of this estimate is similar to that of *Step 2*; see, [96, Appendix I] for the details.

T_1*: core term.* Using the strong stability of the solution $\overline{u}$ together with (6.8.64), we may conclude that, for sufficiently large R, we have

$$\begin{aligned}
\mathrm{T}_1 &= \langle \delta^2 G^R(T_R \overline{u}) v_R^{\mathrm{co}}, v_R^{\mathrm{co}} \rangle \\
&= \langle \delta^2 \mathcal{G}(\overline{u}) v_R^{\mathrm{co}}, v_R^{\mathrm{co}} \rangle - \big\langle \big(\delta^2 \mathcal{G}(\overline{u}) - \delta^2 \mathcal{G}^R(T_R \overline{u}) \big) v_R^{\mathrm{co}}, v_R^{\mathrm{co}} \big\rangle \\
&\geqslant \frac{c_0}{2} \|D v_R^{\mathrm{co}}\|^2_{\ell^2_\Upsilon}.
\end{aligned} \tag{6.8.65}$$

T_2*: cross term.* Now, we show that the cross term in (6.8.63) vanishes in

the $R \to \infty$ limit. Rewriting T_2, we have

$$\begin{aligned}\mathrm{T}_2 &= \left\langle \delta^2\mathcal{G}^R(T_R\overline{u})v_R^{\mathrm{co}}, v_R^{\mathrm{ff}} \right\rangle \\ &= \left\langle \big(\delta^2\mathcal{G}^R(T_R\overline{u}) - \delta^2\mathcal{G}(\overline{u})\big)v_R^{\mathrm{co}}, v_R^{\mathrm{ff}} \right\rangle \\ &\qquad + \left\langle \delta^2\mathcal{G}(\overline{u})(v_R^{\mathrm{co}} - v), v_R^{\mathrm{ff}} \right\rangle + \left\langle \delta^2\mathcal{G}(\overline{u})v, v_R^{\mathrm{ff}} \right\rangle \end{aligned} \tag{6.8.66}$$

By (6.8.64), the first term of (6.8.66) vanishes as $R \to \infty$ and, since $v_R^{\mathrm{co}} \to v$ strongly in $\dot{\mathscr{W}}^{1,2}(\Lambda)$, the second term in (6.8.66) also vanishes:

$$\left\langle \delta^2\mathcal{G}(\overline{u})(v_R^{\mathrm{co}} - v), v_R^{\mathrm{ff}} \right\rangle \leqslant C\|D(v_R^{\mathrm{co}} - v)\|_{\ell^2_\Upsilon}\|Dv_R^{\mathrm{ff}}\|_{\ell^2_\Upsilon} \to 0 \quad \text{as } R \to \infty.$$

Finally, since $\delta^2\mathcal{G}(\overline{u})v$ is a bounded linear functional on $\dot{\mathscr{W}}^{1,2}(\Lambda)$, we may apply the Riesz representation theorem to conclude that there exists $\Phi \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ such that

$$\left\langle \delta^2\mathcal{G}(\overline{u})v, v_R^{\mathrm{ff}} \right\rangle = \left\langle D\Phi, Dv_R^{\mathrm{ff}} \right\rangle_{\ell^2_\Upsilon}.$$

This quantity vanishes as $R \to \infty$ by the weak convergence of $v_R^{\mathrm{ff}} \rightharpoonup 0$ as $R \to \infty$ (see (6.8.61)).

T_3*: far field term.* Since v_R^{ff} only sees the far field behaviour of the test function, and not the point defect, we may replace $\delta^2\mathcal{G}^R(T_R\overline{u})$ by $\delta^2\mathcal{G}^R_{\mathrm{ref}}$ giving an approximation error of $C\|DT_R\overline{u}\|_{\ell^2_\Upsilon(\Lambda_R\setminus B_{S(R)/2})}$. To do this, we extend v_R^{ff} by zero to $\Lambda_R \cup \Lambda_R^{\mathrm{ref}}$ and note that,

$$\begin{aligned}\left|\mathrm{T}_3 - \left\langle \delta^2\mathcal{G}^R_{\mathrm{ref}}v_R^{\mathrm{ff}}, v_R^{\mathrm{ff}} \right\rangle\right| &= \left|\left\langle \big(\delta^2\mathcal{G}^R(T_R\overline{u}) - \delta^2\mathcal{G}^R_{\mathrm{ref}}\big)v_R^{\mathrm{ff}}, v_R^{\mathrm{ff}} \right\rangle\right| \\ &\leqslant C\|DT_R\overline{u}\|_{\ell^2_\Upsilon(\Lambda_R\setminus B_{S(R)/2})}\|Dv_R^{\mathrm{ff}}\|^2_{\ell^2_\Upsilon}.\end{aligned} \tag{6.8.67}$$

It is now sufficient to prove that there exists $c_1 > 0$ such that

$$\left\langle \delta^2\mathcal{G}^R_{\mathrm{ref}}v_R^{\mathrm{ff}}, v_R^{\mathrm{ff}} \right\rangle \geqslant c_1\|Dv_R^{\mathrm{ff}}\|^2_{\ell^2_\Upsilon}. \tag{6.8.68}$$

A proof of this fact for Bravais lattices can be found in [75] which can be adapted

to the multi-lattice setting. We also give an alternative proof in [96, Appendix I].

Therefore, applying (6.8.67) and (6.8.68) we can conclude that

$$\mathrm{T}_3 = \left\langle \delta^2 \mathcal{G}^R(T_R \overline{u}) v_R^{\mathrm{ff}}, v_R^{\mathrm{ff}} \right\rangle \geqslant \frac{c_1}{2} \|Dv_R^{\mathrm{ff}}\|_{\ell^2_\Upsilon}^2$$

for all R sufficiently large.

Using the fact that $\|Dv_R^{\mathrm{co}}\|_{\ell^2_\Upsilon}^2 + \|Dv_R^{\mathrm{ff}}\|_{\ell^2_\Upsilon}^2 \geqslant \frac{1}{2}\|Dv_R\|_{\ell^2_\Upsilon}^2$ for all sufficiently large R, which follows from [47, Lemma 7.9], allows us to conclude the proof of the stability estimate (6.8.59).

Step 4: Application of the Inverse Function Theorem. The consistency (6.8.58) and stability (6.8.59) estimates allow us to apply the inverse function theorem [88, Lemma B.1] to conclude: for sufficiently large R, there exists $\overline{u}_R$ such that

$$\delta \mathcal{G}^R(\overline{u}_R) = 0 \quad \text{and} \quad \|D\overline{u}_R - D\overline{u}\|_{\ell^2_\Upsilon} \to 0 \text{ as } R \to \infty.$$

Moreover, there exists a constant $c_2 > 0$ such that

$$\left\langle \delta^2 \mathcal{G}^R(\overline{u}_R) v, v \right\rangle \geqslant c_2 \|Dv\|_{\ell^2_\Upsilon}^2 .$$

Proof of Proposition 6.8: $R \to \infty$ in the Grand Canonical Ensemble

Since $\sup_j \|D\overline{u}_{R_j}\|_{\ell^2_\Upsilon} < \infty$, there exists a $\overline{u} \in \dot{\mathscr{W}}^{1,2}(\Lambda)$ such that $\overline{u}_{R_j} \rightharpoonup \overline{u}$ along a subsequence as $j \to \infty$. Using Lemma 6.14 and the fact μ is uniformly bounded away from $\sigma(\mathcal{H}^{R_j}(\overline{u}_{R_j}))$, we obtain $\mu \notin \sigma(\mathcal{H}(\overline{u}))$.

We wish to show that $\delta\mathcal{G}(\overline{u}) = 0$. Using the notation from (6.8.40) and noting that $\overline{u}_{R_j}$ solves $(\mathrm{GCE}_\mu^{\infty,R_j})$ we have, for all $v \in \dot{\mathscr{W}}^{1,2}(\Lambda)$,

$$0 = \left\langle \delta G^{R_j}(u_{R_j}), v \right\rangle = \sum_{\ell \in \Lambda_{R_j}} \mathcal{F}_\ell^{R_j}(u_{R_j}) \cdot v(\ell). \tag{6.8.69}$$

It is sufficient to suppose that $\mathrm{supp}(v) \subseteq B_{R_v}$ for some $R_v > 0$ and show that

$\mathcal{F}_\ell^{R_j}(\overline{u}_{R_j}) \to \mathcal{F}_\ell(\overline{u})$ as $j \to \infty$:

$$|\mathcal{F}_\ell^{R_j}(\overline{u}_{R_j}) - \mathcal{F}_\ell(\overline{u})| \leqslant |\mathcal{F}_\ell^{R_j}(\overline{u}_{R_j}) - \mathcal{F}_\ell^{R_j}(\overline{u})| + |\mathcal{F}_\ell^{R_j}(\overline{u}) - \mathcal{F}_\ell(\overline{u})|. \tag{6.8.70}$$

The first term of (6.8.70) may be treated in the exact same way as in (6.8.43) to conclude that $|\mathcal{F}_\ell^{R_j}(\overline{u}_{R_j}) - \mathcal{F}_\ell^{R_j}(\overline{u})| \to 0$ as $j \to \infty$.

For the second term of (6.8.70) we may use the chain rule formula (6.8.44) to write the forces as sums over site energies. Using the fact that $\ell \in B_{R_v}$ and Lemma 6.17, we have

$$\begin{aligned}
&\sum_{\rho \in \Lambda_{R_j} - \ell} \Big(\mathcal{G}_{\ell-\rho,\rho}^{R_j}(Du(\ell)) - \mathcal{G}_{\ell,\rho}(Du(\ell)) \Big) - \sum_{\rho \in \Lambda \setminus \Lambda_{R_j} - \ell} \mathcal{G}_{\ell,\rho}(Du(\ell)) \\
&\qquad \leqslant \sum_{\rho \in \Lambda_{R_j} - \ell} e^{-\eta(\operatorname{dist}(\ell, \Omega_{R_j}^c) + |\rho|)} - \sum_{\rho \in \Lambda \setminus \Lambda_{R_j} - \ell} e^{-\gamma_{\mathrm{CT}}|\rho|} \\
&\qquad \leqslant C e^{-\frac{1}{2}\eta(R_j - R_v)}.
\end{aligned}$$

where $\eta \coloneqq \frac{1}{2}\mathfrak{m} \min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\}$. We can therefore conclude that $|\mathcal{F}_\ell^{R_j}(\overline{u}) - \mathcal{F}_\ell(\overline{u})| \to 0$ as $j \to \infty$. That is, $\mathcal{F}_\ell(\overline{u}) = 0$ for all $\ell \in \Lambda \cap B_{R_v}$.

Proofs of Theorem 6.9 and Proposition 6.10: $R \to \infty$ in the Canonical Ensemble

Proof of Theorem 6.9. We suppose that $\overline{u}$ is a strongly stable solution to $(\mathrm{GCE}_\mu^{\infty,\infty})$. By Theorem 6.7, there is a sequence of solutions $\overline{u}_R$ to $(\mathrm{GCE}_\mu^{\infty,R})$ with $\overline{u}_R \to \overline{u}$ in $\dot{\mathscr{W}}^{1,2}(\Lambda)$ as $R \to \infty$. This strong convergence means that, by Lemmas 6.11 and 6.14, every isolated eigenvalue of $\sigma(\mathcal{H}(\overline{u}))$ is a limit point of a sequence of eigenvalues contained in $\sigma(\mathcal{H}^R(\overline{u}_R))$ and the accumulation points of every such sequence are contained in $\sigma(\mathcal{H}(\overline{u}))$. Since $\mu \notin \sigma(\mathcal{H}(\overline{u}))$, we can find adjacent points $\underline{\nu}, \overline{\nu} \in \sigma(\mathcal{H}(\overline{u}))$ such that $\underline{\nu} < \mu < \overline{\nu}$. Now, choosing the electron number $N_{e,R} \coloneqq N^{\infty,R}\big(\overline{u}_R; \frac{1}{2}(\underline{\nu} + \overline{\nu})\big)$, and by applying Lemma 6.2, we can conclude that $\varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R) \to \frac{1}{2}(\underline{\nu} + \overline{\nu})$ as $R \to \infty$. Further, the interval between $\varepsilon_{\mathrm{F}}^{\infty,R}(\overline{u}_R)$ and $\frac{1}{2}(\underline{\nu} + \overline{\nu})$ does not intersect $\sigma(\mathcal{H}(\overline{u}))$ for all sufficiently large R. That is, for all sufficiently large R, $\overline{u}_R$ solves $(\mathrm{CE}_{N_{e,R}}^{\infty,R})$. □

Proof of Proposition 6.10. Since $\|D\overline{u}_{R_j}\|_{\ell^2_\Upsilon}$ is uniformly bounded, along a subsequence, $\overline{u}_{R_j} \rightharpoonup \overline{u}$ as $j \to \infty$ for some $\overline{u} \in \dot{\mathscr{W}}^{1,2}(\Lambda)$. Now, because $\sigma(\mathcal{H}^{R_j}(\overline{u}_{R_j}))$ is uniformly bounded, $\varepsilon_{\mathrm{F}}^{\infty,R_j}(\overline{u}_{R_j}) \to \mu$ along a further subsequence as $j \to \infty$ for some $\mu \in \mathbb{R}$.

Supposing that $\sigma(\mathcal{H}^{R_j}(\overline{u}_{R_j}))$ is (eventually) bounded away from $\varepsilon_{\mathrm{F}}^{\infty,R_j}(\overline{u}_{R_j})$, we know that μ is eventually bounded away from $\sigma(\mathcal{H}^{R_j}(\overline{u}_{R_j}))$. This means that, for all j sufficiently large, $\overline{u}_{R_j}$ solves $(\mathrm{GCE}_\nu^{\infty,R})$ for all ν in a neighbourhood of μ. Therefore, by Proposition 6.8, $\overline{u}$ is a critical point of $\mathcal{G}(\,\cdot\,;\mu)$.

We remark here that the boundedness of the sequence $(N_{e,R_j} - N_{\mathrm{b}} \cdot |\Lambda_{R_j}|)_j$ is a necessary condition for the limit μ to be contained in the band gap. We do not state this as an assumption in Proposition 6.10 because we require the stronger condition that μ is (eventually) bounded away from $\sigma(\mathcal{H}^{R_j}(\overline{u}_{R_j}))$. $\square$

APPENDIX A

Notation and Assumptions

A.1 Basic Notation

Sets and Functions

- $|\cdot|$: absolute value on $\mathbb{R}^n$ or $\mathbb{C}$ or the Frobenius matrix norm on $\mathbb{R}^{n\times n}$,
- $\mathbb{N} = \{1, 2, 3, \dots\}$: natural numbers,
- $\mathbb{N}_0 \coloneqq \{0\} \cup \mathbb{N}$: natural numbers including zero,
- $\mathbb{R}_+ \coloneqq \{r \in \mathbb{R} \colon r > 0\}$: positive real numbers,
- $|A| = \#A$: cardinality of A,
- $B_r(x; \|\cdot\|_X) \coloneqq \{y \in X \colon \|x - y\|_X < r\}$: open ball of radius r about x in $(X, \|\cdot\|_X)$,
- $\operatorname{dist}(z, A) \coloneqq \inf_{a\in A} |z - a|$: distance between z and the set A,
- $\operatorname{dist}(A, B) \coloneqq \max\{\sup_{a\in A} \operatorname{dist}(a, B), \sup_{b\in B} \operatorname{dist}(b, A)\}$: Hausdorff distance between A and B,
- $B_\varepsilon(A) \coloneqq \{z \colon \operatorname{dist}(z, A) < \varepsilon\}$: open ball of radius ε about A,

- $a + bC \coloneqq \{a + bc \colon c \in C\}$,
- $[a, b] \coloneqq \{(1-t)a + tb \colon t \in [0,1]\}$: closed interval between $a, b \in \mathbb{R}^n$ or $\mathbb{C}$,
- $\operatorname{conv} A \coloneqq \{(1-t)a + tb \colon a, b \in A, t \in [0,1]\}$: convex hull of A,
- $\liminf_{n\to\infty} A_n \coloneqq \{a \colon \exists a_n \in A_n \text{ s.t. } a_n \to a\}$,
- $\limsup_{n\to\infty} A_n \coloneqq \{a \colon \exists a_n \in A_n \text{ s.t. } a_n \to a \text{ along a subsequence}\}$,
- $\lim_{n\to\infty} A_n$: (topological) limit of (A_n); defined and equal to both $\liminf_{n\to\infty} A_n$ and $\limsup_{n\to\infty} A_n$ in the case that these limits agree,
- $\chi_{A_0} \colon A \to \{0,1\}$: characteristic function of A_0 on A; function with $\chi_{A_0} = 1$ on A_0 and $\chi_{A_0} = 0$ on $A \setminus A_0$,
- $f|_{A_0}$: restriction of f to A_0,
- $\operatorname{supp} f$: support of f,
- $\|f\|_{L^\infty(A)} \coloneqq \sup_{x\in A} |f(x)|$: sup-norm of f on A,

Contour Integrals

- $\operatorname{len} \mathscr{C}$: length of the simple closed positively oriented contour $\mathscr{C}$,
- $\|O\|_{\mathscr{C}} \coloneqq \frac{\operatorname{len}\mathscr{C}}{2\pi} \sup_{z\in\mathscr{C}} |O(z)|$,
- $\oint_{\mathscr{C}}$: contour integral around $\mathscr{C}$,
- $\int_a^b \coloneqq \int_{[a,b]}$: integral between a and b in $\mathbb{C}$,

Sequences and Operators

- $\ell^p(\Lambda; \mathbb{R}^n)$: space of sequences ψ for which $\|\psi\|_{\ell^p} \coloneqq \left(\sum_{\ell\in\Lambda} |\psi_\ell|^p\right)^{1/p}$ is finite,
- $\ell^\infty(\Lambda; \mathbb{R}^n)$: space of bounded sequences with $\|\psi\|_{\ell^\infty} \coloneqq \sup_{\ell\in\Lambda} |\psi_\ell|$,
- $\|T\|_{X\to Y} \coloneqq \sup_{x\in X, \|x\|_X = 1} \|Tx\|_Y$: operator norm of $T \colon X \to Y$,
- $\|T\|_{\mathrm{F}}$: Hilbert-Schmidt norm of T, a bounded linear operator on a Hilbert space,

- $\sigma(T)$: spectrum of operator T,
- $\sigma_{\text{disc}}(T)$: discrete spectrum; isolated eigenvalues of finite multiplicity,
- $\sigma_{\text{ess}}(T) \coloneqq \sigma(T) \setminus \sigma_{\text{disc}}(T)$: essential spectrum,
- $\operatorname{Tr} T$: trace of the operator T,
- $\operatorname{tr} T_{ij}$: trace of the (i,j)-block of the block matrix T; i.e. $\operatorname{Tr} T = \sum_i \operatorname{tr} T_{ii}$,
- Id_n : $n \times n$ identity matrix,
- A^{T} : transpose of matrix A,
- $\|A\|_{\max} = \max_{i,j} |A_{ij}|$: maximum-norm of an operator,

Other Notation

- δ_{ij} : Kronecker delta,
- $\delta(\,\cdot\,)$: Dirac delta; distribution with $\delta(f) = \int f(x) \mathrm{d}\delta(x) \coloneqq f(0)$,
- C : generic positive constant that may change in calculations from one line to the next. C will always be independent of important quantities such as Fermi-temperature and the band gap. The dependencies of C will normally be clear from context or stated explicitly,
- $f \lesssim g$: $f \leqslant Cg$ for a generic positive constant as above,
- $f \sim g$ as $x \to x_0 \in \mathbb{R} \cup \{\pm\infty\}$ or $\mathbb{C} \cup \{\infty\}$: there exists an open neighbourhood U of x_0 and positive constants $c_1, c_2 > 0$ such that $c_1 g(x) \leqslant f(x) \leqslant c_2 g(x)$ for all $x \in U$,
- $\operatorname{supp} \nu$: support of the measure ν; set of all x for which every open neighbourhood of x has non-zero measure,
- For multiindices θ, we write $|\theta|_1 \coloneqq \sum_j \theta_j$ and $|\theta|_\infty \coloneqq \max_j \theta_j$,
- $\langle \delta\mathcal{G}(u), v\rangle, \langle \delta^2\mathcal{G}(u)v, w\rangle, \langle \delta^3\mathcal{G}(u)v, w, z\rangle$: first, second, and third variations of $\mathcal{G} \in C^3(X)$.

A.2 Atomic configurations

- $\boldsymbol{r} = \{\boldsymbol{r}_\ell\}_{\ell\in\Lambda} \subseteq \mathbb{R}^d$: atomic positions for some finite or countable index set Λ,

- $\boldsymbol{X}_\ell \coloneqq (\boldsymbol{r}_\ell, v_\ell, Z_\ell)$: state of atom ℓ where v_ℓ is the effective potential and Z_ℓ is the atomic species,

- $\boldsymbol{X}_{\ell k} \coloneqq (\boldsymbol{r}_{\ell k}, v_\ell, v_k, Z_\ell, Z_k)$: state of atom k relative to the central site ℓ where $\boldsymbol{r}_{\ell k} \coloneqq \boldsymbol{r}_k - \boldsymbol{r}_\ell$. Moreover, we write $r_{\ell k} \coloneqq |\boldsymbol{r}_{\ell k}|$,

- $\nabla^j h(\boldsymbol{X}_{\ell k})$: derivatives with respect to relative atomic positions. For functions h, independent of the effective potential, we write $\nabla^0 h(\boldsymbol{X}_{\ell k}) \coloneqq h(\boldsymbol{X}_{\ell k})$ and

$$\big[\nabla^j h(\boldsymbol{X}_{\ell k})\big]_{i_1\dots i_j} \coloneqq \left.\frac{\partial^j \big(\xi \mapsto h((\xi, v_\ell, v_k, Z_\ell, Z_k))\big)}{\partial\xi_{i_1}\dots\partial\xi_{i_j}}\right|_{\xi=\boldsymbol{r}_{\ell k}}$$

  for each $1 \leqslant i_1, \dots, i_j \leqslant d$. We use $\nabla^j t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km})$ for derivatives of the function $(\xi,\zeta) \in \mathbb{R}^{2d} \mapsto t\big((\xi, v_\ell, v_m, Z_\ell, Z_m), (\zeta, v_k, v_m, Z_k, Z_m)\big)$ at $(\xi,\zeta) = (\boldsymbol{r}_{\ell m}, \boldsymbol{r}_{km})$. Sometimes it will be useful to use the following:

$$\begin{aligned}
[\boldsymbol{\nabla}^{\otimes j} t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km})]_{\alpha_1\dots\alpha_j} &\coloneqq \nabla_{\alpha_1}\dots\nabla_{\alpha_j} t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km}), \qquad \text{and} \\
\big\langle \boldsymbol{\nabla}^{\otimes j} t\,; v_1, \dots, v_j\big\rangle &\coloneqq \sum_{1\leqslant\alpha_1,\dots,\alpha_j\leqslant 2} [\boldsymbol{\nabla}^{\otimes j} t]_{\alpha_1\dots\alpha_j} [v_1]_{\alpha_1}\dots[v_j]_{\alpha_j}, \qquad \text{(A.2.1)}
\end{aligned}$$

  where $\boldsymbol{\nabla} \coloneqq (\nabla_1, \nabla_2)^{\mathrm{T}}$ and ∇_ι denotes the derivative with respect to the $\iota \in \{1,2\}$ component.

- $\boldsymbol{X} = \{\boldsymbol{X}_\ell\}_{\ell\in\Lambda} = (\boldsymbol{r}, v, Z)$: whole atomic configuration,

- $\frac{\partial}{\partial \boldsymbol{X}_n}$: derivative with respect to $\boldsymbol{X}_n$. That is, for functions f with values in Y, we denote by $\frac{\partial f(\boldsymbol{X})}{\partial \boldsymbol{X}_n} \in Y^{1+d}$ the following derivative

$$\left[\frac{\partial f(\boldsymbol{X})}{\partial \boldsymbol{X}_n}\right]_l = \begin{cases} \frac{\partial f(\boldsymbol{X})}{\partial v_n} & \text{if } l = 0, \\ \frac{\partial f(\boldsymbol{X})}{\partial [\boldsymbol{r}_n]_l} & \text{if } 1 \leqslant l \leqslant d. \end{cases}$$

- $|\cdot|$: Euclidean norm on $\mathbb{R}^n$ or $\mathbb{C}$ or the Frobenius matrix norm: *e.g.* for a function h with values in a normed space $(Y, |\cdot|_Y)$,

$$\big|\nabla^j h(\boldsymbol{X}_{\ell k})\big| \coloneqq \sqrt{\sum_{i_1,\dots,i_j=1}^{d} \big|\nabla^j h(\boldsymbol{X}_{\ell k})_{i_1\dots i_j}\big|_Y^2}$$

(for us $Y = \mathbb{R}^{N_\mathrm{b}\times N_\mathrm{b}}$ and $|A|_Y \coloneqq \sqrt{\sum_{ab}|A_{ab}|^2}$ again denotes a Frobenius matrix norm).

A.3 Summary of the Assumptions

In this section we summarise the main assumptions of this thesis:

- **(AC)**, p.g. 13 : atomic configurations for which $r_{\ell k} \geqslant \mathfrak{m}$ and $|v_\ell| \leqslant \mathfrak{c}$,
- **(TB)**, p.g. 14 : tight binding Hamiltonian $\mathcal{H}(\boldsymbol{X})_{\ell k} \in \mathbb{R}^{N_\mathrm{b}\times N_\mathrm{b}}$ given by

$$\mathcal{H}(\boldsymbol{X})_{\ell k} = h(\boldsymbol{X}_{\ell k}) + \sum_{m\notin\{\ell,k\}} t(\boldsymbol{X}_{\ell m}, \boldsymbol{X}_{km}) + \delta_{\ell k} v_\ell \mathrm{Id}_{N_\mathrm{b}},$$

- **($\mathbf{P}_\delta$)**, p.g. 16 : a pair $(\boldsymbol{X}, \boldsymbol{X}^\mathrm{d})$ where $\boldsymbol{X}^\mathrm{d}$ is a point defect configuration relative to $\boldsymbol{X}$,
- **(SC)**, p.g. 83 : self-consistency, $\rho_\ell = F_\ell^\beta\big(\boldsymbol{X}(\rho)\big)$ for all $\ell \in \Lambda$,
- **(Stab)**, p.g. 85 : stability, $I - \mathscr{L}(\rho)\colon \ell^2(\Lambda) \to \ell^2(\Lambda)$ is invertible,
- **(Gap)**, p.g. 107 : spectral gap in the homogeneous system,
- **(L)**, p.g. 108 : uniform non-interpeneration condition,
- **($\mathbf{Ref}_R$)**, p.g. 109 : supercell model.

APPENDIX B

Mathematical Formulation of the Tight Binding Models

B.1 Non-constant Number of Atomic Orbitals Per Atom

As noted in §2.2, the number of atomic orbitals per atom should be able to depend on the atomic species. That is, for $\ell \in \Lambda$, the number $N_{\mathrm{b}}(\ell)$ of atomic orbitals corresponding to ℓ may depend on Z_ℓ. In particular, the size of the blocks $\mathcal{H}(\boldsymbol{X})_{\ell k}$ depend on (Z_ℓ, Z_k): the entries $\mathcal{H}(\boldsymbol{X})_{\ell k,ab}$ are well-defined for orbital indices $1 \leqslant a \leqslant N_{\mathrm{b}}(\ell)$ and $1 \leqslant b \leqslant N_{\mathrm{b}}(k)$ (see, (1.2.1)).

We may assume without loss of generality that the spectrum $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$ is bounded below by a positive constant. If not, we may artificially add a constant multiple of the identity $z_0\mathrm{Id}$ to the Hamiltonian to shift the spectrum of $\mathcal{H}(\boldsymbol{X})$ away from $\{0\}$. This modification does not affect the local observables (2.4.1) as long as the integration contour and function arguments are also shifted away from $\{0\}$ by z_0 (i.e. consider $O(\,\cdot\, - z_0)$ and integration over $\mathscr{C}_O + z_0$). We may therefore assume that $\mathscr{C}_O$ does not encircle $\{0\}$.

Now, by defining $N_{\mathrm{b}} \coloneqq \max_{\ell\in\Lambda} N_{\mathrm{b}}(\ell)$, we may extend the definition of the

Hamiltonian by adding additional zero rows and columns:

$$\widetilde{\mathcal{H}}(\boldsymbol{X})_{\ell k,ab} \coloneqq \begin{cases} \mathcal{H}(\boldsymbol{X})_{\ell k,ab} & \text{if } 1 \leqslant a \leqslant N_{\mathrm{b}}(\ell) \text{ and } 1 \leqslant b \leqslant N_{\mathrm{b}}(k) \\ 0 & \text{if } N_{\mathrm{b}}(\ell) < a \leqslant N_{\mathrm{b}} \text{ or } N_{\mathrm{b}}(k) < b \leqslant N_{\mathrm{b}} \end{cases}$$

which possibly introduces 0 as an eigenvalue but does not affect the rest of the spectrum.

Therefore, the modified Hamiltonian $\widetilde{\mathcal{H}}(\boldsymbol{X})$ satisfies **(TB)** and, in addition, we have

$$\begin{aligned} O_\ell(\boldsymbol{X}) &= \operatorname{tr}\Big[\oint_{\mathscr{C}_O} O(z)\big(z - \mathcal{H}(\boldsymbol{X})\big)^{-1} \frac{\mathrm{d}z}{2\pi i}\Big]_{\ell\ell} \\ &= \operatorname{tr}\Big[\oint_{\mathscr{C}_O} O(z)\big(z - \widetilde{\mathcal{H}}(\boldsymbol{X})\big)^{-1} \frac{\mathrm{d}z}{2\pi i}\Big]_{\ell\ell}. \end{aligned} \tag{B.1.1}$$

Here, we have used the fact that the integration contour $\mathscr{C}_O$ does not encircle $\{0\}$. In particular, local observables corresponding to $\mathcal{H}(\boldsymbol{X})$ and $\widetilde{\mathcal{H}}(\boldsymbol{X})$ are identical and we may assume that the number of atomic orbitals per atom is constant.

B.2 Band Structure of a Multi-lattice Reference Configuration

We suppose that Λ^{ref} is a multilattice reference configuration: consider a finite unit cell $\Gamma \subseteq \Lambda^{\mathrm{ref}}$ satisfying $\Lambda^{\mathrm{ref}} = \bigcup_{\gamma\in\mathbb{Z}^d}(\Gamma + \mathsf{A}\gamma)$ and $\Gamma + \mathsf{A}\gamma$ are pairwise disjoint for all $\gamma \in \mathbb{Z}^d$ where $\mathsf{A} \in \mathbb{R}^{d\times d}$ is an invertible matrix. We consider the band structure of general self-adjoint operators $T\colon \ell^2(\Lambda^{\mathrm{ref}};\mathbb{C}^n) \to \ell^2(\Lambda^{\mathrm{ref}};\mathbb{C}^n)$ satisfying $T_{\ell+\mathsf{A}\gamma,k+\mathsf{A}\gamma} = T_{\ell k}$ for all $\ell, k \in \Gamma$ and $\gamma \in \mathbb{Z}^d$.

For $\xi \in \mathbb{R}^d$ and $\psi \in \ell^2(\Lambda^{\mathrm{ref}};\mathbb{C}^n)$, we define $(U\psi)_\xi \in \ell^2(\Lambda^{\mathrm{ref}};\mathbb{C}^n)$ by

$$(U\psi)_\xi(\ell) \coloneqq \sum_{\gamma\in\mathbb{Z}^d} \psi(\ell + \mathsf{A}\gamma) e^{-i(\ell+\mathsf{A}\gamma)\cdot\xi}. \tag{B.2.1}$$

We suppose that $\Gamma^\star \subseteq \mathbb{R}^d$ is a bounded connected domain containing the

origin such that $\mathbb{R}^d$ is the disjoint union of $\Gamma^\star + 2\pi\mathsf{A}^{-\mathrm{T}}\eta$ for $\eta \in \mathbb{Z}^d$. In particular, for $\xi \in \mathbb{R}^d$, there exist unique $\eta \in \mathbb{Z}^d$ and $\xi_0 \in \Gamma^\star$ such that $\xi = \xi_0 + 2\pi\mathsf{A}^{-\mathrm{T}}\eta$ and so $e^{-i\mathsf{A}\gamma\cdot\xi} = e^{-i\mathsf{A}\gamma\cdot\xi_0}e^{-i\mathsf{A}\gamma\cdot 2\pi\mathsf{A}^{-\mathrm{T}}\eta} = e^{-i\mathsf{A}\gamma\cdot\xi_0}$ for any $\gamma \in \mathbb{Z}^d$. We therefore restrict ξ to $\Gamma^\star$ and define $U\colon \ell^2(\Lambda^{\mathrm{ref}};\mathbb{C}^n) \to L^2\big(\Gamma^\star;\ell^2(\Gamma;\mathbb{C}^n)\big)$ by (B.2.1). This operator is unitary between the Hilbert spaces $\ell^2(\Lambda^{\mathrm{ref}};\mathbb{C}^n)$ and $L^2\big(\Gamma^\star;\ell^2(\Gamma;\mathbb{C}^n)\big)$ with inner products

$$\langle\psi,\phi\rangle_{\ell^2(\Lambda^{\mathrm{ref}})} \coloneqq \sum_{\ell\in\Lambda^{\mathrm{ref}}} \psi(\ell)\cdot\overline{\phi(\ell)} = \sum_{\ell\in\Lambda^{\mathrm{ref}}}\sum_{i=1}^{n}\psi(\ell)_i\overline{\phi(\ell)_i} \qquad \text{and}$$
$$\langle\Psi,\Phi\rangle_{L^2(\Gamma^\star;\ell^2)} \coloneqq \fint_{\Gamma^\star}\langle\Psi_\xi,\Phi_\xi\rangle_{\ell^2(\Gamma)}\mathrm{d}\xi = \sum_{\ell\in\Gamma}\fint_{\Gamma^\star}\Psi_\xi(\ell)\cdot\overline{\Phi_\xi(\ell)}\mathrm{d}\xi,$$

respectively. Therefore, we may write

$$\begin{aligned}(UT\psi)_\xi(\ell) &= \sum_{\gamma\in\mathbb{Z}^d}\sum_{k\in\Lambda^{\mathrm{ref}}} T_{\ell+\mathsf{A}\gamma,k}\psi(k)e^{-i(\ell+\mathsf{A}\gamma)\cdot\xi}\\ &= \sum_{k\in\Gamma}\sum_{\eta\in\mathbb{Z}^d}\Big(\sum_{\gamma\in\mathbb{Z}^d} T_{\ell+\mathsf{A}\gamma,k+\mathsf{A}\eta}e^{-i(\ell-k+\mathsf{A}(\gamma-\eta)\cdot\xi}\Big)\psi(k+\mathsf{A}\eta)e^{-i(k+\mathsf{A}\eta)\cdot\xi}\\ &= \sum_{k\in\Gamma}\Big(\sum_{\gamma\in\mathbb{Z}^d} T_{\ell+\mathsf{A}\gamma,k}e^{-i(\ell-k+\mathsf{A}\gamma)\cdot\xi}\Big)(U\psi)_\xi(k) =: \big[T_\xi(U\psi)_\xi\big](\ell)\end{aligned}$$

where T_ξ is the operator $\ell^2(\Gamma;\mathbb{C}^n) \to \ell^2(\Gamma;\mathbb{C}^n)$ with matrix entries $\big[T_\xi\big]_{\ell k} = \sum_{\gamma\in\mathbb{Z}^d} T_{\ell+\mathsf{A}\gamma,k}e^{-i(\ell-k+\mathsf{A}\gamma)\cdot\xi}$.

Therefore, since U is unitary, we have

$$\sigma(T) = \bigcup_{\xi\in\Gamma^\star}\sigma(T_\xi).$$

Moreover, the eigenvalues of T_ξ may be chosen to be continuous functions of $\xi \in \Gamma^\star$ [62].

B.3 Exponential Sums

Throughout this thesis, we frequently apply the following estimate:

Lemma B.1. *Suppose $\boldsymbol{X}$ is a configuration satisfying* **(AC)** *with the constant*

$\mathfrak{m}$. *Then, for* $\gamma \geqslant \eta \geqslant 0$, *we have*

$$\sum_{m\in\Lambda} e^{-\gamma\, r_{\ell m}} e^{-\eta\, r_{mk}} \leqslant \frac{C_d}{(\mathfrak{m}\gamma)^d} e^{-\frac{1}{2}\eta\, r_{\ell k}}$$

where C_d *is a constant depending only on* d.

Proof. Since $\gamma r_{\ell m} + \eta r_{mk} \geqslant \eta r_{\ell k}$ and $\gamma r_{\ell m} + \eta r_{mk} \geqslant \gamma r_{\ell m}$, we obtain

$$\sum_{m\in\Lambda} e^{-\gamma\, r_{\ell m}} e^{-\eta\, r_{mk}} \leqslant \left(\sum_{m\in\Lambda} e^{-\frac{1}{2}\gamma\, r_{\ell m}}\right) e^{-\frac{1}{2}\eta\, r_{\ell k}}. \tag{B.3.1}$$

To conclude, we approximate the summation in (B.3.1) with an integral. To do so, we note that $e^{-\gamma\, r_{\ell m}} \leqslant e^{-\gamma|\boldsymbol{r}-\boldsymbol{r}_\ell|}$ for all $\boldsymbol{r} \in B_{r_{\ell m}}(\boldsymbol{r}_\ell)$, the sets $B_{r_{\ell m}}(\boldsymbol{r}_\ell) \cap B_{\mathfrak{m}/2}(\boldsymbol{r}_m)$ are pairwise disjoint for $m \neq \ell$, and, after denoting the d-dimensional Lebesgue measure by $\mathcal{L}_d$, we have $\mathcal{L}_d\big(B_{r_{\ell m}}(\boldsymbol{r}_\ell) \cap B_{\mathfrak{m}/2}(\boldsymbol{r}_m)\big) \geqslant c_d \mathfrak{m}^d$ where $c_d = \mathcal{L}_d\big(B_1(0) \cap B_{1/2}(\boldsymbol{r})\big)$ for $|\boldsymbol{r}| = 1$. For a schematic plot summarising these properties, see Fig. B.1.

We therefore obtain

$$\begin{aligned}\sum_{m\neq\ell} e^{-\gamma\, r_{\ell m}} &\leqslant \sum_{m\neq\ell} \fint_{B_{r_{\ell m}}(\boldsymbol{r}_\ell)\cap B_{\mathfrak{m}/2}(\boldsymbol{r}_m)} e^{-\gamma|\boldsymbol{r}-\boldsymbol{r}_\ell|}\mathrm{d}\boldsymbol{r} \leqslant \frac{1}{c_d\mathfrak{m}^d}\int_{\mathbb{R}^d} e^{-\gamma|\boldsymbol{r}|}\mathrm{d}\boldsymbol{r} \\ &= \frac{\mathcal{L}_d(B_1)}{c_d\mathfrak{m}^d}\int_0^\infty e^{-\gamma r} r^{d-1}\mathrm{d}r = \frac{\mathcal{L}_d(B_1)}{c_d\mathfrak{m}^d}\frac{(d-1)!}{\gamma^d}\end{aligned}$$

where the final equality can be shown by induction. □

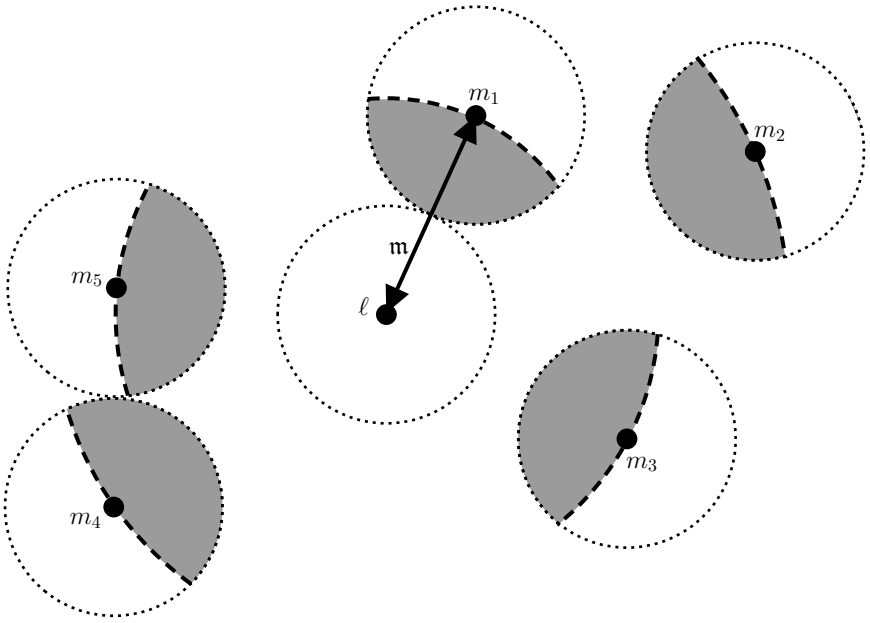


Figure B.1: Schematic plot to demonstrate the proof of Lemma B.1. Dotted circles represent the pairwise disjoint sets $B_{\mathfrak{m}/2}(\boldsymbol{r}_m)$. Dashed arcs lie on $\partial B_{r_{\ell m}}(\boldsymbol{r}_\ell)$. For $\boldsymbol{r}$ in the shaded region nearest m_j (i.e. $\boldsymbol{r} \in B_{\mathfrak{m}/2}(\boldsymbol{r}_{m_j}) \cap B_{r_{\ell m_j}}(\boldsymbol{r}_\ell)$), we have $e^{-\gamma\, r_{\ell m_j}} \leqslant e^{-\gamma|\boldsymbol{r}-\boldsymbol{r}_\ell|}$. Moreover, the volume of each shaded region is bounded below by $c_d\mathfrak{m}^d = \mathcal{L}_d\big(B_{\mathfrak{m}/2}(\boldsymbol{r}_{m_1}) \cap B_{r_{\ell m_1}}(\boldsymbol{r}_\ell)\big)$ since $r_{\ell m_1} = \mathfrak{m}$.

APPENDIX C

Body-ordered Approximations

of the Potential Energy Landscape

C.1 Truncation of the Atomic Environment

We have seen that analytic quantities of interest may be approximated by body-order approximations. However, each polynomial depends on the whole atomic configuration $\boldsymbol{X}$. In this section, we consider the truncation of the approximation schemes to a neighbourhood of the central site ℓ and prove the exponential convergence of the corresponding sparse representation.

C.1.1 Banded Approximation

One intuitive approach is to restrict the interaction range globally and consider the following *banded approximation*:

$$[\widetilde{\mathcal{H}}^{r_\mathrm{c}}]_{km} \coloneqq \begin{cases} h(\boldsymbol{X}_{km}) + \sum\limits_{\substack{m' \notin \{k,m\}: \\ r_{km'}, r_{mm'} \leqslant r_\mathrm{c}}} t(\boldsymbol{X}_{km'}, \boldsymbol{X}_{mm'}) + \delta_{km} v_k \mathrm{Id}_{N_\mathrm{b}} & \text{if } r_{km} \leqslant r_\mathrm{c} \\ 0 & \text{otherwise.} \end{cases} \tag{C.1.1}$$

Therefore, approximating $O_\ell(\boldsymbol{X})$ with a function depending on the first N moments $[(\widetilde{\mathcal{H}}^{r_c})^n]_{\ell\ell}$ (e.g. applying Theorem 4.3 or 4.4 to $\widetilde{\mathcal{H}}^{r_c}$) results in an approximation scheme depending only on finitely many atomic sites in a neighbourhood of ℓ. This can be seen from the fact that

$$[(\widetilde{\mathcal{H}}^{r_c})^n]_{\ell\ell} = \sum_{\substack{\ell_1,\dots,\ell_{n-1} \\ r_{\ell\ell_1}, r_{\ell_1\ell_2},\dots,r_{\ell_{n-1}\ell} \leqslant r_c}} \mathcal{H}_{\ell\ell_1}\mathcal{H}_{\ell_1\ell_2}\dots\mathcal{H}_{\ell_{n-1}\ell}. \tag{C.1.2}$$

Moreover, we obtain appropriate error estimates by combining Theorem 4.3 or 4.4 with the following estimate:

Proposition C.1. *Suppose $\boldsymbol{X}$ satisfies Definition 2.2. Fix $0 < \beta \leqslant \infty$ and suppose that, if $\beta = \infty$, then $\mathsf{g} > 0$. Then, we have*

$$\left| O_\ell(\boldsymbol{X}) - \operatorname{tr} O\big(\widetilde{\mathcal{H}}^{r_c}(\boldsymbol{X})\big)_{\ell\ell} \right| \lesssim e^{-\frac{1}{2}\gamma_0 r_c}.$$

Suppose $\gamma_N(r_c)$ and $\gamma_N^{\mathrm{def}}(r_c)$ are the rates of approximation from Theorems 4.3 and 4.4 when applied to $\widetilde{\mathcal{H}}^{r_c}$. Then $\gamma_N(r_c) \to \gamma_N$ and $\gamma_N^{\mathrm{def}}(r_c) \to \gamma_N^{\mathrm{def}}$ as $r_c \to \infty$, with an exponential rate.

Proof. We first note that

$$\Big[\mathcal{H}(\boldsymbol{X}) - \widetilde{\mathcal{H}}^{r_c}(\boldsymbol{X})\Big]_{km} = \begin{cases} \mathcal{H}(\boldsymbol{X})_{km} & \text{if } r_{km} > r_c \\ \sum_{\substack{m': \\ r_{km'} > r_c \text{ or } r_{mm'} > r_c}} t(\boldsymbol{X}_{km'}, \boldsymbol{X}_{mm'}) & \text{if } r_{km} \leqslant r_c. \end{cases} \tag{C.1.3}$$

Therefore, applying **(TB)**, we obtain

$$\big|[\mathcal{H}(\boldsymbol{X}) - \widetilde{\mathcal{H}}^{r_c}(\boldsymbol{X})]_{km}\big| \lesssim e^{-\frac{1}{2}\gamma_0 r_c} \sum_{m'} e^{-\frac{1}{2}\gamma_0 (r_{km'} + r_{mm'})} \lesssim e^{-\frac{1}{2}\gamma_0 r_c} e^{-\frac{1}{4}\gamma_0 r_{km}}. \tag{C.1.4}$$

To conclude we choose a suitable contour $\mathscr{C}$ and apply the Combes-Thomas

estimate (Lemma 3.3) together with (C.1.4):

$$\begin{aligned}
&\Big|O_\ell(\boldsymbol{X}) - \operatorname{tr} O\big(\widetilde{\mathcal{H}}^{r_\mathrm{c}}(\boldsymbol{X})\big)_{\ell\ell}\Big| \\
&\leqslant \left|\frac{\operatorname{tr}}{2\pi}\oint_{\mathscr{C}} O(z)\Big[(\mathcal{H}(\boldsymbol{X})-z)^{-1}\big(\mathcal{H}(\boldsymbol{X})-\widetilde{\mathcal{H}}^{r_\mathrm{c}}(\boldsymbol{X})\big)(\widetilde{\mathcal{H}}^{r_\mathrm{c}}(\boldsymbol{X})-z)^{-1}\Big]_{\ell\ell}\mathrm{d}z\right| \\
&\lesssim \|O\|_{\mathscr{C}} e^{-\frac{1}{2}\gamma_0 r_\mathrm{c}} \sum_{km} e^{-\gamma_{\mathrm{CT}}(r_{\ell k}+r_{m\ell})} e^{-\frac{1}{4}\gamma_0 r_{km}} \lesssim e^{-\frac{1}{2}\gamma_0 r_\mathrm{c}} \qquad \text{(C.1.5)}
\end{aligned}$$

As a consequence of (C.1.4), we have $\|\mathcal{H}(\boldsymbol{X}) - \widetilde{\mathcal{H}}^{r_\mathrm{c}}(\boldsymbol{X})\|_{\ell^2\to\ell^2} \lesssim e^{-\frac{1}{2}\gamma_0 r_\mathrm{c}}$ and so $\operatorname{dist}\big(\sigma(\mathcal{H}), \sigma(\widetilde{\mathcal{H}}^{r_\mathrm{c}})\big) \lesssim e^{-\frac{1}{2}\gamma_0 r_\mathrm{c}}$ [76]. This means that for sufficiently large r_c, we obtain the same rates of approximation when applying Theorems 4.3 and 4.4 to $\widetilde{\mathcal{H}}^{r_\mathrm{c}}$. □

C.1.2 Truncation

One downside of the banded approximation is that the truncation radius depends on the maximal polynomial degree (e.g. see (C.1.2)). In this section, we consider truncation schemes that only depend on finitely many atomic sites independent of the polynomial degree:

$$\widetilde{\mathcal{H}}^{r_\mathrm{c}} \coloneqq \mathcal{H}\big|_{\ell;\Lambda\cap B_{r_\mathrm{c}}(\ell)} \qquad \text{(C.1.6)}$$

where the restriction of the Hamiltonian has been introduced in (4.5.1).

On defining the quantities

$$I_N\widetilde{O}_\ell(\boldsymbol{X}) \coloneqq \operatorname{tr}\big[I_N O\big(\widetilde{\mathcal{H}}^{r_\mathrm{c}}\big)\big]_{\ell\ell}, \qquad \text{(C.1.7)}$$

where the operators I_N are given by Theorem 4.2, we obtain a sparse representation of the N-body approximation depending only on finitely many atomic sites, independently of the maximal body-order N.

Proposition C.2. *Suppose $\boldsymbol{X}$ satisfies Definition 2.2. Fix $0 < \beta \leqslant \infty$ and suppose that, if $\beta = \infty$, then $\mathsf{g} > 0$. Then,*

$$\big|I_N O_\ell^\beta(\boldsymbol{X}) - I_N\widetilde{O}_\ell^\beta(\boldsymbol{X})\big| \lesssim e^{-\frac{1}{4}\min\{\gamma_{\mathrm{CT}},\gamma_0\}r_\mathrm{c}}$$

where $O^\beta = F^\beta$ or G^β and γ_{CT} is the constant from Lemma 3.3.

Proof. Applying the Hermite integral formula (4.8.1) directly, we conclude that $I_N O^\beta(z)$ is bounded uniformly in N along a suitably chosen contour $\mathscr{C} \coloneqq \{g_E = \gamma\}$ (examples of such contours are given in Figure 4.4). It is important to note that the contour $\mathscr{C}$ must be chosen to encircle both $\sigma(\mathcal{H})$ and $\sigma(\widetilde{\mathcal{H}}^{r_{\mathrm{c}}})$. In the following, we let γ_{CT} be the Combes-Thomas exponent from Lemma 3.3 corresponding to $\mathcal{H}$.

Similarly to (C.1.5), we obtain

$$\begin{aligned}
&\left| I_N O_\ell^\beta(\boldsymbol{X}) - I_N \widetilde{O}_\ell^\beta(\boldsymbol{X}) \right| \\
&\lesssim \|I_N O\|_{\mathscr{C}} \sum_{km} e^{-\gamma_{\mathrm{CT}} r_{\ell k}} \left| \left[\mathcal{H}(\boldsymbol{X}) - \widetilde{\mathcal{H}}^{r_{\mathrm{c}}}(\boldsymbol{X}) \right]_{km} \right| \\
&\lesssim \sum_{\substack{k,m: \\ r_{\ell k} \geqslant r_{\mathrm{c}} \text{ or } r_{\ell m} \geqslant r_{\mathrm{c}}}} e^{-\gamma_{\mathrm{CT}} r_{\ell k}} e^{-\frac{1}{2}\gamma_0 r_{km}} + \sum_{\substack{k,m: \\ r_{\ell k}, r_{\ell m} < r_{\mathrm{c}}}} e^{-\gamma_{\mathrm{CT}} r_{\ell k}} \sum_{\substack{m': \\ r_{\ell m'} \geqslant r_{\mathrm{c}}}} e^{-\gamma_0 (r_{km'} + r_{mm'})} \\
&\lesssim e^{-\frac{1}{2}\min\{\gamma_{\mathrm{CT}}, \frac{1}{2}\gamma_0\} r_{\mathrm{c}}}. \qquad \text{(C.1.8)}
\end{aligned}$$

This concludes the proof. □

C.1.3 Divide-and-conquer Methods

The truncation scheme considered in §C.1.2 is closely related to the divide-and-conquer method for solving the electronic structure problem [132]. In this context the system is split into many subsystems that are only related through a global choice of Fermi level. In our notation, this method consists of constructing N_{DAC} smaller Hamiltonians $\widetilde{\mathcal{H}}^{r_{\mathrm{c}}, \ell_j}$ centred on the atoms ℓ_j (for $j = 1, \ldots, N_{\mathrm{DAC}}$) and approximating the quantities $O_\ell(\boldsymbol{X})$ for ℓ in a small neighbourhood of ℓ_j by calculating $\operatorname{tr} O\big(\widetilde{\mathcal{H}}^{r_{\mathrm{c}}, \ell_j}\big)_{\ell\ell}$. That is, the eigenvalue problem for the whole system is approximated by solving N_{DAC} smaller eigenvalue problems in parallel. In particular, this method leads to linear scaling algorithms [57]. Theorem C.2 then ensures that the error in this approximation decays exponentially with the distance between ℓ and the exterior of the subsystem centred on ℓ_j.

A similar error analysis in the context of divide-and-conquer methods in Kohn-Sham density functional theory can be found in [30].

C.1.4 General truncation operators

It should be clear from the proof of Proposition C.2 that more general truncation operators may be used. Indeed, Proposition C.2 is satisfied for all truncation operators $\widetilde{\mathcal{H}}^{r_c} = \widetilde{\mathcal{H}}^{r_c}(\boldsymbol{X})$ satisfying the following conditions:

(T1) For every polynomial p, the quantity $p\big(\widetilde{\mathcal{H}}^{r_c}\big)_{\ell\ell}$ depends on at most finitely many atomic sites depending on r_c but not p,

(T2) For all $k, m \in \Lambda$, we have $[\widetilde{\mathcal{H}}^{r_c}]_{km} \to \mathcal{H}_{km}$ as $r_c \to \infty$,

(T3) There exists $c_0 > 0$ such that for all $\gamma, r_c > 0$,

$$\sum_{km} e^{-\gamma r_{\ell k}} \Big| \big[\mathcal{H} - \widetilde{\mathcal{H}}^{r_c}\big]_{km} \Big| \leqslant C e^{-c_0 \min\{\gamma_0, \gamma\}\, r_c}$$

for some $C > 0$ depending on γ but not on r_c.

Due to the exponential weighting of the summation, (T3) states that $\widetilde{\mathcal{H}}^{r_c}$ captures the behaviour of the Hamiltonian in a small neighbourhood of the site ℓ. Moreover, when making the approximation $I_N O\big(\mathcal{H}\big)_{\ell\ell} \approx I_N O\big(\widetilde{\mathcal{H}}^{r_c}\big)_{\ell\ell}$, the number of atomic sites involved is finite by (T1).

C.1.5 Non-linear schemes

One may be tempted to approximate the Hamiltonian with the truncation, $\widetilde{\mathcal{H}}^{r_c}$, and then apply the nonlinear scheme of Theorem 4.4. In doing so, we obtain the following error estimates:

$$\begin{aligned}
&\Big| O_\ell(\boldsymbol{X}) - \Theta\big([\widetilde{\mathcal{H}}^{r_c}]_{\ell\ell}, \dots, [(\widetilde{\mathcal{H}}^{r_c})^N]_{\ell\ell}\big) \Big| \\
&\qquad \leqslant \Big| O(\mathcal{H})_{\ell\ell} - O\big(\widetilde{\mathcal{H}}^{r_c}\big)_{\ell\ell} \Big| + \Big| O\big(\widetilde{\mathcal{H}}^{r_c}\big)_{\ell\ell} - \Theta\big([\widetilde{\mathcal{H}}^{r_c}]_{\ell\ell}, \dots, [(\widetilde{\mathcal{H}}^{r_c})^N]_{\ell\ell}\big) \Big| \\
&\qquad \lesssim e^{-\frac{1}{4}\min\{\gamma_0, \gamma_{\mathrm{CT}}\} r_c} + e^{-\widetilde{\gamma}_N(r_c) N}.
\end{aligned} \tag{C.1.9}$$

A problem with this analysis is that the constant $\widetilde{\gamma}_N(r_c)$ in (C.1.9) arises by applying Theorem 4.4 to $\widetilde{\mathcal{H}}^{r_c}$ rather than the original system $\mathcal{H}$. In particular, this means that $\widetilde{\gamma}_N(r_c)$ depends on the spectral properties of $\widetilde{\mathcal{H}}^{r_c}$ rather than $\mathcal{H}$. Since spectral pollution is known to occur when applying naive truncation schemes [84], the choice of $\widetilde{\mathcal{H}}^{r_c}$ is important for the analysis. In particular, it is not clear that $\widetilde{\gamma}_N(r_c) \to \gamma_N$ in general. This is in contrast the the result of Proposition C.1.

C.2 Derivatives in the Nonlinear Scheme

As mentioned in Remark 4.8, the results of this section depend on the "regularity" properties of D_ℓ:

Definition C.1 (Regular n^{th}-root Asymptotic Behaviour)**.** *For a unit measure ν with compact support $E \coloneqq \operatorname{supp}\nu \subseteq \mathbb{R}$, we say ν is regular and write $\nu \in$ **Reg** if the corresponding sequence of orthonormal polynomials $\{p_n(\,\cdot\,;\nu)\}$ satisfy*

$$\lim_{n\to\infty} |p_n(z;\nu)|^{\frac{1}{n}} = e^{g_E(z)}$$

locally uniformly on $\mathbb{C} \setminus \operatorname{conv}(E)$.

Remark C.2. *The regularity condition says that the n^{th}-root asymptotic behaviour of $|p_n(z;\nu)|$ is minimal: in general, we have [113, Theorem 1.1.4]*

$$e^{g_E(z)} \leqslant \liminf_{n\to\infty} |p_n(z;\nu)|^{\frac{1}{n}} \leqslant \limsup_{n\to\infty} |p_n(z;\nu)|^{\frac{1}{n}} \leqslant e^{g_\nu(z)}$$

where $g_\nu \geqslant g_E$ is the minimal carrier Green's function *of ν [113].*

Under the regularity condition of Definition C.1, we obtain results analogous to (4.3.6):

Theorem C.3. *Suppose that $\boldsymbol{X}$ satisfies Definition 2.2 and $\ell \in \Lambda$ is such that $D_\ell \in$ **Reg**. Then, with the notation of Theorem 4.4, we in addition have*

$$\left| \frac{\partial}{\partial \boldsymbol{X}_m} \Big(O_\ell^\beta(\boldsymbol{X}) - \Theta\big(\mathcal{H}_{\ell\ell}, [\mathcal{H}^2]_{\ell\ell}, \ldots, [\mathcal{H}^N]_{\ell\ell}\big) \Big) \right| \lesssim e^{-\frac{1}{2}\gamma_N N} e^{-\eta\, r_{\ell m}}.$$

More generally, if the regularity assumption is not satisfied, it may still be the case that Theorem C.3 holds but with reduced locality exponent η. To formulate this result, we require the notion of *minimal carrier capacity*:

Definition C.3 (Minimal carrier capacity)**.** *For arbitrary Borel sets C, the capacity of C is defined as*

$$\operatorname{cap}(C) \coloneqq \sup\{\operatorname{cap}(K)\colon K \subseteq C, \text{compact}\},$$

where $\operatorname{cap}(K)$ *is defined as in §4.8.1.*

For a unit measure ν with compact support $E \coloneqq \operatorname{supp}\nu \subseteq \mathbb{R}$, the set of carriers of ν *and the* minimal carrier capacity *are defined as*

$$\Gamma(\nu) \coloneqq \{C \subseteq \mathbb{C}\colon C \text{ Borel and } \nu(\mathbb{C} \setminus C) = 0\}, \quad \text{and} \tag{C.2.1}$$

$$c_\nu \coloneqq \inf\{\operatorname{cap}(C)\colon C \in \Gamma(\nu), C \text{ bounded}\} \leqslant \operatorname{cap}(E), \tag{C.2.2}$$

respectively.

Under these definitions, we have the following [113, p. 8-10]:

Remark C.4. *For a unit measure ν with compact support $E \coloneqq \operatorname{supp}\nu \subseteq \mathbb{R}$, we have*

(i) The set of minimal carriers $\Gamma_0(\nu) \coloneqq \{C \in \Gamma(\nu)\colon \operatorname{cap}(C) = c_\nu, C \subseteq E\}$ *is nonempty,*

(ii) If $c_\nu > 0$, then there exists a minimial carrier equilibrium distribution *ω_ν, a (uniquely defined) unit measure with* $\operatorname{supp}\omega_\nu \subseteq E$ *satisfying*

$$g_\nu(z) = -\int \log\frac{1}{|z-t|}\mathrm{d}\omega_\nu(t) - \log c_\nu,$$

(iii) $g_\nu \equiv g_E$ if and only if $c_\nu = \operatorname{cap}(E)$,

*(iv) In particular, if $c_\nu = \operatorname{cap}(E)$, then $\nu \in$ **Reg** (although the converse is false [113, Example 1.5.4]),*

(v) Suppose $c_\nu > 0$. Then, on defining ν_n to be the discrete unit measure

giving equal weight to each of the zeros of $p_n(\,\cdot\,;\nu)$*, the condition that*

$$\nu_n \rightharpoonup^\star \omega_E,$$

where ω_E *is the equilibrium distribution for* E*, is equivalent to* $\nu \in \mathbf{Reg}$ *[113, Thm. 3.1.4]. In particular, this justifies* (4.8.8)*.*

We therefore arrive at the corresponding result for $\ell \in \Lambda$ for which the corresponding LDOS has positive minimal carrier capacity:

Proposition C.4. *Suppose that* $\boldsymbol{X}$ *satisfies Definition 2.2 and* $\ell \in \Lambda$ *such that* $c_{D_\ell} > 0$*. Then, with the notation of Theorem 4.4, we in addition have*

$$\left| \frac{\partial}{\partial \boldsymbol{X}_m} \Big(O_\ell^\beta(\boldsymbol{X}) - \Theta\big(\mathcal{H}_{\ell\ell}, [\mathcal{H}^2]_{\ell\ell}, \dots, [\mathcal{H}^N]_{\ell\ell}\big) \Big) \right| \lesssim e^{-\frac{1}{2}\gamma_N N} e^{-\eta_\ell \, r_{\ell m}}$$

where $\eta_\ell > 0$*,*

$$\eta_\ell \to \eta \quad \text{as } c_{D_\ell} \to \operatorname{cap}(\operatorname{supp} D_\ell),$$

and $\eta > 0$ *is the constant from Theorem C.3.*

The proofs of Theorem C.3 and Proposition C.4 follow from the following estimates on the derivatives of the recursion coefficients $\{a_n, b_n\}$, and the locality of the tridiagonal operators T_N, together with the asymptotic upper bounds (i.e. Definition C.1 or Remark C.2).

Lemma C.5. *Suppose* $\boldsymbol{X}$ *satisfies Definition 2.2. Then, for a simple closed positively oriented contour* $\mathscr{C}'$ *encircling the spectrum* $\sigma\big(\mathcal{H}(\boldsymbol{X})\big)$*, there exists* $\eta = \eta(\mathscr{C}') > 0$ *such that*

$$\left| \frac{\partial b_n}{\partial \boldsymbol{X}_m} \right| \leqslant C \|p_n\|^2_{L^\infty(\mathscr{C}')} e^{-\eta \, r_{\ell m}} \qquad \textit{and}$$
$$\left| \frac{\partial a_n}{\partial \boldsymbol{X}_m} \right| \leqslant C \sum_{l=0}^{n} \|p_l\|^2_{L^\infty(\mathscr{C}')} e^{-\eta \, r_{\ell m}}$$

where $\eta \sim \mathfrak{d}$ *as* $\mathfrak{d} \to 0$ *where* $\mathfrak{d} \coloneqq \operatorname{dist}\big(\mathscr{C}', \sigma\big(\mathcal{H}(\boldsymbol{X})\big)\big)$*.*

In the following, we denote by T_∞ the infinite symmetric matrix on $\mathbb{N}_0$ with diagonal $(a_n)_{n\in\mathbb{N}_0}$ and off-diagonal $(b_n)_{n\in\mathbb{N}}$.

Lemma C.6. *Fix $N \in \mathbb{N} \cup \{\infty\}$. Suppose that $z \in \mathbb{C}$ such that $\mathfrak{d}_N := \operatorname{dist}\big(z, \sigma(T_N)\big) > 0$. Then, for each $i, j \in \mathbb{N}_0$, we have*

$$\Big|(T_N - z)^{-1}_{ij}\Big| \leqslant C e^{-\gamma_{|i-j|,N}|i-j|}.$$

(i) For each $r \in \mathbb{N}$, we have $\gamma_{r,N} \sim \mathfrak{d}_N$ as $\mathfrak{d}_N \to 0$.

(ii) We have $\lim_{r\to\infty} \gamma_{r,\infty} = \lim_{N\to\infty} \gamma_{N,N} = g_{\sigma(T_\infty)}(z)$ where $g_{\sigma(T_\infty)}$ is the Green's function for the set $\sigma(T_\infty)$ as defined in (4.8.8).

Remark C.5. *The fact that $g_{\sigma(T_\infty)}$ does not depend on the discrete eigenvalues of T_∞ means that asymptotically the locality estimates do not depend on defect states in the band gap arising due to perturbations satisfying Proposition 2.3, for example. Indeed, this has been shown in Lemma 3.4. We show an alternative proof using logarithmic potential theory.*

We will assume Lemmas C.5 and C.6 for now and return to their proofs below.

We first add on a constant multiple of the identity, cI, to the operators $\{T_N\}$ so that the spectra are contained in an interval bounded away from $\{0\}$. Moreover, we translate the integrand by the same constant: $\widetilde{O}(z) := O(z - c)$. Then, we extend T_N to an operator on $\ell^2(\mathbb{N}_0)$ by defining $[T_N\psi]_i = \sum_{j=0}^{N}[T_N]_{ij}\psi_j$ for $0 \leqslant i \leqslant N$ and $[T_N\psi]_i = 0$ otherwise. We therefore choose a simple closed contour (or system of contours) $\mathscr{C}$ encircling $\bigcup_N \sigma(T_N)$ so that

$$\begin{aligned}
&\frac{\partial\big[O_\ell(\boldsymbol{X}) - O(T_N)_{00}\big]}{\partial \boldsymbol{X}_m} \\
&= \frac{1}{2\pi i}\oint_{\mathscr{C}} \widetilde{O}(z)\frac{\partial}{\partial \boldsymbol{X}_m}\Big[(T_\infty - z)^{-1}_{0,N+1} b_{N+1}(T_N - z)^{-1}_{N0}\Big]\mathrm{d}z \\
&= \frac{1}{2\pi i}\oint_{\mathscr{C}} \widetilde{O}(z)\Big[\big[(T_\infty - z)^{-1}\frac{\partial T_\infty}{\partial \boldsymbol{X}_m}(T_\infty - z)^{-1}\big]_{0,N+1} b_{N+1}(T_N - z)^{-1}_{N0} \\
&\qquad + (T_\infty - z)^{-1}_{0,N+1}\frac{\partial b_{N+1}}{\partial \boldsymbol{X}_m}(T_N - z)^{-1}_{N0} \\
&\qquad + (T_\infty - z)^{-1}_{0,N+1} b_{N+1}\big[(T_N - z)^{-1}\frac{\partial T_N}{\partial \boldsymbol{X}_m}(T_N - z)^{-1}\big]_{N0}\Big]\mathrm{d}z. \quad \text{(C.2.3)}
\end{aligned}$$

Therefore, applying Lemma C.5, a simple calculation reveals

$$\begin{aligned}
&\left|\frac{\partial\big[O_\ell(\boldsymbol{X}) - O(T_N)_{00}\big]}{\partial \boldsymbol{X}_m}\right| \\
&\leqslant C\sum_{n=0}^{\infty}\Big[\Big|\frac{\partial a_n}{\partial \boldsymbol{X}_m}\Big| + \Big|\frac{\partial b_n}{\partial \boldsymbol{X}_m}\Big|\Big]e^{-\min\{\gamma_{n,N},\gamma_{n,\infty}\}n}e^{-\min\{\gamma_{N,N},\gamma_{N+1,\infty}\}N} \\
&\leqslant C\Big[\sum_{n=0}^{\infty}\sum_{l=0}^{n}\|p_l\|^2_{L^\infty(\mathscr{C}')}e^{-\min\{\gamma_{n,N},\gamma_{n,\infty}\}n}\Big]e^{-\min\{\gamma_{N,N},\gamma_{N+1,\infty}\}N}e^{-\eta\, r_{\ell m}}
\end{aligned} \tag{C.2.4}$$

where $\gamma_{r,N} = \gamma_{r,N}(\mathscr{C})$ is the constant from Lemma C.6. We therefore may conclude by choosing $\mathscr{C}' \coloneqq \{g_E = \gamma\}$ if $D_\ell \in \mathbf{Reg}$ and $\mathscr{C}' \coloneqq \{g_{D_\ell} = \gamma\}$ otherwise for some constant $\gamma > 0$ sufficiently small such that the summation in the square brackets converges.

Proof of Lemma C.5. The proof follows from the following identities:

$$\frac{\partial(b_n^2)}{\partial \boldsymbol{X}_m} = \oint_{\mathscr{C}} b_n^2 p_n(z)^2\Big[(\mathcal{H}-z)^{-1}\frac{\partial \mathcal{H}(\boldsymbol{X})}{\partial \boldsymbol{X}_m}(\mathcal{H}-z)^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i} \quad \text{and} \tag{C.2.5}$$

$$\begin{aligned}
\frac{\partial a_n}{\partial \boldsymbol{X}_m} = \oint_{\mathscr{C}} &\Big((z-a_n)p_n(z)^2 + \sum_{k=0}^{n-1}(-1)^{n-k}(2z-3a_k)p_k(z)^2\Big) \\
&\cdot\Big[(\mathcal{H}-z)^{-1}\frac{\partial \mathcal{H}(\boldsymbol{X})}{\partial \boldsymbol{X}_m}(\mathcal{H}-z)^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}.
\end{aligned} \tag{C.2.6}$$

To do this, it will be convenient to renormalise the orthogonal polynomials as in Remark 4.9 (that is, we consider $P_n(x) \coloneqq b_n p_n(x)$). Moreover, we define $b_{-1} \coloneqq 1$. Using the shorthand $\partial \coloneqq \frac{\partial}{\partial \boldsymbol{X}_m}$, we therefore obtain: $\partial b_{-1} = \partial b_0 = 0$, $\partial P_{-1}(x) = \partial P_0(x) = 0$, and

$$\begin{aligned}
&\partial P_{n+1}(x) \\
&= \frac{x-a_n}{b_n}\partial P_n(x) - \frac{b_n}{b_{n-1}}\partial P_{n-1}(x) - \partial\Big(\frac{a_n}{b_n}\Big)P_n(x) - \partial\Big(\frac{b_n}{b_{n-1}}\Big)P_{n-1}(x),
\end{aligned} \tag{C.2.7}$$

for all $n \geqslant 0$.

By noting $\partial P_1(x) = -\partial a_0$ and applying (C.2.7), we can see that ∂P_n is a polynomial of degree $n-1$ for all $n \geqslant 0$. Therefore, since P_n is orthogonal to

all polynomials of degree $n-1$, we have

$$\begin{aligned}\partial(b_n^2) &= 2\int P_n(x)\partial P_n(x)\mathrm{d}D_\ell + \oint_{\mathscr{C}} P_n(z)^2\Big[(\mathcal{H}-z)^{-1}\frac{\partial\mathcal{H}}{\partial \boldsymbol{X}_m}(\mathcal{H}-z)^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}\\ &= \oint_{\mathscr{C}} P_n(z)^2\Big[(\mathcal{H}-z)^{-1}\frac{\partial\mathcal{H}}{\partial \boldsymbol{X}_m}(\mathcal{H}-z)^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}\end{aligned}$$

which concludes the proof of (C.2.6).

To prove a similar formula for the derivatives of a_n, we first state a useful identity which will be proved after the conclusion of the proof of (C.2.6):

$$x\partial P_n(x) = \sum_{k=0}^{n} c_{nk}P_k(x), \quad \text{where} \quad c_{nn} = \sum_{k=0}^{n-1}\Big(a_k\frac{\partial b_k}{b_k} - \partial a_k\Big). \tag{C.2.8}$$

Therefore, we have

$$\begin{aligned}\partial a_n &= \frac{1}{b_n^2}\oint_{\mathscr{C}} zP_n(z)^2\Big[(\mathcal{H}-z)^{-1}\frac{\partial\mathcal{H}}{\partial \boldsymbol{X}_m}(\mathcal{H}-z)^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}\\ &\qquad + \frac{2}{b_n^2}\int xP_n(x)\partial P_n(x)\mathrm{d}D_\ell(x) - a_n\frac{\partial(b_n^2)}{b_n^2}\\ &= \frac{1}{b_n^2}\oint_{\mathscr{C}} (z-a_n)P_n(z)^2\Big[(\mathcal{H}-z)^{-1}\frac{\partial\mathcal{H}}{\partial \boldsymbol{X}_m}(\mathcal{H}-z)^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}\\ &\qquad + \sum_{k=0}^{n-1}\Big(a_k\frac{\partial(b_k^2)}{b_k^2} - 2\partial a_k\Big).\end{aligned} \tag{C.2.9}$$

Applying (C.2.8) for $k \leqslant n-1$, we can see that ∂a_n can be written as

$$\begin{aligned}\partial a_n = \oint_{\mathscr{C}} &\Big((z-a_n)p_n(z)^2 + \sum_{k=0}^{n-1}(d_{1,k}z + d_{0,k})p_k(z)^2\Big)\\ &\cdot\Big[(\mathcal{H}-z)^{-1}\frac{\partial\mathcal{H}}{\partial \boldsymbol{X}_m}(\mathcal{H}-z)^{-1}\Big]_{\ell\ell}\frac{\mathrm{d}z}{2\pi i}.\end{aligned}$$

for some coefficients $d_{1,k}, d_{0,k}$. Using (C.2.8) and assuming the result for $k \leqslant n-1$, we have

$$\begin{aligned}d_{1,k}z + d_{0,k} &= a_k - 2(z-a_k) - 2\sum_{l=k+1}^{n-1}(-1)^{l-k}(2z-3a_k)\\ &= -2z + 3a_k - (-1)^k\big((-1)^{k+1} + (-1)^{n-1}\big)(2z-3a_k)\\ &= (-1)^{n-k}(2z-3a_k).\end{aligned}$$

for all $k \leqslant n-1$. □

Proof of (C.2.8). We have

$$x\partial P_n(x) = \frac{x}{b_{n-1}} x\partial P_{n-1}(x) - \partial\Big(\frac{a_{n-1}}{b_{n-1}}\Big) xP_{n-1}(x) + \text{l.o.t.} \tag{C.2.10}$$

$$= \frac{1}{b_{n-1}} c_{n-1,n-1} xP_{n-1}(x) - \partial\Big(\frac{a_{n-1}}{b_{n-1}}\Big) b_{n-1}P_n(x) + \text{l.o.t.} \tag{C.2.11}$$

$$= c_{n-1,n-1}P_n(x) - \partial\Big(\frac{a_{n-1}}{b_{n-1}}\Big) b_{n-1}P_n(x) + \text{l.o.t.} \tag{C.2.12}$$

where l.o.t. ("lower order term") denotes a polynomial of degree strictly less than n that changes from one line to the next. That is, since $c_{11} = -\partial a_0 = \partial\big(\frac{a_0}{b_0}\big) b_0$, we apply an inductive argument to conclude

$$c_{nn} = c_{n-1,n-1} - \partial\Big(\frac{a_{n-1}}{b_{n-1}}\Big) b_{n-1} = -\sum_{k=0}^{n-1} \partial\Big(\frac{a_k}{b_k}\Big) b_k$$
$$= \sum_{k=0}^{n-1} \Big(a_k \frac{\partial b_k}{b_k} - \partial a_k\Big) = \sum_{k=0}^{n-1} \Big(\frac{a_k}{2} \frac{\partial(b_k^2)}{b_k^2} - \partial a_k\Big).$$

□

Proof of Lemma C.6. The first statement is the Combes-Thomas resolvent estimate (Lemma 3.3) for tridiagonal operators (which, in particular, satisfy the off-diagonal decay assumptions of Lemma 3.3).

To obtain the asymptotic estimates of *(ii)*, we apply a different approach based on the banded structure of the operators. Since T_N is tri-diagonal, $[(T_N)^n]_{ij} = 0$ if $|i-j| > n$. Therefore, for any polynomial P of degree at most $|i-j|-1$, we have [12]

$$|(T_N - z)^{-1}_{ij}| = \Big|\big[(T_N - z)^{-1} - P(T_N)\big]_{ij}\Big| \leqslant \Big\|\frac{1}{\cdot - z} - P\Big\|_{L^\infty(\sigma(T_N))}. \tag{C.2.13}$$

We may apply the results of logarithmic potential theory (see (4.8.13)), to conclude. Here, it is important that $|\sigma(T_\infty) \setminus \sigma(T_N)|$ remains bounded independently of N so that, asymptotically, (C.2.13) has exponential decay with exponent $g_{\sigma(T_\infty)}$.

The proof that $|\sigma(T_\infty) \setminus \sigma(T_N)|$ is uniformly bounded can easily be shown when considering the sequence of orthogonal polynomials generated by T_∞. A full proof is given in parts *(ii)* and *(iv)* of Lemma C.7. □

C.3 Quadrature Method

The quadrature method as outlined in this section was introduced in [93] to approximate the LDOS. For a comparison of various nonlinear approximation schemes, see [68] and [56]. The former is a practical comparison of quadrature and BOP methods, while the later also discusses the maximum entropy method [90].

We now give an alternative proof of Theorem 4.4 by introducing the quadrature method [93].

Recall that D_ℓ is the local density of states (LDOS) satisfying (4.2.1) and $\{p_n\}$ is the corresponding sequence of orthogonal polynomials generated via the recursion method:

$$[p_n(\mathcal{H})p_m(\mathcal{H})]_{\ell\ell} = \int p_n(x)p_m(x)\mathrm{d}D_\ell(x) = \delta_{nm}.$$

We use the set of zeros of p_{N+1}, denoted by $\mathcal{X}_N = \{\varepsilon_0, \ldots, \varepsilon_N\}$, as the basis for the following quadrature rule:

$$O(\mathcal{H})_{\ell\ell} = \int O(x)\mathrm{d}D_\ell(x) \approx \int I_{X_N}O(x)\mathrm{d}D_\ell(x) = \sum_{j=0}^{N} w_j O(\varepsilon_j), \qquad \text{where}$$
$$w_j = \int \ell_j(x)\mathrm{d}D_\ell(x) = \ell_j(\mathcal{H})_{\ell\ell}, \quad \text{and} \quad \ell_j(x) = \prod_{i\neq j}\frac{x-\varepsilon_i}{\varepsilon_j-\varepsilon_i}.$$

Here, ℓ_j is the polynomial of degree N with $\ell_j(\varepsilon_i) = \delta_{ij}$.

The following lemma highlights the fundamental properties of Gauss quadrature and allows us to show that the approximation scheme given by

$$\Theta^{\mathrm{q}}\Big(\mathcal{H}_{\ell\ell}, [\mathcal{H}^2]_{\ell\ell}, \ldots, [\mathcal{H}^{2N+1}]_{\ell\ell}\Big) \coloneqq \sum_{j=0}^{N} w_j O(\varepsilon_j). \tag{C.3.1}$$

satisfies Theorem 4.4:

Lemma C.7. *Suppose that $\{p_n\}$ is the sequence of polynomials generated by the recursion method* (4.8.25)*, $\mathcal{X}_N$ is the set of zeros of p_{N+1}, and $\{w_j\}$ are the weights satisfying $\int I_{\mathcal{X}_N} O(x) \mathrm{d}D_\ell(x) = \sum_{j=0}^{N} w_j O(\varepsilon_j)$. Then,*

(i) $\mathcal{X}_N \subseteq \mathbb{R}$ is a set of $N+1$ distinct points,

(ii) If P_{2N+1} is a polynomial of degree at most $2N+1$, then

$$P_{2N+1}(\mathcal{H})_{\ell\ell} = \sum_{j=0}^{N} w_j P_{2N+1}(\varepsilon_j),$$

(iii) The weights $\{w_j\}$ are positive and sum to one.

Proof. The idea behind the proofs are standard in the theory of Gauss quadrature (e.g. see [55]) but, for the convenience of the reader, they are collected together in C.3.3. □

Remark C.6. *The quadrature rule discussed in this section can be seen as the exact integral with respect to the following approximate LDOS*

$$D_\ell^{N,\mathrm{q}} \coloneqq \sum_{j=0}^{N} w_j \delta(\,\cdot - \varepsilon_j).$$

Lemma C.7 (ii)-(iii) allows us to conclude that the first $2N+1$ moments of $D_\ell^{N,\mathrm{q}}$ are given by $[\mathcal{H}^n]_{\ell\ell}$ for $n = 1, \ldots, 2N+1$, and that $D_\ell^{N,\mathrm{q}}$ is positive.

In the following two sections we prove error estimates and show that the functional form is analytic on an open set containing $\big(\mathcal{H}_{\ell\ell}, \ldots, [\mathcal{H}^{2N+1}]_{\ell\ell}\big)$.

C.3.1 Error Estimates.

Applying Remark C.6, together with (4.2.2), we have: for every polynomial P_{2N+1} of degree at most $2N+1$,

$$\Big| O_\ell(\boldsymbol{r}) - \sum_{j=0}^{N} w_j O(\varepsilon_j) \Big| \leqslant 2 \| O - P_{2N+1} \|_{L^\infty(\sigma(\mathcal{H}) \cup \mathcal{X}_N)}. \tag{C.3.2}$$

Now, since $\sigma(\mathcal{H}) \subseteq I_- \cup \{\lambda_j\} \cup I_+$ where $\{\lambda_j\}$ is a finite set, we may apply Lemma 4.5 *(iii)* together with the fact $\mathcal{X}_N = \sigma(T_N)$ where T_N is the matrix (4.8.27), to conclude that the number of points in $\mathcal{X}_N \setminus \big(I_- \cup I_+\big)$ is bounded independently of N. Accordingly, we may apply (4.8.13) with $E = I_- \cup I_+$, to obtain the desired asymptotic error estimates.

C.3.2 Analyticity.

To conclude the proof of Theorem 4.4, we show that Θ^{q} as defined in (C.3.1) is analytic in a neighbourhood of $(\mathcal{H}_{\ell\ell}, [\mathcal{H}^2]_{\ell\ell}, \dots, [\mathcal{H}^{2N+1}]_{\ell\ell})$. Recall that in (4.8.37) we have extended the definition of T_N to an analytic function on $U \coloneqq \{\boldsymbol{z} \in \mathbb{C}^{2N+1} \colon b_n^2(\boldsymbol{z}_{1:2n}) \neq 0 \ \forall n = 1, \dots, N\}$.

We define $\mathcal{X}_N(\boldsymbol{z})$ to be the set of eigenvalues of $T_N(\boldsymbol{z})$. Since $\mathcal{X}_N = \mathcal{X}_N\big(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^{2N+1}]_{\ell\ell}\big)$ is a set of $N+1$ distinct points (Lemma C.7 *(i)*), there exists a continuous choice of eigenvalues $\mathcal{X}_N(\boldsymbol{z}) = \{\varepsilon_0(\boldsymbol{z}), \dots, \varepsilon_N(\boldsymbol{z})\}$ such that $\mathcal{X}_N(\boldsymbol{z})$ is a set of $N+1$ distinct points in a neighbourhood, U_0, of $(\mathcal{H}_{\ell\ell}, \dots, [\mathcal{H}^{2N+1}]_{\ell\ell}) \in U$ and each ε_j is analytic on U_0 [76, 125]. With this in hand, we define $\Theta^{\mathrm{q}} \colon U_0 \to \mathbb{C}$ by

$$\Theta^{\mathrm{q}}(\boldsymbol{z}) \coloneqq \mathcal{L}\big(x \mapsto I_{\mathcal{X}_N(\boldsymbol{z})} O(x)\big)(\boldsymbol{z}_{1:N}) = \sum_{j=0}^{N} \mathcal{L}\Big(x \mapsto \prod_{i \neq j} \frac{x - \varepsilon_i}{\varepsilon_j - \varepsilon_i}\Big) \cdot O \circ \varepsilon_j, \tag{C.3.3}$$

which is analytic on $\{\boldsymbol{z} \in U_0 \colon O \text{ analytic at } \varepsilon_j(\boldsymbol{z}) \ \forall j = 0, \dots, N\}$.

C.3.3 Proof of Lemma C.7

Proof of (i). Since T_N is symmetric, the spectrum is real. Now, for each $\varepsilon_j \in \mathcal{X}_N = \sigma(T_N)$, the matrix $(T_N - \varepsilon_j)_{\neg N \neg 0}$ formed by removing the N^{th} row and 0^{th} column is lower-triangular with diagonal $(b_1, \dots, b_N)$. Since each $b_i > 0$, $(T_N - \varepsilon_j)_{\neg N \neg 0}$ has full rank and thus ε_j is a simple eigenvalue of T_N.

Proof of (ii). We may write $P_{2N+1} = p_{N+1} q_N + r_N$ where q_N, r_N are polynomials of degree at most N and note that $[p_{N+1}(\mathcal{H}) q_N(\mathcal{H})]_{\ell\ell} = 0$ by Lemma 4.5 *(i)* and $P_{2N+1}(\varepsilon_j) = r_N(\varepsilon_j)$ since $\mathcal{X}_N$ is the set of zeros of p_{N+1}.

Therefore,

$$\int P_{2N+1}(x)\mathrm{d}D_\ell(x) = \int \Big[p_{N+1}(x)q_N(x) + r_N(x)\Big]\mathrm{d}D_\ell(x) \tag{C.3.4}$$

$$= \int r_N(x)\mathrm{d}D_\ell(x) = \int I_{\mathcal{X}_N} r_N(x)\mathrm{d}D_\ell(x) \tag{C.3.5}$$

$$= \sum_{j=0}^{N} w_j r_N(\varepsilon_j) = \sum_{j=0}^{N} w_j P_{2N+1}(\varepsilon_j). \tag{C.3.6}$$

In (C.3.5) we have used the fact that polynomial interpolation in $N+1$ distinct points is exact for polynomials of degree at most N.

Proof of (iii). $\ell_j(x)^2$ is a polynomial of degree $2N$ and so, by *(ii)*, we have

$$0 \leqslant \int \ell_j(x)^2 D_\ell(x)\mathrm{d}x = \sum_{i=0}^{N} w_i \ell_j(\varepsilon_i)^2 = w_j.$$

Moreover, $\sum_{j=0}^{N} \ell_j(x)$ is a polynomial of degree N equal to one on $\mathcal{X}_N$ (a set of $N+1$ distinct points) and so $\sum_{j=0}^{N} \ell_j(x) \equiv 1$. Finally, $\sum_{j=0}^{N} w_j = \int \big(\sum_{j=0}^{N} \ell_j(x)\big) D_\ell(x)\mathrm{d}x = 1$.

C.4 Numerical Bond-Order Potentials (BOP)

In mathematical terms, the idea behind BOP methods is to replace the local density of states (LDOS) with an approximation using only the information from the truncated tri-diagonal matrix T_N (and possibly additional hyper-parameters). Since the first N coefficients contain the same information as the first $2N+1$ moments $\mathcal{H}_{\ell\ell}, \ldots, [\mathcal{H}^{2N+1}]_{\ell\ell}$, this approach is closely related to the method of moments [34].

Equivalently, the resolvent $[(z-\mathcal{H})^{-1}]_{\ell\ell}$, which can be written conveniently

as the continued fraction expansion

$$[(z-\mathcal{H})^{-1}]_{\ell\ell} = \cfrac{1}{z - a_0 - \cfrac{b_1^2}{z - a_1 - \cfrac{b_2^2}{z - a_2 - \ddots}}}, \tag{C.4.1}$$

is replaced with an approximation G_ℓ^N only involving the coefficients from T_N. For example, for fixed *terminator* t_∞, we may define

$$G_\ell^N(z) \coloneqq \cfrac{1}{z - a_0 - \cfrac{b_1^2}{z - a_1 - \cfrac{b_2^2}{\ddots \quad - \cfrac{b_N^2}{z - a_N - t_\infty(z)}}}}. \tag{C.4.2}$$

Truncating (C.4.1) to level N, which is equivalent to replacing the far-field of the linear chain with vacuum and choosing $t_\infty = 0$, results in a rational approximation to the resolvent and thus a discrete approximation to the LDOS. We have seen that truncation of the continued fraction in this way leads to an approximation scheme satisfying Theorem 4.4.

Alternatively, the far-field may be replaced with a constant linear chain with $a_{N+j} = a_\infty$ and $b_{N+j} = b_\infty$ for all $j \geqslant 1$ leading to the square root terminator $t_\infty(z) = \frac{b_\infty^2}{z - a_\infty - t_\infty(z)}$ [53, 66, 126].

More generally, one may choose any "approximate" local density of states $\widetilde{D}_\ell$ and construct a corresponding terminator that encodes the information from $\widetilde{D}_\ell$ [69, 87]. For example, $\widetilde{D}_\ell(x) \coloneqq \frac{1}{b_\infty \pi}\sqrt{1 - \left(\frac{x - a_\infty}{2b_\infty}\right)^2}$ results in the square root terminator. While we are unaware of any rigorous results, there is numerical evidence [69] to suggest that the error in the approximation scheme is related to the smoothness of the difference $D_\ell - \widetilde{D}_\ell$.

Equivalently, we may choose any bounded symmetric tri-diagonal (Jacobi) operator $\widetilde{T}_N$ with diagonal $a_0, a_1, \ldots, a_N, \widetilde{a}_{N+1}, \ldots$ and off-diagonal entries

$b_1, \ldots, b_N, \widetilde{b}_{N+1}, \ldots$. That is, we may evaluate the recursion method exactly to level N and append the far-field boundary condition $\{\widetilde{a}_n, \widetilde{b}_n\}_{n \geqslant N+1}$ to the semi-infinite linear chain. This approach also includes the case $t_\infty = 0$ as in §4.8.3 by choosing $\widetilde{a}_n = \widetilde{b}_n = 0$ for all n.

With this in hand, we define

$$O_\ell^{N,\mathrm{BOP}}(\boldsymbol{X}) \coloneqq O(\widetilde{T}_N)_{00} = \int O \,\mathrm{d}\widetilde{D}_\ell^{N,\mathrm{BOP}} \tag{C.4.3}$$

where $\widetilde{D}_\ell^{N,\mathrm{BOP}}$ is the appropriate spectral measure corresponding to $\widetilde{T}_N$.

C.4.1 Error estimates

Since $[(\widetilde{T}_N)^n]_{00} = [(T_N)^n]_{00} = [(T_\infty)^n]_{00}$ is independent of the far-field coefficients $\{\widetilde{a}_j, \widetilde{b}_j\}$ for all $n \leqslant 2N+1$, we can immediately see that the first $2N+1$ moments of $\widetilde{D}_\ell^{N,\mathrm{BOP}}$ agree with those of D_ℓ. In particular, we may immediately apply (4.2.2) to obtain error estimates that depend on $\operatorname{supp}\big(D_\ell - \widetilde{D}_\ell^{N,\mathrm{BOP}}\big)$.

Therefore, as long as the far-field boundary condition is chosen so that there are only finitely many discrete eigenvalues in the band gap independent of N, the more complicated BOP schemes converge at least as quickly as the $t_\infty = 0$ case. Intuitively, if the far-field boundary condition is chosen to capture the behaviour of the LDOS (e.g. the type and location of band-edge singularities), then the integration against the signed measure $D_\ell - \widetilde{D}_\ell^{N,\mathrm{BOP}}$ as in (4.2.2) may lead to improved error estimates. A rigorous error analysis to this affect is left for future work.

C.4.2 Analyticity

Since $\widetilde{T}_N$ is bounded and symmetric, the spectrum $\sigma(\widetilde{T}_N)$ is contained in a bounded interval of the real line. In particular, we can apply the same arguments as in (4.8.38) to conclude that (C.4.3) defines a nonlinear approximation scheme given by an analytic function on an open subset of $\mathbb{C}^{2N+1}$.

C.5 Kernel Polynomial Method & Analytic Bond Order Potentials

We first introduce the Kernel Polynomial Method (KPM) for approximating the LDOS [110, 111, 128]. In this section, we scale the spectrum and assume that $\sigma(\mathcal{H}) \subseteq [-1, 1]$.

For a sequence of *kernels* $K_N(x, y)$, we define the approximate quantities of interest

$$O_\ell^N \coloneqq \int K_N \star O \,\mathrm{d}D_\ell =: \iint K_N(x,y) O(y) \,\mathrm{d}y \,\mathrm{d}D_\ell(x). \tag{C.5.1}$$

Under the choice $K_N(x, y) \coloneqq \frac{2}{\pi}\sqrt{1-y^2}\sum_{n=0}^{N} U_n(x)U_n(y)$ (where U_n denotes the n^{th} Chebyshev polynomial of the second kind), we arrive at a projection method similar to that discussed in §4.8.1: if $O(x) = \sum_{m=0}^{\infty} c_m U_m(x)$, then

$$K_N \star O(x) = \sum_{m,n} c_m U_n(x) \frac{2}{\pi} \int_{-1}^{1} U_n(y) U_m(y) \sqrt{1-y^2} \,\mathrm{d}y = \sum_{n=0}^{N} c_n U_n(x). \tag{C.5.2}$$

Equivalently, we may consider the corresponding approximate LDOS

$$O_\ell^N = \int O(x) D_\ell^N(x) \mathrm{d}x \quad \text{where} \quad D_\ell^N(x) = \frac{2}{\pi}\sqrt{1-x^2}\sum_{n=0}^{N} U_n(\mathcal{H})_{\ell\ell} U_n(x).$$

However, truncation of the Chebyshev series in this way leads to artificial oscillations in the approximate LDOS known as Gibbs oscillations [61]. Moreover, without *damping* these oscillations, the approximate LDOS need not be positive. However, on defining

$$K_N^{\text{Fejer}}(x,y) \coloneqq \frac{1}{N}\sum_{n=1}^{N} K_n(x,y) = \frac{2}{\pi}\sqrt{1-y^2}\sum_{n=0}^{N}\left(1-\tfrac{n}{N}\right) U_n(x)U_n(y), \tag{C.5.3}$$

we obtain a positive approximate LDOS [128] where the *damping coefficients* $d_n \coloneqq (1 - \frac{n}{N})$ reduce the effect of Gibbs oscillations. In practice, one may instead choose the *Jackson kernel* [65].

The problem with the above analysis in practice is that the damping factors that we have introduced mean that more moments $[\mathcal{H}^n]_{\ell\ell}$ are required in order to obtain good approximations to the LDOS. Instead, analytic BOP methods [101, 107] compute the first N rows of the tridiagonal operator T_∞, thus obtaining the first $2N+1$ moments exactly. Then, a far-field boundary condition (such as a constant infinite linear chain) is appended to form a corresponding Jacobi operator $\widetilde{T}_N$ as in Appendix C.4. Now, since higher order moments of $\widetilde{T}_N$ can be efficiently computed, we may evaluate the following approximate LDOS

$$D_\ell^{N,M}(x) \coloneqq \frac{2}{\pi}\sqrt{1-x^2}\sum_{n=0}^{M} d_n U_n(\widetilde{T}_N)_{00} U_n(x) \tag{C.5.4}$$

where d_n are damping coefficients and $M > 2N+1$. The damping is chosen so that the lower order moments which are computed exactly and are more important for the reconstruction of the LDOS are only slightly damped. With this choice of kernel, the approximate quantities of interest take the form

$$O_\ell^{N,M} = \sum_{n=0}^{2N+1} d_n c_n U_n(\mathcal{H})_{\ell\ell} + \sum_{n=2N+2}^{M} d_n c_n U_n(\widetilde{T}_N)_{00}$$

Efficient implementation of analytic BOP methods can be carried out using the BOPfox program [65].

Bibliography

[1] B. Aupetit, *A Primer on Spectral Theory*, Springer, 10 1991.

[2] M. Bachmayr, G. Csanyi, R. Drautz, G. Dusson, S. Etter, C. van der Oord, and C. Ortner, *Atomic cluster expansion: Completeness, efficiency and stability*, ArXiv e-prints, arXiv:1911.03550, (2019).

[3] J. Bak and D. J. Newman, *Complex Analysis*, Springer, 08 2010.

[4] A. P. Bartók, J. Kermode, N. Bernstein, and G. Csányi, *Machine Learning a General-Purpose Interatomic Potential for Silicon*, Phys. Rev. X, 8 (2018), p. 041048.

[5] A. P. Bartók, R. Kondor, and G. Csányi, *On representing chemical environments*, Physical Review B, 87 (2013).

[6] A. P. Bartók, M. C. Payne, R. Kondor, and G. Csányi, *Gaussian approximation potentials: The accuracy of quantum mechanics, without the electrons*, Phys. Rev. Lett., 104 (2010), p. 136403.

[7] M. I. Baskes, *Modified embedded-atom potentials for cubic materials and impurities*, Phys. Rev. B Condens. Matter, 46 (1992), pp. 2727–2742.

[8] M. Z. Bazant, E. Kaxiras, and J. F. Justo, *Environment-dependent interatomic potential for bulk silicon*, Phys. Rev. B Condens. Matter, 56 (1997), pp. 8542–8552.

[9] J. Behler, *Atom-centered symmetry functions for constructing high-dimensional neural network potentials*, The Journal of Chemical Physics, 134 (2011), p. 074106.

[10] J. Behler, *Representing potential energy surfaces by high-dimensional neural network potentials*, Journal of Physics: Condensed Matter, 26 (2014), p. 183001.

[11] J. Behler and M. Parrinello, *Generalized neural-network representation of high-dimensional potential-energy surfaces*, Phys. Rev. Lett., 98 (2007), p. 146401.

[12] M. Benzi, P. Boito, and N. Razouk, *Decay properties of spectral projectors with applications to electronic structure*, SIAM Rev., 55 (2013), pp. 3–64.

[13] N. Bernstein, G. Csanyi, and J. Kermode, *QUantum mechanics and Interatomic Potentials (QUIP)*. https://github.com/libAtoms/QUIP, 2006.

[14] R. Biswas and D. R. Hamann, *New classical models for silicon structural energies*, Phys. Rev. B, 36 (1987), pp. 6434–6445.

[15] X. Blanc, C. Le Bris, and P.-L. Lions, *The energy of some microscopic stochastic lattices*, Arch. Ration. Mech. Anal., 184 (2007), pp. 303–339.

[16] B. J. Braams and J. M. Bowman, *Permutationally invariant potential energy surfaces in high dimensionality*, Int. Rev. Phys. Chem., 28 (2009), pp. 577–606.

[17] E. Cancès, A. Deleurence, and M. Lewin, *A new approach to the modeling of local defects in crystals: The reduced Hartree-Fock case*, Commun. Math. Phys., 281 (2008), pp. 129–177.

[18] E. Cancès and V. Ehrlacher, *Local defects are always neutral in the Thomas–Fermi–von Weiszäcker theory of crystals*, Arch. Ration. Mech. Anal., 202 (2011), pp. 933–973.

[19] E. Cancès, V. Ehrlacher, D. Gontier, A. Levitt, and D. Lombardi, *Numerical quadrature in the Brillouin zone for periodic Schrödinger operators*, Numer. Math., 144 (2020), pp. 479–526.

[20] E. Cancès, G. Kemlin, and A. Levitt, *Convergence analysis of direct minimization and self-consistent iterations*, SIAM J. Matrix Anal. A, 42 (2021), pp. 243–274.

[21] E. Cancès and C. Le Bris, *Mathematical modeling of point defects in materials science*, Math. Models Methods Appl. Sci., 23 (2013), pp. 1795–1859.

[22] E. Cancès, V. Ehrlacher, and Y. Maday, *Periodic Schrödinger operators with local defects and spectral pollution*, SIAM J. Numer. Anal., 50 (2012), pp. 3016–3035.

[23] I. Catto, C. Le Bris, and P.-L. Lions, *The mathematical theory of thermodynamic limits: Thomas-Fermi type models*, Clarendon Press, 1998.

[24] ——, *On the thermodynamic limit for Hartree–Fock type models*, Ann. I. H. Poincare, An., 18 (2001), pp. 687–760.

[25] ——, *On some periodic Hartree-type models for crystals*, Ann. I. H. Poincare, An., 19 (2002), pp. 143–190.

[26] H. Chen, J. Lu, and C. Ortner, *Thermodynamic limit of crystal defects with finite temperature tight binding*, Arch. Ration. Mech. Anal., 230 (2018), pp. 701–733.

[27] H. Chen, F. Nazar, and C. Ortner, *Geometry equilibration of crystalline defects in quantum and atomic descriptions*, Math. Models Methods Appl. Sci., 29 (2019), pp. 419–492.

[28] H. Chen and C. Ortner, *SKTB.jl.git*. https://github.com/cortner/SKTB.jl.git.

[29] ——, *QM/MM methods for crystalline defects. Part 1: Locality of the tight binding model*, Multiscale Model. Simul., 14 (2016), pp. 232–264.

[30] J. Chen and J. Lu, *Analysis of the divide-and-conquer method for electronic structure calculations*, Math. Comput., 85 (2016), pp. 2919–2938.

[31] M. Chupin, M.-S. Dupuy, G. Legendre, and Éric Séré, *Convergence analysis of adaptive DIIS algorithms with application to electronic ground state calculations*, ArXiv e-prints, arXiv:2002.12850, (2020).

[32] R. Cohen, M. Mehl, and D. Papaconstantopoulos, *Tight-binding total-energy method for transition and noble metals*, Phys. Rev. B, 50 (1994), pp. 14694–14697.

[33] J. M. Combes and L. Thomas, *Asymptotic behaviour of eigenfunctions for multiparticle Schrödinger operators*, Comm. Math. Phys., 34 (1973), pp. 251–270.

[34] F. Cyrot-Lackmann, *On the electronic structure of liquid transitional metals*, Adv. Phys., 16 (1967), pp. 393–400.

[35] E. B. Davies and M. Plum, *Spectral pollution*, IMA J. Numer. Anal., 24 (2004), pp. 417–438.

[36] M. S. Daw and M. I. Baskes, *Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals*, Phys. Rev. B Condens. Matter, 29 (1984), pp. 6443–6453.

[37] P. A. M. Dirac, *Quantum mechanics of many-electron systems*, Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 123 (1929), pp. 714–733.

[38] R. Drautz, *Atomic cluster expansion for accurate and transferable interatomic potentials*, Phys. Rev. B, 99 (2019), p. 014104.

[39] ——, *From electrons to interatomic potentials for materials simulations*, in Topology, Entanglement, and Strong Correlations, E. Pavarini and E. Koch, eds., Forschungszentrum Jülich GmbH, Institute for Advanced Simulation, 2020, ch. 3.

[40] R. Drautz, M. Fähnle, and J. M. Sanchez, *General relations between many-body potentials and cluster expansions in multicomponent systems*, J. Phys. Condens. Matter, 16 (2004), pp. 3843–3852.

[41] T. A. Driscoll, *Algorithm 756: A MATLAB toolbox for Schwarz-Christoffel mapping*, ACM T. Math. Software, 22 (1996), pp. 168–186.

[42] ——, *Schwarz-Christoffel toolbox*. https://github.com/tobydriscoll/sc-toolbox, 2007.

[43] T. A. Driscoll, K.-C. Toh, and L. N. Trefethen, *From potential theory to matrix iterations in six steps*, SIAM Rev., 40 (1998), pp. 547–578.

[44] T. A. Driscoll and L. N. Trefethen, *Schwarz-Christoffel Mapping*, Cambridge University Press, June 2002.

[45] W. E and J. Lu, *Electronic structure of smoothly deformed crystals: Cauchy-Born rule for the nonlinear tight-binding model*, Comm. Pure Appl. Math., 63 (2010), pp. 1432–1468.

[46] ——, *The electronic structure of smoothly deformed crystals: Wannier functions and the Cauchy-Born rule*, Arch. Ration. Mech. Anal., 199 (2011), pp. 407–433.

[47] V. Ehrlacher, C. Ortner, and A. V. Shapeev, *Analysis of boundary conditions for crystal defect atomistic simulations*, ArXiv e-prints, arXiv:1306.5334, (2013).

[48] ——, *Analysis of boundary conditions for crystal defect atomistic simulations*, Arch. Ration. Mech. An., 222 (2016), pp. 1217–1268.

[49] M. Elstner and G. Seifert, *Density functional tight binding*, Philos. T. Roy. Soc. A, 372 (2014), p. 20120483.

[50] M. Embree and L. N. Trefethen, *Green's functions for multiply connected domains via conformal mapping*, SIAM Rev., 41 (1999), pp. 745–761.

[51] F. Ercolessi and J. B. Adams, *Interatomic potentials from first-principles calculations: The force-matching method*, EPL, (1994).

[52] S. Etter, *Polynomial and Rational Approximation for Electronic Structure Calculations*, PhD thesis, University of Warwick, UK, June 2019.

[53] M. Finnis, *Interatomic Forces in Condensed Matter*, Oxford University Press, 2003.

[54] ——, *Bond-order potentials through the ages*, Prog. Mater. Sci., 52 (2007), pp. 133–153.

[55] G. Freud, *Orthogonal Polynomials*, Elsevier, 05 2014.

[56] S. Glanville, A. T. Paxton, and M. W. Finnis, *A comparison of methods for calculating tight-binding bond energies*, J. Phys. F Met. Phys., 18 (1988), pp. 693–718.

[57] S. Goedecker, *Linear scaling electronic structure methods*, Rev. Mod. Phys., 71 (1999), pp. 1085–1123.

[58] S. Goedecker and M. Teter, *Tight-binding electronic-structure calculations and tight-binding molecular dynamics with localized orbitals*, Phys. Rev. B, 51 (1995), pp. 9455–9464.

[59] D. Gontier and S. Lahbabi, *Convergence rates of supercell calculations in the reduced Hartree–Fock model*, Math. Model. Num. Anal., 50 (2016), pp. 1403–1424.

[60] ——, *Supercell calculations in the reduced Hartree–Fock model for crystals with local defects*, Appl. Math. Res. eXpress, 2017 (2016), pp. 1–64.

[61] L. Grafakos, *Classical Fourier Analysis*, Springer, 08 2016.

[62] A. Greenbaum, R.-C. Li, and M. L. Overton, *First-order perturbation theory for eigenvalues and eigenvectors*, SIAM Rev., 62 (2020), pp. 463–482.

[63] R. C. Gunning and H. Rossi, *Analytic Functions of Several Complex Variables*, Prentice-Hall, 04 1965.

[64] T. Haliciogli, H. O. Pamuk, and S. Erkoc, *Interatomic potentials with multi-body interactions*, Phys. Status Solidi B, 149 (1988), pp. 81–92.

[65] T. Hammerschmidt, B. Seiser, M. Ford, A. Ladines, S. Schreiber, N. Wang, J. Jenke, Y. Lysogorskiy, C. Teijeiro, M. Mrovec, M. Cak, E. Margine, D. Pettifor, and R. Drautz, *BOPfox program for tight-binding and analytic bond-order potential calculations*, Comput. Phys. Commun., 235 (2019), pp. 221–233.

[66] R. Haydock, V. Heine, and M. J. Kelly, *Electronic structure based on the local atomic environment for tight-binding bands*, J. Phys. C Solid State, 5 (1972), pp. 2845–2858.

[67] ——, *Electronic structure based on the local atomic environment for tight-binding bands. II*, J. Phys. C Solid State, 8 (1975), pp. 2591–2605.

[68] R. Haydock and C. M. M. Nex, *Comparison of quadrature and termination for estimating the density of states within the recursion method*, J. Phys. C Solid State, 17 (1984), pp. 4783–4789.

[69] ——, *A general terminator for the recursion method*, J. Phys. C Solid State, 18 (1985), pp. 2235–2248.

[70] M. F. Herbst and A. Levitt, *Black-box inhomogeneous preconditioning for self-consistent field iterations in density functional theory*, J. Phys. Condens. Matter, 33 (2020), p. 085503.

[71] P. Hislop and I. Sigal, *Introduction to Spectral Theory: With Applications to Schrödinger Operators (Applied Mathematical Sciences)*, Springer, 1995.

[72] P. Hohenberg and W. Kohn, *Inhomogeneous electron gas*, Phys. Rev., 136 (1964), pp. B864–B871.

[73] R. Horn and C. Johnson, *Matrix Analysis*, Cambridge University Press, 1991.

[74] A. P. Horsfield, A. M. Bratkovsky, M. Fearn, D. G. Pettifor, and M. Aoki, *Bond-order potentials: Theory and implementation*, Phys. Rev. B, 53 (1996), pp. 12694–12712.

[75] T. Hudson and C. Ortner, *On the stability of Bravais lattices and their Cauchy–Born approximations*, ESAIM: Math. Model. Num., 46 (2011), pp. 81–110.

[76] T. Kato, *Perturbation Theory for Linear Operators*, Springer-Verlag Berlin Heidelberg, 2nd ed., 1995.

[77] C. Kittel, *Introduction to Solid State Physics*, Wiley, 8th ed., 2004.

[78] W. Kohn and L. J. Sham, *Self-consistent equations including exchange and correlation effects*, Phys. Rev., 140 (1965), pp. A1133–A1138.

[79] P. Koskinen and V. Mäkinen, *Density-functional tight-binding for beginners*, Comp. Mater. Sci., 47 (2009), pp. 237–253.

[80] S. Krantz, *Function Theory of Several Complex Variables*, American Mathematical Society, Jan. 2001.

[81] C. Lanczos, *An iteration method for the solution of the eigenvalue problem of linear differential and integral operators*, J. Res. Nat. Bur. Stand., (1950).

[82] E. Levin and E. B. Saff, *Potential theoretic tools in polynomial and rational approximation*, in Harmonic Analysis and Rational Approximation. Lecture Notes in Control and Information Science, Springer-Verlag, 2006, pp. 71–94.

[83] A. Levitt, *Screening in the finite-temperature reduced Hartree–Fock model*, Arch. Rat. Mech. Anal., 238 (2020), pp. 901–927.

[84] M. Lewin and É. Séré, *Spectral pollution and how to avoid it*, P. Lond. Math. Soc., 100 (2009), pp. 864–900.

[85] E. H. Lieb and B. Simon, *The Thomas-Fermi theory of atoms, molecules and solids*, Adv. Math., 23 (1977), pp. 22–116.

[86] L. Lin, J. Lu, and L. Ying, *Numerical methods for Kohn–Sham density functional theory*, Acta Numerica, 28 (2019), p. 405–539.

[87] M. U. Luchini and C. M. M. Nex, *A new procedure for appending terminators in the recursion method*, J. Phys. C Solid State, 20 (1987), pp. 3125–3130.

[88] M. Luskin and C. Ortner, *Atomistic-to-continuum coupling*, Acta Numerica, 22 (2013), p. 397–508.

[89] Y. Lysogorskiy, C. van der Oord, A. Bochkarev, S. Menon, M. Rinaldi, T. Hammerschmidt, M. Mrovec, A. Thompson, G. Csányi,

C. Ortner, and R. Drautz, *Performant implementation of the atomic cluster expansion (PACE) and application to copper and silicon*, npj Comput. Mater., 7 (2021).

[90] L. R. Mead and N. Papanicolaou, *Maximum entropy in the problem of moments*, J. Math. Phys., 25 (1984), pp. 2404–2417.

[91] M. Mehl and D. Papaconstantopoulos, *Applications of a tight-binding total-energy method for transition and noble metals: Elastic constants, vacancies, and surfaces of monatomic metals*, Phys. Rev. B, 54 (1996), pp. 4519–4530.

[92] F. Q. Nazar and C. Ortner, *Locality of the Thomas–Fermi–von Weizsäcker equations*, Arch. Ration. Mech. Anal., 224 (2017), pp. 817–870.

[93] C. M. M. Nex, *Estimation of integrals with respect to a density of states*, J. Phys. A Math. Gen., 11 (1978), pp. 653–663.

[94] D. Olson and C. Ortner, *Regularity and locality of point defects in multilattices*, Appl. Math. Res. eXpress, 1-41 (2017).

[95] C. Ortner and J. Thomas, *Point defects in tight binding models for insulators*, Math. Models Methods Appl. Sci., 30 (2020), pp. 2753–2797.

[96] ——, *Point defects in tight binding models for insulators*, ArXiv e-prints, arXiv:2004.05356, (2020).

[97] C. Ortner, J. Thomas, and H. Chen, *Locality of interatomic forces in tight binding models for insulators*, ArXiv e-prints, arXiv:1906.11740, (2019).

[98] ——, *Locality of interatomic forces in tight binding models for insulators*, ESAIM: Math. Model. Num. Anal., 54 (2020), pp. 2295–2318.

[99] D. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids, From Z = 1 To Z = 112*, Springer New York, 2015.

[100] D. Papaconstantopoulos, M. Mehl, S. Erwin, and M. Pederson, *Tight-binding hamiltonians for carbon and silicon*, Symposium R – Tight Binding Approach to Computational Materials Science, 491 (1997), p. 221.

[101] D. Pettifor, *New many-body potential for the bond order*, Phys. Rev. Lett., 63 (1989), pp. 2480–2483.

[102] C. Pisani, *Quantum-mechanical treatment of the energetics of local defects in crystals: A few answers and many open questions*, Phase Transit., 52 (1994), pp. 123–136.

[103] T. Ransford, *Potential Theory in the Complex Plane*, Cambridge University Press, Mar. 1995.

[104] E. B. Saff, *Logarithmic potential theory with applications to approximation theory*, Surveys in Approximation Theory, 5 (2010), pp. 165–200.

[105] E. B. Saff and V. Totik, *Logarithmic Potentials with External Fields*, Springer Berlin Heidelberg, 1997.

[106] G. Seifert and J.-O. Joswig, *Density-functional tight binding—an approximate density-functional theory method*, Wiley Interdiscip. Rev. Comput. Mol. Sci., 2 (2012), pp. 456–465.

[107] B. Seiser, D. G. Pettifor, and R. Drautz, *Analytic bond-order potential expansion of recursion-based methods*, Phys. Rev. B, 87 (2013), p. 094105.

[108] A. Shapeev, *Moment tensor potentials: A class of systematically improvable interatomic potentials*, Multiscale Model. Simul., 14 (2016), pp. 1153–1173.

[109] J. Shen, G. Strang, and A. J. Wathen, *The potential theory of several intervals and its applications*, Appl. Math. Opt., 44 (2001), pp. 67–85.

[110] R. Silver and H. Roder, *Densities of states of mega-dimensional Hamiltonian matrices*, Int. J. Mod. Phys. C, 05 (1994), pp. 735–753.

[111] R. Silver, H. Roeder, A. Voter, and J. Kress, *Kernel polynomial approximations for densities of states and spectral functions*, J. Comput. Phys., 124 (1996), pp. 115–130.

[112] J. C. Slater and G. F. Koster, *Simplified LCAO method for the periodic potential problem*, Phys. Rev., 94 (1954), pp. 1498–1524.

[113] H. Stahl and V. Totik, *General Orthogonal Polynomials*, Encyclopedia of Mathematics and its Applications, Cambridge University Press, 1992.

[114] F. H. Stillinger and T. A. Weber, *Computer simulation of local order in condensed phases of silicon*, Phys. Rev. B Condens. Matter, 31 (1985), pp. 5262–5271.

[115] A. M. Stoneham, *Theory of defects in solids: Electronic structure of defects in insulators and semiconductors*, Clarendon Press, 2001.

[116] P. Suryanarayana, K. Bhattacharya, and M. Ortiz, *Coarse-graining Kohn–Sham density functional theory*, Journal of the Mechanics and Physics of Solids, 61 (2013), pp. 38–60.

[117] P. Suryanarayana, P. P. Pratapa, A. Sharma, and J. E. Pask, *SQDFT: Spectral quadrature method for large-scale parallel O(N) Kohn–Sham calculations at high temperature*, Computer Physics Communications, 224 (2018), pp. 288–298.

[118] A. P. Sutton, *Electronic Structure of Materials*, Oxford University Press, 05 1993.

[119] R. Taylor and V. Totik, *Lebesgue constants for Leja points*, IMA J. Num. Anal., 30 (2008), pp. 462–486.

[120] G. Teschl, *Jacobi operators and completely integrable nonlinear lattices*, Mathematical Surveys and Monographs, 72 (2000).

[121] ——, *Mathematical Methods in Quantum Mechanics*, The American Mathematical Society, 11 2014.

[122] J. Thomas, *Locality of interatomic interactions in self-consistent tight binding models*, J. Nonlinear Sci., 30 (2020), pp. 3293–3319.

[123] J. Thomas, H. Chen, and C. Ortner, *Rigorous body-order approximations of an electronic structure potential energy landscape*, ArXiv e-prints, arXiv:2106.12572, (2021).

[124] L. N. Trefethen, *Approximation Theory and Approximation Practice, Extended Edition*, SIAM, Jan. 2019.

[125] N.-K. Tsing, M. K. Fan, and E. I. Verriest, *On analyticity of functions involving eigenvalues*, Linear Algebra Appl., 207 (1994), pp. 159–180.

[126] P. Turchi, F. Ducastelle, and G. Treglia, *Band gaps and asymptotic behaviour of continued fraction coefficients*, J. Phys. C Solid State, 15 (1982), pp. 2891–2924.

[127] C. van der Oord, G. Dusson, G. Csanyi, and C. Ortner, *Regularised atomic body-ordered permutation-invariant polynomials for the construction of interatomic potentials*, 2019.

[128] A. F. Voter, J. D. Kress, and R. N. Silver, *Linear-scaling tight binding from a truncated-moment approach*, Phys. Rev. B, 53 (1996), pp. 12733–12741.

[129] N. D. Woods, M. C. Payne, and P. J. Hasnip, *Computing the self-consistent field in Kohn-Sham density functional theory*, J. Phys. Condens. Matter, 31 (2019).

[130] X. Xie, K. A. Persson, D. W. Small, and D. W. Small, *Incorporating electronic information into machine learning potential energy surfaces via approaching the ground-state electronic energy as a function of atom-based electronic populations*, J. Chem. Theory Comput., 16 (2020), pp. 4256–4270.

[131] T. Yamamoto, *A convergence theorem for Newton's method in Banach spaces*, Japan Journal of Applied Mathematics, 3 (1986), pp. 37–52.

[132] W. Yang, *Direct Calculation of Electron Density in Density-Functional Theory*, Phys. Rev. Lett., 66 (1991), p. 1438.

[133] H. Zhengda, *A note on the Kantorovich theorem for Newton iteration*, J. Comput. Appl. Math., 47 (1993), pp. 211 – 217.

[134] Y. Zuo, C. Chen, X. Li, Z. Deng, Y. Chen, J. Behler, G. Csányi, A. V. Shapeev, A. P. Thompson, M. A. Wood, and S. P. Ong, *Performance and cost assessment of machine learning interatomic potentials*, J. Phys. Chem. A, 124 (2020), pp. 731–745.