MODEL REDUCTION BY DIRICHLET-TO-NEUMANN MAP FOR
MOLECULAR DYNAMICS AND QUANTUM MECHANICS.

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Abstract

This dissertation studies model reduction techniques in the context of classical molecular dynamics and quantum mechanical models. Both the spatial and temporal reductions are considered. The model reduction is formulated as the Dirichlet-to-Neumann (DtN) map. In this dissertation, we restrict ourself into the systems where the number of degrees of freedoms is overwhelming, but the systems exhibit periodic structures, such as, lattice structure in crystalline solids or finite difference structure of the Laplace operator. In these special cases, we are able to take the advantage of the periodic structure, and evaluate the DtN map efficiently. The full model is reduced to a problem on the boundary of the computational domain. The main numerical tool used to compute the DtN map is the boundary element method. Since the lattice Green’s function is computable for the system with the periodic structure, the boundary element method is practical.

The boundary element method not only is crucial to static problems, where we seek the mechanical equilibrium, but also plays an important role in wave propagation problems. In wave propagation problems, the reduced model is the problem in a truncated domain with absorbing boundary conditions. The approximation of the dynamic DtN map provides such absorbing boundary condition. In this case, the stability of the reduced model must be ensured. The stability requirements will be presented.

The same ansatz is applied to time-dependent Schrödinger equation and the time-dependent Hartree-Fock equation. For continuous equations, we start from the discretized model by finite difference. The periodic structure of the nodal points are mathematically equivalent to the lattice structure. Lattice Green’s function and the DtN map can be computed using a similar approach. Stable approximations will be presented. This approach can be naturally extended to the time-dependent Hartree-Fock equation when the potential is neglectable in the exterior region.

The idea of model reduction is verified by several numerical experiments: fracture in atomistic model, phonons propagation in molecular dynamics, one-dimensional time-dependent Schrödinger equation, and $^{16}\text{O}^{+}\text{O}$ colisions.
# Table of Contents

List of Figures vii
List of Tables x
List of Symbols xi
Acknowledgments xiii

Chapter 1
Overview and introduction 1
1.1 Molecular dynamics simulations 2
1.2 Quantum mechanical simulation: Hartree-Fock method 3
1.3 Classical boundary element method 6

Chapter 2
Static problems: domain reduction 9
2.1 Introduction 9
2.2 Mathematical formulations of ABEM 11
2.3 Numerical implementation 17
2.3.1 Adaptive quadrature 17
2.3.2 The Dirichlet-Neumann coupling method 21
2.4 Numerical results 23
2.4.1 A comparison with full-atomistic simulation 23
2.4.2 A system with a long crack 27
2.5 Conclusion and discussion 30

Chapter 3
Dynamic problems: spatial & temporal reduction using absorbing boundary conditions 31
3.1 Introduction 31
3.2 The formulation of absorbing boundary conditions . . . . . . . . . . 34
3.3 Approximations of the DtN map $\Theta$ . . . . . . . . . . . . . . . . . . 41
  3.3.1 Approximation by rational functions . . . . . . . . . . . . . 41
  3.3.2 Evaluation of the DtN map . . . . . . . . . . . . . . . . . . 44
3.4 Stability of absorbing boundary conditions (ABCs) . . . . . . . . . 45
3.5 Implementation of ABCs and partial-harmonic approximation of MD 49
3.6 Numerical simulations . . . . . . . . . . . . . . . . . . . . . . . . 51
  3.6.1 Waves in homogeneous systems . . . . . . . . . . . . . . . . 53
  3.6.2 Waves in a system with dislocations . . . . . . . . . . . . . 53
3.7 Conclusion . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 54

Chapter 4
Absorbing boundary conditions in quantum mechanics 56
4.1 Introduction . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 56
4.2 Formulation of the DtN map for Schrödinger equation . . . . . . . 58
4.3 Approximation of the discrete DtN map . . . . . . . . . . . . . . . 61
  4.3.1 Galerkin projection . . . . . . . . . . . . . . . . . . . . . . . 62
  4.3.2 Approximation by interpolation . . . . . . . . . . . . . . . 66
4.4 Applications & numerical experiments . . . . . . . . . . . . . . . . 66
  4.4.1 1d TDSE model . . . . . . . . . . . . . . . . . . . . . . . . . 68
  4.4.2 3d TDSE model . . . . . . . . . . . . . . . . . . . . . . . . . 70
  4.4.3 3d TDHF model . . . . . . . . . . . . . . . . . . . . . . . . . 71

Chapter 5
Conclusion and future work 75
5.1 Conclusion . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 75
5.2 Coarse grained MD using ABCs at finite temperature . . . . . . . . 75
5.3 Atomistic-to-continuum coupling for elastic wave interactions . . . 76

Appendix A
Dynamic lattice Green’s function 78

Appendix B
Discrete Green’s function for Schrödinger equation 82
  B.1 Discrete Green’s function for 1D Schrödinger equation . . . . . . . 82
  B.2 Discrete Green’s function for 3D Schrödinger equation . . . . . . . 84

Appendix C
Derivation of the time-dependent Hartree-Fock equation for the nucleon system 86
List of Figures

2.1 An illustration of the definitions of different regions. The atoms that are shown in the interior are in the atomistic regions $\Omega_\alpha$. Also highlighted are the atoms along the boundary of $B$.

2.2 Representative atoms and weighted summation for the quadrilateral elements. In this example, each cell contains 4 atoms. For the two different elements, we choose the atoms in the intact cells (green) with weight $L/(2l)$ and fragmented cells (blue) with weight 1.

2.3 An illustration of adaptive quadrature. A diagonal block of the stiffness matrix is shown. The colors from white to black indicate the density of selected representative atoms, e.g., the entries close to the diagonals were computed using many representative atoms, and the remaining entries were computed using very few representative atoms due to the facts that those elements are far from each other.

2.4 An illustration of the coupling method. In this example, the system contains two atomistic regions. The atoms on the different boundaries contribute the corresponding terms to the ABEM equation.

2.5 A system with two cracks. The two rectangular domains (colored red) are atomistic regions (upper). All atoms in the entire domain are colored with local atomic strain (bottom).

2.6 Relative error ($\|(u - u^*)/\|u^*\|_\infty\|)$ with $\epsilon_{22} = 2\%$. $u^*$ is the exact solution of full-atomistic simulation. $u$ is the solution by proposed coupling method. $x$-component (left upper) and $y$-component (right upper) of the displacement are shown separately. The positions of four atoms with maximum displacement on crack faces are shown as functions of strain (bottom four).
2.7 Snapshots of crack propagation under increasing load using full-atomistic simulation (Top) and our coupling method (Bottom). All snapshots under different strains are put together for comparison. Full-atomistic region is cropped according to atomistic region in the coupling model. The crack-propagation distance is shown as a function of the strain in the right figures.

2.8 Strain-stress curve. The crack propagation part is shown only. The strain-stress response is a straight line before the cracks propagate.

2.9 The setup of the simulation. The figure on the left shows the entire sample and the crack, along with the elements. Right figure is a close-up view of the crack with the solid circles representing the atoms.

2.10 The simulation of the long crack: Stress-strain curve (upper) and elastic modulus (bottom).

2.11 Snapshots of crack propagation under increasing loading (the crack tip on the right). From left to right, the values of the strain: 0.04%, 0.043%, 0.04312%, 0.04321%, 0.04338%, 0.04347%, 0.04373%, and 0.04383%.

3.1 An illustration of the domain decomposition.

3.2 An illustration of the interface regions $\Gamma_I$ and $\Gamma_{II}$.

3.3 Wave propagations in the homogeneous system. The color indicates the velocity in the x direction.

3.4 Wave propagations in the system with dislocations, the color indicates the value of velocity.

4.1 An illustration of the model reduction for 1d Schrödinger equation.

4.2 The solutions by ABC using interpolation and the exact solution.

4.3 The decay of the norm of the wave function.

4.4 The solutions by various absorbing boundary conditions and the exact solution.

4.5 The decay of the particle density.

4.6 # of electron as a function of time step.

4.7 3d tdse solutions.

4.8 The loss of the total energy and the loss of nucleons.

4.9 Contour plot of the nucleon density in time evolution of $^{16}O + ^{16}O$ collision with ABC (top). The difference of the nucleon density in time evolution by ABC and Dirichlet boundary condition.
5.1 One-dimensional simulation of the dynamical atomistic-to-continuum coupling. The Lennard-Jones potential is used in the MD region. The interactions are linearized in the continuum region. The continuum region is discretized for a more accurate approximation of the DtN map. $T = 0, 1 \times 10^4, 2 \times 10^5, 3 \times 10^5$ from top to bottom. The coupling method filters phonons and passing elastic waves in dynamics simulation of concurrent atomistic-continuum method.

B.1 1D discrete Green’s function vs 1D continuum Green’s function, $s=1, h=1$ .................................................. 84

B.2 3D discrete Green’s function vs 3D continuum Green’s function, $h=0.01, s=10$ .................................................. 85
List of Tables

3.1 Kernel functions in the Laplace domain. . . . . . . . . . . . . . . . . . . 37
3.2 Computational time of the three approximate ABCs imposed on
the same problem, same computer, for 200,000 time steps. . . . . . . 52
List of Symbols

\( \Omega \) \hspace{1cm} \text{the computational domain} \\
\( \Omega_a \) \hspace{1cm} \text{the truncated region in model reduction} \\
\( D_{ij} \) \hspace{1cm} \text{force constant matrix between atom } i \text{ and } j \\
\( \tilde{D}_{ij} \) \hspace{1cm} \text{shifted force constant } \tilde{D}_{ij} = D_{ij} + s^2 \delta_{ij} \\
\( G_{nj} \) \hspace{1cm} \text{lattice Green’s function at atom } j \text{ relative to atom } n \\
\( R_i \) \hspace{1cm} \text{reference coordinate of atom } i \\
\( r_i \) \hspace{1cm} \text{current position of atom } i \\
\( u_i \) \hspace{1cm} \text{displacement of atom } i \\
\( f_i \) \hspace{1cm} \text{force on atom } i \\
\( s \) \hspace{1cm} \text{Laplace transform variable} \\
\( U_i \) \hspace{1cm} \text{Laplace transform of the displacement of atom } i \\
\( F_i \) \hspace{1cm} \text{Laplace transform of the force on atom } i \\
\( V \) \hspace{1cm} \text{potential energy of the system} \\
\( t_i \) \hspace{1cm} \text{traction on the atom } i \\
\( \sigma_i \) \hspace{1cm} \text{local stress on atom } i \\
\( A_i \) \hspace{1cm} \text{coefficients of rational functions on the numerator} \\
\( B_i \) \hspace{1cm} \text{coefficients of rational functions on the denominator}
\( \sigma_i \)  local stress on atom \( i \)

\( \hat{H} \)  Hamiltonian operator in a quantum system

\( H_{ij} \)  discretization of Laplace operator

\( \Psi \)  wave function in a quantum system

\( \rho \)  nucleon density

\( t_0 \)  coefficient of the Skyrme interaction

\( t_3 \)  coefficient of the Skyrme interaction

\( V_0 \)  coefficient of the Skyrme interaction

\( W_Y \)  Yukawa potential

\( W_C \)  Coulomb potential
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Chapter 1  
Overview and introduction

Modeling and simulation of materials are of general interest in various scientific fields. In each field, a systematic mathematical framework is constructed to study the specific physical phenomena. The levels of simulations mainly vary from classical continuum mechanics, molecular dynamics (MD), and quantum mechanics (QM) in terms of the accuracy [1]. One single model usually is insufficient to model the entire complicated phenomena. Lots of efforts have been devoted to balance the computational cost and accuracy among different models.

The bottom-up approach always be preferred as a neat framework. Due to the assumption of the models, it is more practical from microscopic models to macroscopic models by proper approximations. However, the reverse path is mostly a rocky road. The modification of the fundamental assumption in a macroscopic model is more challenging than coarsening the corresponding microscopic model. Throughout this dissertation, the philosophy is deriving macroscopic models from the microscopic models, namely from molecular dynamics to continuum mechanics, or from quantum mechanics to continuum mechanics. During this process, the existing ideas in the macroscopic models might be applied to the microscopic model. The connections between any two channels and derivation from a microscopic model to a macroscopic model trigger our interest most.

This chapter presents the least amount of prerequisite knowledge of this dissertation. Section 1.1 introduces the background of molecular dynamics. The Hartree-Fock model is introduced in Section 1.2. In Section 1.3 the idea of the boundary element method will be discussed.
1.1 Molecular dynamics simulations

Molecular dynamics (MD) is a computer simulation method for studying the physical movements of atoms and molecules. The trajectories of atoms and molecules are determined by Newton’s equations of motion. For a system of $N$ particles with coordinates $\mathbf{x}$ and velocities $\mathbf{v}$, the positions and velocities follow

$$\begin{aligned}
    m\ddot{\mathbf{v}}(t) &= -\nabla_x V(\mathbf{x}) \\
    \dot{\mathbf{x}}(t) &= \mathbf{v}(t)
\end{aligned} \tag{1.1}$$

The potential energy function $V(\mathbf{x})$ of the system is a function of the particles coordinates $\mathbf{x}$. It is referred to the potential in physics, or force field in chemistry. $m$ is the mass matrix, which is diagonal. Given the initial positions and velocities, the above ordinary differential equation has an unique solution for $\mathbf{v}$ and $\mathbf{x}$, namely, all the future velocities and positions are determined. In mathematics, all the quantities are determined by the initial conditions (positions and velocities) for any given system.

The potential energy function is the key of success in MD. It is the key characteristic of a MD system. In general, the total potential energy can be expressed as

$$V = \sum_i^N V_1(\mathbf{x}_i) + \sum_{i,j}^N V_2(\mathbf{x}_i, \mathbf{x}_j) + \sum_{i,j,k}^N V_3(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) + \cdots \tag{1.2}$$

here $V_1$ is the one-body potential. $V_2$ is the two-body interaction, which depends on the distance between two atoms. $V_3$ is the three-body potential, which can be a function of angles between bonds and distances between atoms. Different potentials are used for different purposes and different materials. Most interactions in MD are short-ranged interactions, that is, there is some cutoff distance $r_{cut}$, such that, the force calculation will be restricted in a small region for each atom. In this case, the MD algorithm is an $O(N)$ algorithm. For the long-range interactions, e.g. electrostatic interactions, the computational complexities of MD can be reduced to $O(N^2)$ or $O(N \log N)$ by the Ewald summation [2]. The typical potentials in MD include the Lennard-Jones potentials, embedded-atom potential (EAM) for metals, Tersoff potential for silicon and carbon, and etc.

From physical viewpoint, many constraints can be applied to MD. Most of them
are implemented by boundary conditions. The typical constraints of MD include the number of particles (N), volume (V), energy (E), and temperature (T). For instance, in the microcanonical ensemble (NVE), particles (N), volume (V) and energy (E) of the system do not change. In the canonical ensemble, particles (N), volume (V), and temperature (T) of the system do not change. To connect the mathematical theory, NVE ensemble can be implemented by imposing Dirichlet boundary condition or Neumann boundary conditions. The temperature control is slightly more complicated. Most thermostat algorithm control the temperature by adding or removing energy from the boundaries from a MD simulation. The popular methods include Nosé-Hoover thermostat, Nosé-Hoover chains, the Berendsen thermostat, the Andersen thermostat and Langevin dynamics.

1.2 Quantum mechanical simulation: Hartree-Fock method

The Hartree-Fock (HF) method is a method of approximation for the quantum many-body system. The Hartree-Fock theory is applied to the Schrödinger equation for various physical systems, such as atoms, molecules, and nuclear structures. In this dissertation, the time-dependent Hartree-Fock method in nuclear physics will be presented. As an introduction, the idea of the Hartree-Fock method will be explained by the electronic structure calculation.

Consider the following nonrelativistic Hamiltonian of the system of \( I \) electrons and \( J \) nuclei,

\[
H = T_e + V_{ne}(\mathbf{r}_1, \cdots, \mathbf{r}_I, \mathbf{R}_1, \cdots, \mathbf{R}_J) + V_{ee}(\mathbf{R}_1, \cdots, \mathbf{R}_J) \tag{1.3}
\]

The kinetic energy operator \( T_e \) is defined as

\[
T_e = \sum_{i=1}^{I} -\frac{\hbar^2}{2m_e} \nabla_i^2 
\tag{1.4}
\]

The nuclei-electron interaction \( V_{ne} \), which depends on the nuclei positions \((\mathbf{R}_1, \cdots, \mathbf{R}_J)\)
and the coordinates of the electrons \((r_1, \cdots, r_I)\), is formulated as

\[
V_{ne} = \sum_{i=1}^{I} \sum_{j=1}^{J} \frac{Z_j e^2}{4\pi\epsilon_0 |r_i - R_j|} \tag{1.5}
\]

where \(\epsilon_0 = 8.85 \times 10^{-12} C^2/Jm\) is the permittivity of space. The electron-electron interaction \(V_{ee}\) is expressed as

\[
V_{ee} = \sum_{i=1}^{I} \sum_{j>i}^{I} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} \tag{1.6}
\]

In the typical electron structure calculation, the nuclei positions are fixed. Hence, the nuclei-nuclei interaction is just a constant. To simplify the notations, let us define

\[
H = \sum_{i=1}^{I} h_1(r_i) + \frac{1}{2} \sum_{i \neq j} h_2(r_i, r_j) \tag{1.7}
\]

If we ignore the spin of electrons, the many-body wave function generally takes the form

\[
\Psi(r_1, r_2, \cdots, r_I) \tag{1.8}
\]

where \(r_i\) is the coordinate of the electron \(i\). The wave function certainly depends on the nuclear positions \(R_i\). In electron structure calculation, the nuclear positions are given beforehand. To simplify the notations, the dependence does not appear in the form of the many-body wave function.

The exact fermionic wave function is an element in the Fock space,

\[
F_- (H) = \bigoplus_{n=0}^{\infty} S_- H^\otimes n = \mathbb{C} \oplus H \oplus (S_- (H \times H)) \oplus (S_- (H \otimes H \otimes H)) \oplus \cdots \tag{1.9}
\]

where \(H\) is a single-particle Hilbert space. One typical example is the free particle with \(H = L_2(\mathbb{R}^3, \mu)\). \(S_-\) is the operator which antisymmetrizes a tensor, that is, for a general wave function \(\psi\),

\[
\Psi(r_1, \cdots, r_i, \cdots, r_j, \cdots, r_I) = -\Psi(r_1, \cdots, r_j, \cdots, r_i, \cdots, r_I) \tag{1.10}
\]

In order to satisfy the antisymmetry condition, the Hartree-Fock approximation
adopts the following Slater determinant as the wave function:

$$
\Psi(r_1, r_2, \cdots, r_n) = \frac{1}{\sqrt{I!}} \begin{vmatrix}
\psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_I(r_1) \\
\psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_I(r_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(r_I) & \psi_2(r_I) & \cdots & \psi_I(r_I)
\end{vmatrix} \quad (1.11)
$$

The factor $\frac{1}{\sqrt{I!}}$ is introduced to ensure normalization. The single-particle wave function $\phi_i$ are the unknowns, which will be determined by solving the Hartree-Fock equations. The Hartree-Fock equations are derived by the variational principle. The expectation value of the Hamiltonian (the total energy) under the Hartree-Fock approximation is

$$
\langle \Psi | H | \Psi \rangle = \sum_{i=1}^{I} \langle \psi_i | \hat{h}_1 | \psi_i \rangle + \frac{1}{2} \sum_{i,j} \left[ \langle \psi_i \psi_j | \hat{h}_2 | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{h}_2 | \psi_i \psi_j \rangle \right] \quad (1.12)
$$

These single-particle wave functions minimize the above energy. Also, the set of those basis function should remain orthogonal, that is, the wave functions satisfy

$$
\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \text{for all } i, j = 1, \ldots, I \quad (1.13)
$$

The constrains are added to the minimization by Lagrange multipliers. Overall, the single-particle wave functions satisfy

$$
\frac{\delta}{\delta \psi_i^*(x)} \left[ \langle \psi | H | \psi \rangle - \sum_{i,j} \lambda_{ij} \langle \psi_i | \psi_j \rangle \right] = 0 \quad (1.14)
$$

By evaluating the functional differentiation, Eq. 4.49 turns out to be

$$
\hat{h}_1 \psi_k(r_1) + \sum_i \left\{ \int \psi_i^* \hat{h}_2[\psi_i(r_2)\psi_k(r_1)]dr_2 - \int \psi_i^* \hat{h}_2[\psi_i(r_1)\psi_k(r_2)]dr_2 \right\} = \sum_i \lambda_{ki} \psi_i(r_1) \quad (1.15)
$$
This equation can be written as a compact form,

\[ \hat{F}_k \psi = \sum_{i=1}^{I} \lambda_{ki} \psi_i \]  \hspace{1cm} (1.16)

where \( \hat{F} \) is called Fock operator. \( \psi_i \) are one-electron wave functions, called the Hartree-Fock molecular orbitals. In modern Hartree-Fock calculations, the one-electron wave functions are approximated by a linear combination of atomic orbitals (LCAO), such as Gaussian-type orbitals. Other basis sets are also used in the interests of saving computation time. When the basis functions are not orthogonal, the right hand side of (4.4) becomes the overlap matrix. Instead of performing the Gram-Schmidt process, the more common approach is to solve the generalized eigenvalue problem.

1.3 Classical boundary element method

The idea of the boundary element method (BEM) is reformulating the partial differential equation into a boundary integral equation when the Green’s function can be calculated. BEM is more efficient than the widely-used finite element method if the discretization of the entire domain requires too many elements. Here, we will derive the BEM by an example of a two-dimensional problem.

Let us consider the boundary value problem

\[ \Delta u = 0 \quad \text{in } \Omega, \]
\[ u(x, y) = u_0 \quad \text{on } \partial \Omega \]  \hspace{1cm} (1.17)

The Green’s function (fundamental solution) is defined by

\[ \Delta G(x - \xi, y - \eta) = \delta(x - \xi, y - \eta) \]  \hspace{1cm} (1.18)

where \( (\xi, \eta) \) is a point source of infinite strength. In this particular example, the Green’s function can be explicitly expressed as

\[ G(x - \xi, y - \eta) = \ln r + C, \quad r = \sqrt{(\xi - x)^2 + (\eta - y)^2}. \]  \hspace{1cm} (1.19)
where $C$ can be any constant number.

The original problem (C.10) is reduced to the boundary integral equation by taking advantage of Green's function and Green's second identity. The Green's second identity is formulated as follow: If $\varphi$ and $\psi$ are both twice continuously differentiable on $U$, then

$$
\int_U (\psi \Delta \varphi - \varphi \Delta \psi) dV = \oint_{\partial U} \left( \psi \frac{\partial \varphi}{\partial n} - \varphi \frac{\partial \psi}{\partial n} \right) (1.20)
$$

For the point $(\xi, \eta) \in \Omega$ is not on the boundary, if we choose $\varphi = G$ and $U = \Omega$,

$$
\int_\Omega u \Delta G dV = \int_\Omega u \delta(x - \xi, y - \eta) dV = u(\xi, \eta) (1.21)
$$

The boundary integral equation is written as

$$
u(\xi, \eta) = \oint_{\partial \Omega} (u \frac{\partial G}{\partial n} - G \frac{\partial u}{\partial n}) (1.22)
$$

For the case when the point $P(\xi, \eta)$ is on the boundary $\partial \Omega$), the boundary integral equation can be derived by some analysis. For the point where the boundary is smooth, there exists a small disk around $P$, $U(p, \epsilon)$. Let us denote $\Omega_\epsilon = \Omega \cup U(p, \epsilon)$. If we apply the Green’s second identity with $\varphi = G$ and $U = \Omega$,

$$
u(\xi, \eta) = \oint_{\partial \Omega_\epsilon} (u \frac{\partial G}{\partial n} - G \frac{\partial u}{\partial n}) (1.23)
$$

by the same trick above. At this point, we divide $\partial \Omega_\epsilon$ into two parts $\partial \Omega_{-\epsilon}$ and $\Gamma$, where $\partial \Omega_{-\epsilon} = \partial \Omega \cap \partial \Omega_\epsilon$ and $\Gamma = \partial \Omega_\epsilon - \partial \Omega_{-\epsilon}$ is a half circle. By the mean value theorem,

$$
\lim_{\epsilon \to 0} \int_{\Gamma} u \frac{\partial G}{\partial n} ds = u(P), (1.24)
$$

and

$$
\lim_{\epsilon \to 0} \int_{\Gamma} G \frac{\partial u}{\partial n} ds = 0. (1.25)
$$

On the boundary $\Omega_\epsilon$, the limits of two integrals are

$$
\lim_{\epsilon \to 0} \int_{\partial \Omega_\epsilon} u \frac{\partial G}{\partial n} ds = \int_{\partial \Omega} u \frac{\partial G}{\partial n} ds (1.26)
$$
and
\[
\lim_{\epsilon \to 0} \int_{\partial \Omega_\epsilon} G \frac{\partial u}{\partial n} \, ds = \int_{\partial \Omega} G \frac{\partial u}{\partial n} \, ds \tag{1.27}
\]

Therefore, for any point \(P(\xi, \eta)\), the boundary integral equation is
\[
C(P)u(P) = \int_{\partial \Omega} u \frac{\partial G}{\partial n} \, ds - \int_{\partial \Omega} G \frac{\partial u}{\partial n} \, ds \tag{1.28}
\]

where
\[
C(P) = \begin{cases} 
1 & P \in \Omega \\
1/2 & P \in \partial \Omega, \text{ smooth} \\
1 - \alpha/(2\pi) & P \in \partial \Omega, \text{ not smooth}
\end{cases} \tag{1.29}
\]

The boundary integral equation is closed when we consider all the points on the boundary. Let us discretize the boundary, denote \(q = \frac{\partial u}{\partial n}\). \(u, q,\) and \(F\) are the discretizations of \(u, q\) and \(\frac{\partial G}{\partial n}\) on the boundary. The discretization of the boundary integral equation is written as
\[
Cu = Gq + Fu. \tag{1.30}
\]

The equation is determined when the proper boundary conditions, namely partial components of \(u\) or \(q\) are given. The unknowns are the remaining components of \(u\) and \(q\) which are not given. For the information of other points inside the domain (not on the boundary) can be evaluated by (B.11) when (B.13) is solved.
Chapter 2  
Static problems: domain reduction

2.1 Introduction

The problem of fracture is of central importance in material science, and it has a major subject of interest in computational mechanics. A remarkable success in fracture mechanics is the development of boundary element method (BEM) [3, 4]. By employing the fundamental solutions — the Green’s function, the formulation reduces the full elastostatic problem to a coupled system of equations along the crack faces as well as the remote boundary, where the external loads can be applied. This effectively simplifies the problem to one in a lower dimension. In sharp contrast to traditional finite element discretizations, BEM eliminates the computational burden associated with the non-uniform meshes around the cracks. The BEM has also been extended to anisotropic elasticity models, e.g., [5, 6]. Another important development is the incorporation of $J-$integrals in the BEM formulation [7].

A recently emerging method for fracture simulations is based on atomistic models. Starting with an interatomic potential, either empirically fitted or derived from more fundamental considerations, one can seek the mechanical equilibrium by minimizing the total potential energy. This model is known as the molecular mechanics (MM) model. For example, Cheung and Yip [8] considered the BCC-iron structures and studied the brittle-ductile transition along three different crystal orientations. There have been many recent works on the atomistic simulations of fracture, e.g., [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. With standard software
packages, such as LAMMPS [20], performing such a simulation has become a rather straightforward task.

Atomistic models naturally incorporate crystal configurations and defect structures [21, 22]. Therefore, they often offer much greater modeling accuracy. For example, cracks may have different propagation properties along different crystal planes [8]. Of particular importance from a modeling perspective is that fracturing criterion is not needed in such a model. A notable finding is lattice trapping associated with crack propagation [23]. On the other hand, direct simulations using atomistic models inevitably introduce huge number of atoms, and the system is often too large for a practical computation. For static problems, where one finds the mechanical equilibrium by minimizing the total energy, the usual optimization algorithms take huge number of iterations to converge, due to the large dimensionality. For dynamics problems, many time steps are needed to reach the time scale of interest. To overcome the difficulty, many hybrid models have been proposed in the last two decades to combine an atomistic model near local defects and a continuum description to model the elastic deformation away from the defects [24, 25, 26, 27, 28, 29, 30, 31, 32]. In particular, in [33], the MM model is interfaced with a finite element model of elasticity. Later, the quasicontinuum method [34, 35, 36] was developed, which has been applied to the fracture problems to study the emission of dislocations from the crack tip [37].

Nevertheless, the ability of existing hybrid methods to handle a system on the micron scale, and more importantly, cracks that extend to hundreds of nanometers, has not been reported. One crucial difficulty is associated with the mesh generation: Due to the small spatial scale associated with the MM model, one has to refine the mesh from a much larger scale to Angstrom ($10^{-10}$m) scale.

Motivated by the success of the conventional BEM in continuum mechanics, we propose to address this issue by using a discrete BEM. This approach starts with the full MM model, and following the formulation of continuum BEM, it derives a reduced model, in which only those atoms near the crack tips and those atoms along the remote boundary are involved. As a result, the dimension of the problem is significantly reduced. Further, the reduced model is mesh-less, and no mesh generation or re-generation is needed. This formulation has been presented in our previous work [38, 39], and it has been referred to as the atomistic-based boundary element method (ABEM). This project will focus on brittle materials.
For ductile cracks, the fracture process is accompanied by dislocations emission, and new methodologies are needed to keep track of the dislocation loops, e.g., a method along the line of the new discrete dislocation dynamics (DDD) method [40].

In order to consider systems at least on the micron scale and longer cracks, we propose an adaptive quadrature approximation along the boundaries and along the crack faces. With these further approximations, the dimension of the reduced model is insensitive to the size of the entire system. Meanwhile, the ABEM will serve as a boundary condition for the atomistic models near the crack tips. Consequently, the influence of the remote boundary conditions on the crack regions are directly manifested. In addition, the MM models for each crack tip can be solved in parallel. To facilitate the coupling between the ABEM and the MM models, we propose a Dirichlet-Neumann coupling method, in which the two components exchange displacement and tractions, respectively, without having to introduce an overlapping region. This also greatly simplifies the implementation.

2.2 Mathematical formulations of ABEM

Consider a system with \(N\) atoms, occupying a domain \(D\) with boundary \(\partial D\). Throughout this project, \(\mathbf{R}_i\) and \(\mathbf{u}_i\) will be used to designate the reference coordinate and the displacement of \(i\)-th atom respectively: \(\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i\) is the current position. We first start with the full atomistic model, where we seek the mechanical equilibrium by minimizing the total potential energy,

\[
\min V(\mathbf{u}_1, \mathbf{u}_2, \cdots, \mathbf{u}_N),
\]

subject to appropriate loading condition along the boundary. In terms of force balance, the model can be expressed as,

\[
f_i := -\frac{\partial}{\partial \mathbf{u}_i} V = 0, \quad 1 \leq i \leq N,
\]

again subject to the boundary conditions along \(\partial D\). This force balance can also be formulated in terms of the stress by defining appropriate atomic expressions of the first Piola-Kirchhoff stress [41], making an immediate connection to conventional
continuum mechanics. However, we prefer to keep the formulation at the discrete level, which offers several advantages in terms of the implementation. This will be explained in detail in the next section.

For crystalline solids, various models for the potential energy, known as empirical potentials, have been developed. Several representative examples can be found in [42, 43, 44]. Most empirical potentials are short-ranged: They come with a cut-off distance $r_{\text{cut}}$, which is usually about $2 \sim 4$ atomic spacings.

As alluded to in the introduction, we are interested in a micron scale system, which for atomistic models, would involve a huge number of atoms e.g., $N \sim 10^9$. Since direct simulations are impractical, we introduce a reduction procedure to remove the excessive atomic degrees of freedom. As an example, we show in Fig.

2.1 a system with two sub-domains which may contain micro cracks. The first key step is to partition the system into sub-domains. In particular, we denote the sub-domains that contain the micro cracks as $\Omega_1$ and $\Omega_2$. These two regions will be referred to as atomistic regions, since the atomistic model (2.2) will be retained to resolve the micro-structures. Further, we let $B$ be the remaining part of the system, where the atomistic model (2.2) will be simplified. A natural approximation is to switch to a continuum approximation in $B$, e.g., a finite element discretization of the elasticity model. This is essentially the idea of the quasi-continuum approximation [34]. An inevitable issue in such an approach is the coupling between the finite element nodal values in $B$ and the atom positions in the atomistic regions. The fact that the region $B$ is multi-connected further complicates the implementation procedure.

Here we use the atomistic-based boundary element method (ABEM) [38], in which a mesh-less model is derived, without having to go through a continuum approximation. The mathematical formulation is briefly described here. We make the assumption that the displacement of the atoms in $B$ is smooth. Therefore, the atomistic model in this region can be reduced. A natural approximation is the harmonic approximation, which linearizes the force between the atoms [45, 46]. Namely,

$$-\frac{\partial V}{\partial u_i} \approx \sum_j D_{i,j}(u_i - u_j).$$  \hspace{1cm} (2.3)

Here $D_{i,j}$ is known as the force constant. It can be defined as the second order
Figure 2.1. An illustration of the definitions of different regions. The atoms that are shown in the interior are in the atomistic regions $\Omega_\alpha$. Also highlighted are the atoms along the boundary of $B$.

derivative of the potential energy around the reference state (perfect lattice),

$$D_{i-j} = \frac{\partial^2}{\partial u_i \partial u_j} V(0, 0, \cdots, 0). \tag{2.4}$$

The force constant does not depend on the particular atoms, but is related to the relative position. Therefore, it has been customary to write it as $D_{i,j} = D_{i-j}$. Because of the short-range interactions between atoms, the force constant is only nonzero when the two atoms are within the cut-off radius.

It is worthwhile to point out that the continuum limit of the linearized model is the anisotropic linear elasticity model. In particular, the elastic moduli can be expressed in terms of the force constant matrices \cite{46}.

Let us define the outer and inner boundary of $B$ respectively as follows,

$$\partial B^+ = \{ \mathbf{R}_i \notin B, |\mathbf{R}_i - \mathbf{R}_j| \leq r_{cut}, \text{for some } j \in B \}, \tag{2.5}$$

and

$$\partial B^- = \{ \mathbf{R}_i \in B, |\mathbf{R}_i - \mathbf{R}_j| \leq r_{cut}, \text{for some } j \notin B \}. \tag{2.6}$$

A pictorial illustration can be found in Figure 1. These two sets of atoms have to be distinguished due to the discrete nature of the model.

With this linearization, the atomistic model in the region $B$ has been reduced
to the following boundary value problem,

$$\sum_{j} D_{i,j} (u_i - u_j) = 0, \quad i \in B, \quad (2.7)$$

supplemented with the following boundary conditions,

$$u_i = u_0^i, \quad i \in \partial B^+, \quad \text{(given the displacement of atom } i), \quad (2.8)$$

$$t_j = t_0^j, \quad j \in \partial B^-, \quad \text{(given the external force of atom } j). \quad (2.9)$$

Here the two boundary conditions are the discrete analogue of the Dirichlet and Neumann boundary conditions in continuum mechanics. For instance, we may apply Dirichlet boundary condition along the remote boundary (i.e., $\partial D^+$), and Neumann boundary condition along the interfaces with the atomistic region. Namely,

$$\partial B^-_N = \{i | i \in \partial B^- \text{ and } \text{dist}(R_i, \Omega_\alpha) \leq r_{\text{cut}}, \text{ for some } \alpha \geq 1\}. \quad$$

Equations (2.7) and (2.8) summarized the simplified molecular mechanics model in the domain $B$. Meanwhile, the displacement of the atoms in the atomistic region still follow the nonlinear molecular statics model, i.e., the force on each atom vanishes,

$$f_i = 0, \quad \text{for each } i \in \Omega_\alpha. \quad$$

Using the usual additivity of the empirical potentials, for each atomistic region $\Omega_\alpha$, we can write this as a minimization problem,

$$\min E_\alpha, \quad E_\alpha := \sum_{i \in \Omega_\alpha} V_i, \quad (2.10)$$

subject to the boundary condition along $\partial \Omega_\alpha^+$.

Up to this point, the number of unknowns is the same as before. The reduction of the degrees of freedom will be achieved by using the lattice Green’s function, which is similar to the derivation of the boundary element methods for continuum mechanics [6].

The lattice Green’s function is defined as the solution of the finite-difference
equations (2.7),
\[
\sum_k D_k G_{j+k|n} = I \delta_{jn},
\]  
subject to a point force. Here \( G_{j|n} \) represents the displacement of the atoms at lattice point \( j \), in response to a force applied to lattice site \( n \). It is the fundamental solution of the difference equations (2.7). Due to the translational symmetry, the function only depends on the relative position \( \mathbf{R}_j - \mathbf{R}_n \). At this point, we assume that this Green’s function is accessible for any two atoms \( j \) and \( n \). Interested readers are referred to [38] regarding the method for calculating the Green’s function.

The general formulation of the atomistic-based boundary element method (ABEM) was first established in [38], which essentially involves multiplying the equation (2.7) and summation by parts. If we impose the Dirichlet boundary condition on \( \partial B_D \), and Neumann boundary condition on \( \partial B_N \). The ABEM can be summarized as the following equation: For any \( n \in \partial B^- \), we have
\[
\mathbf{u}_n = - \sum_{j \in \partial B^-_N} S_{n,j} \mathbf{u}_j + \sum_{j \in \partial B^-_N} G_{j|n} \mathbf{t}_j + \sum_{j \in \partial B^-_D} K^-_{n,j} \mathbf{u}_j - \sum_{i \in \partial B^+_D} K^+_{n,i} \mathbf{u}_i,
\]  
where the coefficient matrices are given by,
\[
K^+_{n,i} = \sum_{j \in \partial B^-} G_{j|n} D_{i-j},
K^-_{n,j} = \sum_{i \in \partial B^+} G_{i|n} D_{i-j},
S_{n,j} = - \sum_{i \in \partial B^+} (G_{i|n} - G_{j|n}) D_{i-j}.
\]  
These formulae are exact under the harmonic approximation. We can write the above formulae into a more compact form,
\[
\mathbf{u}_- = K \mathbf{u}_- + \mathbf{b}_-,
\]  
where
\[
\begin{align*}
\mathbf{u}_- &= [\mathbf{u}_{j_1}^T, \mathbf{u}_{j_2}^T, \ldots, \mathbf{u}_{j_n}^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial B^-,
\mathbf{u}_+ &= [\mathbf{u}_{j_1}^T, \mathbf{u}_{j_2}^T, \ldots, \mathbf{u}_{j_n}^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial B^+_D,
\mathbf{t}_- &= [\mathbf{t}_{j_1}^T, \mathbf{t}_{j_2}^T, \ldots, \mathbf{t}_{j_n}^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial B^-.
\end{align*}
\]
and the remaining terms are given by,

\[ K = \begin{bmatrix} -S & K^- \end{bmatrix}, \quad b_- = Gt_- - K^+ u_+, \quad \text{and} \quad G_{n,j} = G_{j|n}. \]

This is reminiscent of the conventional BEM. The unknowns are the displacement of the atoms along \( \partial B^- \), and the input is the displacement along \( \partial B_D^+ \) and traction along \( \partial B_N^- \).

Equation (2.12) is the main result of the ABEM. It eliminates all the atomic degrees of freedom in the interior of the domain \( B \), which for many material defect problems, leads to a significant reduction. Further, it directly couples the displacement along the remote boundaries and the traction along the interfaces with the atomistic regions. Despite the similarity to the conventional BEMs, the current method is directly based on the discrete atomistic model. In particular, the Green’s function associated with the lattice model remains finite at the origin. As a result, no singular integral would arise from the present framework. Further, since the model is already discrete, no geometric singularity, such as corners, would come up, either.

The current project aims to further improve the ABEM. In particular, we address the following issues.

1. In the domain-decomposition algorithm, where we alternate between the linear equations (2.12) and the nonlinear equations (2.2) in the atomistic regions until convergence. This is done by using a Dirichlet-Neumann coupling, motivated by the technique in domain decomposition method [47].

2. The second issue for simulating a crack is when the length of the crack is long, a direct treatment is to include the entire crack in an atomistic region \( \Omega/ \), which clearly increases the computational cost due to the large number of atoms involved. Here we propose to only resolve the atoms near the crack tips, and treat the crack faces as an internal interface. This will be explained in the next two sections.
2.3 Numerical implementation

Compared to the original ABEM, we have made several improvements, including an adaptive quadrature formula, a non-overlapping coupling with the atomistic regions, and a quadrature approximation along the crack faces for longer cracks, which is specifically designed for fracture simulations. Here will explain the implementation of these steps.

2.3.1 Adaptive quadrature

In equation (2.12), all summations are over atoms along the boundaries. For a large system, e.g., one on the micron scale, the summations would involve many atoms and the computation becomes expensive. In practice, most "external/far field" boundary conditions are smooth enough to be approximated by standard shape functions, e.g., piecewise polynomials. In this case, the displacement of the atoms and the traction will be approximated by a linear combination of some shape functions, here denoted by $\varphi$. To better explain the notations, the boundaries are divided into $\partial B^+ = \partial R^+ \cup \partial L^+$ and $\partial B^- = \partial R^- \cup \partial L^-$. Here $\partial R$ is the remote boundary where an approximation of the summations will be introduced, and $\partial L$ is the local boundary surrounding the atomistic regions $\Omega_\alpha$ where atom-by-atom summation is retained. For all $i \in \partial R^+$ and $j \in \partial R^-$, we can define the subspace approximations,

\begin{align}
    u_i & \approx \sum_{k \in \partial R^+} u^h_{k \varphi_k}(R_i), \\
    u_j & \approx \sum_{\ell \in \partial R^-} u^h_{\ell \varphi_\ell}(R_j), \\
    t_j & \approx \sum_{\ell \in \partial R^-} t^h_{\ell \varphi_\ell}(R_j),
\end{align}

where, $u^h_k$ and $u^h_\ell$ are the displacement of $k$-th outside nodal point and $\ell$-th inside nodal point, respectively.

To proceed, we define

\begin{align}
    u^h_{in} &= [(u^h_{j_1})^T, \ldots, (u^h_{j_n})^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial R^-, \\
    u^h_{out} &= [(u^h_{j_1})^T, \ldots, (u^h_{j_n})^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial R^+_D,
\end{align}
where,

\[ t_{in}^h = [(t_{j_1}^h)^T, \ldots, (t_{j_n}^h)^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial \mathcal{R}_N, \]

and similarly

\[ u_{in} = [u_{j_1}^T, \ldots, u_{j_n}^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial \mathcal{L}^-, \]
\[ u_{out} = [u_{j_1}^T, \ldots, u_{j_n}^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial \mathcal{L}^+_D, \]
\[ t_{in} = [t_{j_1}^T, \ldots, t_{j_n}^T]^T, \text{ for all } j_1, \ldots, j_n \in \partial \mathcal{L}^-_N. \]

We also define two matrices,

\[ \Phi_+ := (\varphi_k(\mathbf{R}_i))_{i \in \mathbb{R}^+, k \in \partial \mathbb{R}^+}, \Phi_- := (\varphi_\ell(\mathbf{R}_j))_{j \in \mathbb{R}^-, \ell \in \partial \mathbb{R}^-}. \quad (2.18) \]

For all atoms at the remote boundary, we can substitute the equation (2.15) into equation (2.12). For \( n \in \partial \mathcal{R}^- \), we multiply \( \varphi_m(\mathbf{R}_n) \) and sum up these equations over \( n \), yielding,

\[
\begin{pmatrix}
\mathbf{u}_{in} \\
\mathbf{C} \mathbf{u}_{in}^h
\end{pmatrix} = -\tilde{S} \begin{pmatrix}
\mathbf{u}_{in} \\
\mathbf{u}_{in}^h
\end{pmatrix} + \tilde{G} \begin{pmatrix}
\mathbf{t}_{in} \\
\mathbf{t}_{in}^h
\end{pmatrix} + \tilde{K}^- \begin{pmatrix}
\mathbf{u}_{in} \\
\mathbf{u}_{in}^h
\end{pmatrix} - \tilde{K}^+ \begin{pmatrix}
\mathbf{u}_{out} \\
\mathbf{u}_{out}^h
\end{pmatrix} \quad (2.19)
\]

where,

\[ \mathbf{C} = \Phi_-^T \Phi_- \]
\[ \tilde{S} = \begin{bmatrix}
(S_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N} & (S_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N} \\
\Phi_-^T(S_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N} & \Phi_-^T(S_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N}
\end{bmatrix}, \]
\[ \tilde{G} = \begin{bmatrix}
(G_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N} & (G_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N} \\
\Phi_-^T(G_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N} & \Phi_-^T(G_{nj})_{n \in \partial \mathcal{L}^-_N, j \in \partial \mathcal{L}^-_N}
\end{bmatrix}, \]
\[ \tilde{K}^- = \begin{bmatrix}
(K_{nj}^-)_{n \in \partial \mathcal{L}^-_D, j \in \partial \mathcal{L}^-_D} & (K_{nj}^-)_{n \in \partial \mathcal{L}^-_D, j \in \partial \mathcal{L}^-_D} \\
\Phi_-^T(K_{nj}^-)_{n \in \partial \mathcal{L}^-_D, j \in \partial \mathcal{L}^-_D} & \Phi_-^T(K_{nj}^-)_{n \in \partial \mathcal{L}^-_D, j \in \partial \mathcal{L}^-_D}
\end{bmatrix}, \]
\[ \tilde{K}^+ = \begin{bmatrix}
(K_{nj}^+)_{n \in \partial \mathcal{L}^+_D, j \in \partial \mathcal{L}^+_D} & (K_{nj}^+)_{n \in \partial \mathcal{L}^+_D, j \in \partial \mathcal{L}^+_D} \\
\Phi_-^T(K_{nj}^+)_{n \in \partial \mathcal{L}^+_D, j \in \partial \mathcal{L}^+_D} & \Phi_-^T(K_{nj}^+)_{n \in \partial \mathcal{L}^+_D, j \in \partial \mathcal{L}^+_D}
\end{bmatrix}. \]

This is typically a Galerkin projection of the equation (2.12) onto a subspace spanned by the shape functions. In standard boundary element methods, singular integrals come up and they are approximated by numerical quadratures, such as the Gauss-Legendre quadrature. For the problem here, a similar issue arises. Namely,
one needs to approximate a ‘long’ sum using a ‘short’ sum. Therefore, here we present an adaptive summation method to reduce the computational cost of the summation calculation in assembling the ABEM equation.

From equation (2.19), the summation formulae will be applied to the elements in the matrices $C$, $\tilde{S}$, $\tilde{G}$, $\tilde{K}^-$, and $\tilde{K}^+$. To explain, we consider a sub-matrix (e.g., of the matrices $\tilde{C}$, $\tilde{S}$, $\tilde{G}$, $\tilde{K}^-$, and $\tilde{K}^+$) with the following structure,

$$A = \begin{bmatrix} A_{pp} & A_{pe} \\ A_{ep} & A_{ee} \end{bmatrix}. \quad (2.20)$$

In particular, $A_{pp}$ is the interactions between atoms, i.e., no shape function. We can compute this term directly. $A_{pe}$ and $A_{ep}$ are the interactions between atoms and elements and $A_{ee}$ represents the interactions between elements. Usually, we have many atoms in the elements. Hence, the computational cost of $A$ comes mainly from $A_{ee}$. Some of the terms in the long sum involve atoms that are far away, in which case, they can be well approximated by a short sum. On the other hand, they may involve the interactions of atoms that are close by, which have to be computed directly. Motivated by this observation, we propose to compute the summations adaptively.

To illustrate the idea, consider an entry $A_{pe}$ in matrix $A$, we select several representative atoms and compute the weighted summation. The selection of representative atoms is shown as Fig 2.2. In this project, we only consider quadrilateral elements. In addition, owing to the crystal symmetry, atoms are arranged in primitive cells, and each rectangular element along the remote boundary is aligned with the crystal planes, so that each element is filled with a stack of primitive cells. Those intact cells that are close to the two ends are selected as summation points or representative atoms (similar to quadrature points in numerical integrations). The weight is $L/(2l)$. $L$ is the length of the element and $l$ is the size of primitive cell. Since the interactions between the inside atoms and outside atoms are localized, the width of the element is selected to be in the same order of magnitude as the size of primitive cell. This approach is similar to the trapezoid rule for integrals in the continuous case. For the fragmented cells, only some atoms are contained in the element. The remaining atoms in the element are counted with weight 1.

Let $e_0$ be the initial element with length $L$, as shown in Fig 2.2. For the adaptivity, we first divide the element $e_0$ into two smaller elements $e_1$ and $e_2$. For
In this example, each cell contains 4 atoms. For the two different elements, we choose the atoms in the intact cells (green) with weight \( L/(2l) \) and fragmented cells (blue) with weight 1.

If the error
\[
\frac{|A_{pe_0} - A_{pe_1} - A_{pe_2}|}{|A_{pe_0}|} > TOL,
\]
the two subelements will be divided again until the relative error is less than \( TOL \) or subelements are too small. If the subelement is too small, we select all atoms as the representative atoms. For an entry \( A_{e_1 e_2} \) in matrix \( A \), we can divide \( e_1 \) into \( e_{11} \) and \( e_{12} \), divide \( e_2 \) into \( e_{21} \) and \( e_{22} \). If the relative error
\[
\frac{|A_{e_1 e_2} - A_{e_{11} e_{21}} - A_{e_{11} e_{22}} - A_{e_{12} e_{21}} - A_{e_{12} e_{22}}|}{|A_{e_1 e_2}|} > TOL,
\]
we will divide the four sub-elements again until the error is less than \( TOL \) or the elements are too small. In practice, the entire process is implemented as Fig. 2.3. When the two elements are getting close, those elements are divided into smaller elements. Since we always select fixed number of atoms for each sub-element as Fig. 2.2, more representative atoms are involved at this point. If two elements are far away from each other, we do not need to select many representative atoms. Eventually, most computational resources are spent on the computation of the diagonal entries and near-diagonal entries of the stiffness matrix.
Figure 2.3. An illustration of adaptive quadrature. A diagonal block of the stiffness matrix is shown. The colors from white to black indicate the density of selected representative atoms, e.g., the entries close to the diagonals were computed using many representative atoms, and the remaining entries were computed using very few representative atoms due to the facts that those elements are far from each other.

2.3.2 The Dirichlet-Neumann coupling method

In deriving the ABEM, it has been assumed that the position of the atoms in the atomistic regions $\Omega_\alpha$ is given. On the other hand, when solving the nonlinear equations (2.2) in the atomistic regions, we regard the positions of the atoms outside $\Omega_\alpha$, i.e., $\partial \Omega_\alpha^+$ as boundary conditions. Thus, the ABEM equations (2.12) and the nonlinear equations (2.2) in the atomistic regions are coupled. The coupled system can be expressed as follows,

$$u_+ = u|_{\partial \mathcal{L}^+}; \quad u = \arg\min_{\mathcal{L}^+} E_\alpha(u), \text{ for each } \alpha,$$

subject to $u_- = (I - K)^{-1}(Gt_\alpha - K^+u_+)$. (2.23)

Instead of solving these two sets of equations simultaneously, we alternate between the two models. This is motivated by the fact that these two sets of problems are defined in different regions, and the success of domain decomposition method. More specifically, we solve the nonlinear equations in the atomistic region...
with the boundary condition from the ABEM solution. Namely, we solve,

$$\min E_\alpha, \text{ with } u_j \text{ fixed, } j \in \partial \Omega_\alpha^+, \text{ for each } \alpha.$$  \hspace{1cm} (2.24)

Then, for the atoms around the interfaces, we update the Neumann boundary condition for the ABEM model using

$$t_j = - \sum_{i \in \partial B^+} D_{i-j} (u_i - u_j), j \in \partial B^-_N,$$  \hspace{1cm} (2.25)

and solve the ABEM equations again. In practice, a relaxation factor is often needed to guarantee the coupling method is converged. Namely, for the $n$th iteration, we have,

$$u^{(n)}_{-} = \gamma (I - K)^{-1} (Gt^{(n-1)}_{-} - K^+ u^{(n-1)}_{+}) + (1 - \gamma) u^{(n-1)}_{-},$$  \hspace{1cm} (2.26)

$$u^{(n)} = \arg\min E_\alpha(u), \text{ s.t. } u_{-} = u^{(n)}_{-},$$  \hspace{1cm} (2.27)

where $\gamma$ is the relaxation factor. This procedure has been illustrated in Fig. 2.4.

**Figure 2.4.** An Illustration of the coupling method. In this example, the system contains two atomistic regions. The atoms on the different boundaries contribute the corresponding terms to the ABEM equation.
2.4 Numerical results

We now present results from several simulation tests. As an example, we consider fractures in bcc iron. The interaction between atoms is modeled by the EAM potential, developed by Shastry and Farkas [9]. The equilibrium atomic spacing is 2.8663. The atoms are oriented in three orthogonal directions [110], [1\bar{1}0] and [001]. We apply periodic boundary condition in the third direction for the whole system to mimic a plane strain condition. The lattice Green's function is computed using the Fourier integral for short distances, and for atoms that are far apart, the Green’s function is approximated by the Green’s function for anisotropic elasticity [38, 48].

Meanwhile, to prepare an initial crack, we adopt the analytical solution based on the Stroh’s formalism [48]. When multiple cracks are present, we take the linear superpositions of the corresponding displacement. When the system is equilibrated, we measure the traction along the upper boundary, given by,

$$\sigma = \frac{1}{A} \sum_{i \in \Gamma} \sum_{j} D_{ij}(u_i - u_j).$$  \hspace{1cm} (2.28)

Here \( \Gamma \) is the top surface of the rectangular domain; \( A \) is the area of the surface \( \Gamma \). The results in atomistic region is visualized by Ovito [49]. The color indicates the atomic strain component \( \epsilon_{11} \).

2.4.1 A comparison with full-atomistic simulation

In the first test, we initialized the position of two cracks randomly. In this project, the modeling error will be assessed via numerical tests. The atomistic regions are chosen based on the local atomic strain (Fig. 2.5). To minimize the size of the atomistic regions, we kept the atoms around the crack tips and crack faces. The size of the entire system is \([-200, 200] \times [-240, 240]\). For a larger system where the crack tips are far apart, one can also choose a dumbbell-shaped domain for each crack. In this particular example, we just choose two rectangular regions for the cracks. There are about 11,000 atoms in each atomistic region. The entire system, on the other hand, contains 50,214 atoms. The setup of the system is shown in Fig. 2.5. Quasi-static loads are applied in the vertical direction. The loading increment
is implemented by increasing the strain $\epsilon_{22}$ of the system. For each step in the quasi-static loading, the displacement along the boundary is adjusted in accordance to the strain value.

Figure 2.5. A system with two cracks. The two rectangular domains (colored red) are atomistic regions (upper). All atoms in the entire domain are colored with local atomic strain (bottom).

We use the Dirichlet-Neumann coupling to combine the atomistic model in the two subdomains with cracks and the surrounding region $B$. The relaxation factor of the coupling method is set to 0.01. Initially, we increased the load with 1% increment, and we found that the crack underwent large extensions. So a subsequent run was conducted with smaller increment before the transition occurs. Fig. 2.7 shows the beginning of crack propagation, and we observe the crack growth with respect to the increased load.
As part of verification of our coupling method, we compare our results with full-atomistic simulation, which for the current system, is still computationally accessible. First, a quantitative comparison is made to verify the numerical techniques. From Fig. 2.6, greater error around the crack-tips is observed. Those error is distributed in atomistic regions where local atomic strain is significantly larger. Such error is expected to decrease when we increase the size of atomistic regions. In Fig. 2.7, we show the change of atomic positions around both cracks as the strain is being increased. We observe that in the full simulation, the upper crack extends to the right and the lower crack extends to the left, implying an interesting interaction mechanism between the two cracks, and the solution from the coupling method exhibits a consistent pattern. In both simulations, we can also observe that two cracks will reduce the local strain for each other. Since the local strain is the main mechanism of crack propagation, one crack will prevent the other from propagating.

Here, we roughly record the performances of the two methods. In these two simulations, full-atomistic simulation will take 2 minutes CPU time when the load increment is 0.01%. Meanwhile, the coupling method will cost 10 minutes CPU time for the same simulation. But this does not mean that the coupling method is always slower than the full-atomistic simulation. In this particular example, the entire system is quite small, so that we can assess the error directly. We selected almost half domain as atomistic regions. Another factor is that the coupling is implemented using the alternating Schwarz iteration, which can clearly be sped up. The coupling method is expected to outperform the full-atomistic simulation for larger systems.

Now we turn to the resulting strain-stress response curve, shown in Fig 2.8. The stress increases initially as the strain is increased. But the stress drops when the system arrives at the first bifurcation point. Then, subsequent drops of the stress were observed, which implies that the system experienced other bifurcation points. These bifurcation points correspond to the growth of the cracks, which is accompanied by bond-breaking events along the crack faces [50, 51].
Figure 2.6. Relative error \( (\mathbf{u} - \mathbf{u}^*) / \|\mathbf{u}^*\|_\infty \) with \( \epsilon_{22} = 2\% \). \( \mathbf{u}^* \) is the exact solution of full-atomistic simulation. \( \mathbf{u} \) is the solution by proposed coupling method. \( x \)-component (left upper) and \( y \)-component (right upper) of the displacement are shown separately. The positions of four atoms with maximum displacement on crack faces are shown as functions of strain (bottom four).
Figure 2.7. Snapshots of crack propagation under increasing load using full-atomistic simulation (Top) and our coupling method (Bottom). All snapshots under different strains are put together for comparison. Full-atomistic region is cropped according to atomistic region in the coupling model. The crack-propagation distance is shown as a function of the strain in the right figures.

2.4.2 A system with a long crack

Next, we consider a larger system with a much longer crack inside. The entire domain is a square region having side length of $1\mu m$, and it contains more than 2 billion atoms. A crack with initial length of $0.04\mu m$ is introduced at a random position inside the system. Two atomistic regions with width and height $1nm$ are introduced to surround the two crack tips.

To avoid tracking all the atoms along the crack faces, which in this case would amount to much larger atomistic regions, we treat the crack faces as internal interfaces and introduce rectangular elements along the crack faces to simplify the representation of the displacement along the crack faces. Therefore we only have to define the atomistic regions to be around the crack tips. More specifically, every side of the face is divided into 20 elements equally. Essentially, they are handled in the same manner as the remote boundary $\partial D$, but with homogeneous Neumann boundary conditions (traction free). The quadrature points along the crack faces
Figure 2.8. Strain-stress curve. The crack propagation part is shown only. The strain-stress response is a straight line before the cracks propagate.

are shown in Fig. 2.9.

Similar to the simulation of the two-crack case, we apply an increasing load on the system vertically and impose Dirichlet boundary condition along $\partial D$. The adaptive quadrature method has been applied to compute the matrices more efficiently to model the interaction between atoms and elements, as well as the interaction between elements. The relative tolerance $TOL$ is set to $10^{-4}$ in this calculation. Fig. 2.9 shows the setup of the system.

Figure 2.9. The setup of the simulation. The figure on the left shows the entire sample and the crack, along with the elements. Right figure is a close-up view of the crack with the solid circles representing the atoms.

The mechanical response is shown in Fig. 2.10. The stress is seen to increase when we increase the load. In this case, the stress-strain curve remains monotone for this loading range. However, if we consider the elastic modulus (the slope of
the stress-strain curve), we find the elastic modulus is decreasing, as shown in the right Figure.

![Stress-strain curve and elastic modulus graphs](image)

**Figure 2.10.** The simulation of the long crack: Stress-strain curve (upper) and elastic modulus (bottom).

In contrast to classical fracture mechanics that is based on continuum mechanics models, our model can provide the micro-structural information around the crack tips. In particular, we have observed the crack growth as the loading increases, accompanied by the separation of atoms above and below the crack faces. In Fig. 2.11, we show the growth of the right-half crack. As the loading increases, the crack tip moves one atomic spacing, stays there for a few steps, then moves another atomic spacing again. This result is aligned with the change in the elastic modulus: When the crack tip moves for one atomic spacing, the elastic modulus decreases slightly. If the crack tip does not move, the elastic modulus remains nearly as a...
constant, as indicated by the figure in the right panel in Fig. 2.10. In each stage of the propagation, the distribution of the local strain is almost the same except for the shift of the crack tip. Our simulation ends when the crack tips almost touch the boundary of atomistic regions.

Figure 2.11. Snapshots of crack propagation under increasing loading (the crack tip on the right). From left to right, the values of the strain: 0.04% 0.043%, 0.04312%, 0.04321%, 0.04338%, 0.04347%, 0.04373%, and 0.04383%.

2.5 Conclusion and discussion

This chapter presented a new framework for the numerical simulation of fracture. The new methodology combines an atomistic model around the crack tips and a reduced atomistic model in the surrounding region. The goal is to maintain the high precision of the atomistic model for the description of crack initiation and extension, and at the same time, reduce the computational complexity to an extent that is similar to conventional boundary element method. In particular, the inclusion of the atomistic models makes it possible to take into account the detailed atomic interaction near crack tips. As a result, one can bypass conventional fracturing criteria. Further, the computational cost is further reduced by introducing adaptive quadrature and a non-overlapping domain decomposition method. The method can potentially be applied to mechanical problems at the micro-scales, in which the toughness is of main interest. To our knowledge, problems of this magnitude have not been considered by existing atomistic-to-continuum coupling methods.
Chapter 3
Dynamic problems: spatial & temporal reduction using absorbing boundary conditions

3.1 Introduction

Absorbing boundary conditions (ABCs) are extremely important numerical tools [52, 53, 54] to efficiently simulate wave propagation phenomena in large or infinite domains. In these methods, the computational cost is greatly reduced by truncating the entire domain into a much smaller region of interest. The boundaries of the truncated region are specifically treated to retain the characteristics of the full system. Mathematically, an exact boundary condition (BC) can often be derived, which tends to be nonlocal. For instance, in the work of Engquist and Majda [55], the exact BC is represented via pseudo-differential operators. They can be approximated by Padé approximations, which lead to local ABCs. Another popular approach is to introduce an artificial absorbing layer to facilitate the propagation to the exterior. The most well-known method of this type is the perfectly matched layer (PML) method, which is originally formulated by Berenger [56] for Maxwell’s equations.

In the context of molecular dynamics (MD), the role of the ABCs is again critical: typical MD simulations involve a huge number of atoms and the computation tends to be prohibitively expensive. Therefore, ABCs are much needed to minimize the computational cost. It is worthwhile to first point out that the ABCs for MD
models are different from those for continuous PDEs, since the dispersion relations are quite different. There has been a lot of recent development of ABCs for MD models. There are mainly three approaches:

**Exact ABCs.** The exact ABC can be derived for planar boundaries using Fourier/Laplace transform, or the lattice Green’s functions [57, 58, 59, 60, 61]. The main computational challenge is due to the convolutional integral in time, which has to be evaluated at each step. To the best of our knowledge, the best solution is given by the rational approximation of the continuum Green’s function [62]. Nevertheless, these exact BCs are limited to planar boundaries, and the explicit forms break down at corners.

**Approximate ABCs by minimizing the total phonon reflection.** In this approach, the reflection coefficient [63, 64] is calculated at boundaries of the truncated region. An approximate ABC, typically with a small number of previous time steps involved, is sought by minimizing the total reflection, in the form of energy fluxes [65]. This idea is extended to the cases of finite temperature [66]. A similar idea is the matching boundary conditions, proposed by Tang and his co-workers in a series of works [67, 68, 69]. They assume that the time history kernel can be approximated by an artificial local boundary condition. The unknowns are determined by a matching procedure at some pre-selected wave numbers.

**Discrete PML.** The PML method was extended to MD models by To and Li [70, 71]. Another extension based on continuum PML was performed by Guddati and co-workers [72]. Their approach is based on Guddati’s previous work, perfectly matched discrete layers (PMDL) [73], which is a more accurate implementation of PML. Similar to continuous PML, discrete PML is adaptable to complex geometries, for example, one does not need to treat the corner issue explicitly. The main subtlety is how to determine the parameters in PML. For examples, if they are too small or too large, significant reflections will occur.

The stability of ABCs necessarily is crucial to the numerical robustness and reliability of long-term simulations. While there are plentiful results in the context of wave equations, e.g., [74, 75, 76, 77, 78, 79, 80], for MD, such results are rather scarce [81, 69].

In this project, we propose a systematic approach to formulate and approximate the ABCs for domains with general geometry. In particular, we adopt an impulse/response perspective. More specifically, the impulse corresponds to the
displacement (or traction) of the atoms at the boundary, which will induce a mechanical field in the surround region. This influence will in turn exert a kick-back force on the atoms at the boundary. Therefore, the response, which would exhibit a history-dependence, corresponds to these forces (or displacement). This can be formulated more precisely using the dynamic Dirichlet-to-Neumann (DtN) map. This idea has been pursued for the wave equation and Schrödinger equation in [82, 83, 84]. Our proposed method involves the following steps:

(a) To convert the dynamics problem to a static one, we take the Laplace transform in time.

(b) We reduce the computational domain by using an atomistic-based boundary element method (ABEM). This eliminates the degrees of freedom associated with the surrounding atoms.

(c) The dynamic DtN map can be obtained by an inverse Laplace transform. Instead of implementing this exact ABC, we approximate the Laplace transform by rational functions.

(d) The rational function approximation reduces the nonlocal ABCs to local ODEs, which can be easily implemented.

We emphasize that the use of the ABEM method in (a) allows us to treat domains with general geometry, including multi-connected domains. Meanwhile, since the full MD model is a Hamiltonian system, a naive approximation of the BCs can lead to a unstable model. Our observation is that the formulation via the DtN map in step (b) makes the stability analysis more amenable. The rational approximation in step (d) eliminates the need to perform an inverse Laplace transform numerically.

The layout of this project is as follows. The exact ABC is presented in section 3.2. We discuss the evaluation of the DtN map, along with its approximation in section 3.3. The stability of the ABCs is established in section 3.4. The approximate ABC is extended to the nonlinear MD model under a partial-harmonic approximation in section 3.5. We present two numerical experiments to demonstrate the effectiveness of these methods in section 3.6.
3.2 The formulation of absorbing boundary conditions

Consider a system with \( N \) atoms in a domain \( \Omega \). Atoms in the domain have positions denoted by \( \mathbf{X} \) and displacement \( \mathbf{u} \). The entire domain \( \Omega \) is divided into two regions \( \Omega_1 \) and \( \Omega_\text{II} \), \( \Omega_1 \cup \Omega_\text{II} = \Omega \), as illustrated by Fig. 3.1. Here \( \Omega_1 \) can be multi-connected regions, e.g., around multiple local lattice defects. \( \Omega_1 \) refers to the computational domain, where the MD model is actually being implemented, and \( \Omega_\text{II} \) indicates the surrounding region that is to be removed. We denote \( \mathbf{u}_1 \) as the displacement of atoms in \( \Omega_1 \) and \( \mathbf{u}_\text{II} \) as the displacement of atoms in \( \Omega_\text{II} \). \( \text{dim}(\mathbf{u}_1) = n_1 \), and \( \text{dim}(\mathbf{u}_\text{II}) = n_\text{II} \). In realistic problems, \( \Omega_\text{II} \) involves much more atoms than those in the region \( \Omega_1 \), i.e., \( n_\text{II} \gg n_1 \).

The ABCs can be derived when the interactions with \( \mathbf{u}_\text{II} \) are linearized (but the interactions in \( \Omega_1 \) are kept nonlinear). This can be justified by the observation that away from local defects, the displacement field is often smooth. In this case, the potential energy can be written as,

\[
V = \Phi(\mathbf{u}_1) + \frac{1}{2} \sum_{i \in \Omega_1} \sum_{j \in \Omega} \mathbf{u}_i^T D_{ij} \mathbf{u}_j.
\]  

(3.1)

where \( D_{ij} = \frac{\partial^2 V}{\partial \mathbf{u}_i \partial \mathbf{u}_j} \) corresponds to the Hessian matrix of the exact potential energy \( V \) in the MD model. It is known as the force constant matrix [85]. Typically
these models have short-range interactions, with the cut-off radius denoted by \( r_{\text{cut}} \). This implies that \( D = [D_{ij}] \) is a sparse matrix. The energy \( \Phi(u_i) \) represents the interactions among the atoms in the computational domain \( \Omega \). The derivation will be presented in section 5.

Atoms in region \( \Omega \) and \( \Omega_\Omega \) follow the equations of motion,

\[
\begin{align*}
\ddot{u}_i &= -\nabla \Phi(u_i) - D_{i,\Omega} u_\Omega, \\
\ddot{u}_\Omega &= -D_{\Omega,\Omega} u_i - D_{\Omega,\Omega} u_\Omega.
\end{align*}
\]

Here, we set the mass to unity and defined \( D_{i,\Omega} = [D_{ij}] \), where \( X_i \in \Omega \), and \( X_j \in \Omega_\Omega \). The matrices \( D_{\Omega,\Omega} \) and \( D_{\Omega,\Omega} \) are defined similarly. We have \( D_{i,\Omega} = D_{\Omega,\Omega}^T \).

We will also define \( D_{i,\Omega} = \nabla^2 \Phi(0) \) for the linear stability analysis. The dynamics (3.2) is stable, since the energy is conserved. This also implies that the coefficient matrix

\[
D = \begin{bmatrix} D_{1,1} & D_{1,\Omega} \\ D_{\Omega,1} & D_{\Omega,\Omega} \end{bmatrix}
\]

is symmetric positive definite due to the structural stability.

To build up the Dirichlet-to-Neumann (DtN) map, we take the Laplace transform of the second equation of (3.2) and get,

\[
s^2 U_\Omega = -D_{\Omega,\Omega} U_i - D_{\Omega,\Omega} U_\Omega, \quad s > 0, \tag{3.3}
\]

where \( U_i(s) = \mathcal{L}\{u_i(t)\} \), and \( U_\Omega(s) = \mathcal{L}\{u_\Omega(t)\} \), which are the Laplace transforms of \( u_i(t) \) and \( u_\Omega(t) \), respectively. Here, we assume that \( u_i \) and \( u_\Omega \) are bounded functions, such that the Laplace transformations are well-defined. In the Laplace domain, we are able to formally solve the equations because \( (s^2I + D_{\Omega,\Omega}) \) is positive definite. The solution of Eq. (B.2) is the mapping from \( U_\Omega \) to \( U_i \), that is,

\[
U_\Omega(s) = B_{\Omega,1}(s) U_i = -\tilde{D}_{\Omega,\Omega}^{-1}(s) D_{\Omega,1} U_i(s), \tag{3.4}
\]

where we denote \( \tilde{D}_{ij} = D_{ij} + s^2 \delta_{ij}I \), and let \( \tilde{D}_{\Omega,\Omega}(s) = s^2I + D_{\Omega,\Omega} \). In the time domain, Eq. (B.3) becomes,

\[
u_\Omega = \int_0^t \beta_{\Omega,1}(t-s) u_i(s) ds, \tag{3.5}
\]
where $\beta_{\Pi,1}(s) = \mathcal{L}^{-1}\{B_{\Pi,1}(t)\}$. Clearly, the matrix $\beta_{\Pi,1}$ has $n_{\Pi}$ rows, and it is too large to work with. Fortunately, the interactions have short range and this representation can be simplified to only involve atoms close to the boundary.

$$
\Omega_{\Pi}
$$

Figure 3.2. An illustration of the interface regions $\Gamma_1$ and $\Gamma_{\Pi}$.

The influence of $u_\Pi$ on $u_1$, $f_{1,\Pi} = -D_{1,\Pi}u_\Pi$, corresponds to the Neumann boundary condition on $\Omega_1$. Similarly, we define $f_{\Pi,1} = -D_{\Pi,1}u_1$ as the influence of $u_1$ on $u_\Pi$. Due to the short-range interactions and the translational invariance of the force constant matrices among the atoms, $D_{1,\Pi}$ is a sparse matrix, that is, most entries in the matrices $D_{1,\Pi}$ and $D_{\Pi,1}$ are zeros. The following notations are motivated by the domain decomposition method, and they are useful to reveal the sparsity of the matrices and the nearsightedness of the interactions. We define the sets of boundary atoms as

$$
\Gamma_1 = \{i \in \Omega_1 | D_{ij} \neq 0, \text{ for any } j \in \Omega_\Pi\}, \text{ and }
\Gamma_{\Pi} = \{i \in \Omega_\Pi | D_{ij} \neq 0, \text{ for any } j \in \Omega_1\}.
$$

They are the collections of the atoms at the inner and outer boundaries, as indicated in Fig. (3.2). We now use $u_{1,\Gamma}$ and $u_{\Pi,\Gamma}$ to represent the displacement of atoms in $\Gamma_1$ and $\Gamma_{\Pi}$, respectively. $u_{1,\Gamma}$ has a dimension of $m_1$, and $u_{\Pi,\Gamma}$ has a dimension of $m_{\Pi}$. We have $m_1, m_{\Pi} \ll n_1$. With these notations, the short-range interactions can be revealed by writing the two matrices as

$$
D_{1,\Pi} = \begin{bmatrix} D_{1,\Gamma} & 0 \end{bmatrix}, \text{ and } D_{\Pi,1} = \begin{bmatrix} D_{\Pi,\Gamma} & 0 \end{bmatrix}.
$$

(3.6)

It is also natural to introduce the matrices $E_1$ and $E_{\Pi}$ such that $u_{1,\Gamma} = u_1|_{\Gamma_1} = E_1u_1$, and $u_{\Pi,\Gamma} = u_\Pi|_{\Gamma_\Pi} = E_{\Pi}u_\Pi$. Furthermore, we define $f_{1,\Gamma} = -E_1D_{1,\Gamma}u_{\Pi,\Gamma}$, and
\( f_{\|,\Gamma} = -E_{\|} D_{\|,\|} u_{1,\Gamma} \) to denote the forces at the inner and outer boundaries.

<table>
<thead>
<tr>
<th># of rep.</th>
<th>equations</th>
<th>kernel functions</th>
<th>interpretations</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>( U_{|,\Gamma} = B U_{1,\Gamma} )</td>
<td>( B(s) = -E_{|} \tilde{D}<em>{|,|}^{-1}(s) D</em>{|,\Gamma} )</td>
<td>ABEM [86, 87]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Theta(s) = E_{|} \tilde{D}<em>{|,|}^{-1}(s) E^{T}</em>{|} )</td>
<td>Target kernel</td>
</tr>
<tr>
<td>2</td>
<td>( F_{1,\Gamma} = T U_{1,\Gamma} )</td>
<td>( T(s) = D_{|,\Gamma} \tilde{D}<em>{|,|}^{-1}(s) D^{T}</em>{|,\Gamma} )</td>
<td>DtN map in ( \Omega_{|} ) [88]</td>
</tr>
<tr>
<td>3</td>
<td>( F_{1,\Gamma} = K s U_{1,\Gamma} + \Theta(0) U_{1,\Gamma} )</td>
<td>( K(s) = \frac{\Theta(s) - \Theta(0)}{s} )</td>
<td>GLE in ( \Omega_{|} ) [89, 90]</td>
</tr>
</tbody>
</table>

Table 3.1. Kernel functions in the Laplace domain.

We now turn to the general forms of the boundary conditions. There are various ways to express the boundary conditions based on Eq. (B.3). Their forms in the Laplace domain are summarized in Table 3.1, along with references where these representations can be found. We will briefly go through the derivation of these formulas.

**Representation 1.** The first kernel function can be immediately obtained if we premultiply both sides of Eq. (B.3) by \( E_{\|} \). This kernel function corresponds to a mapping between the displacement at the inner and outer boundaries.

**Representation 2.** To derive the second representation, one notices that the influence of \( u_1 \) on \( u_{\|} \) can be expressed as

\[
 f_{\|,1} = \begin{bmatrix} f_{\|,\Gamma} \\ 0 \end{bmatrix}. \tag{3.7}
\]

Further notice that the right hand side of Eq. (B.3) can be written as

\[
 \tilde{D}_{\|,\|}^{-1} F_{\|,1} = \left[ \tilde{D}_{\|,\|}^{-1} E^{T}_{\|} \ast \right] \begin{bmatrix} F_{\|,\Gamma} \\ 0 \end{bmatrix} = \tilde{D}_{\|,\|}^{-1} E^{T}_{\|} F_{\|,\Gamma}, \tag{3.8}
\]

where \( F_{\|,1}(s) = \mathcal{L}\{f_{\|,1}(t)\} \) is the Laplace transform of \( f_{\|,1}(t) \), and \( F_{\|,1}(s) = -D_{\|,1} U_1 \) is the force from atoms in region \( \Omega_1 \) to atoms in region \( \Omega_{\|} \).
To proceed, we premultiply both sides of Eq. (B.3) by $E$, and get

$$ U_{\Pi,\Gamma}(s) = E_{\Pi} \tilde{D}_{\Pi,\Pi}^{-1}(s) E_{\Pi}^T F_{\Pi,\Gamma}(s). $$

This way, only the atoms outside the boundary are involved in Eq. (4.30). This DtN map connects the displacement and traction at the outer boundary. Numerically, the kernel function $\Theta(s)$ is amenable to numerical and analytical treatments, because it is symmetric positive definite for all $s$. (It is a principle submatrix of $\tilde{D}_{\Pi,\Pi}(s)$.) It is much more convenient to approximate a symmetric positive definite matrix-valued matrix by interpolations. The matrix $\tilde{D}_{\Pi,\Pi}(s)$ corresponds to a continuum screened Poisson operator or Klein-Gordon operator [91].

**Representation 3.** To arrive at the third expression, one can premultiply $D_{\Pi,\Gamma}$ to both sides of Eq. (B.3), which leads to,

$$ F_{I,\Gamma}(s) = D_{\Pi,\Gamma} \tilde{D}_{\Pi,\Pi}^{-1}(s) D_{\Pi,\Gamma}^T U_{I,\Gamma}(s). $$

In this case, the DtN operator is given by

$$ T(s) = D_{\Pi,\Gamma} \tilde{D}_{\Pi,\Pi}^{-1}(s) D_{\Pi,\Gamma}^T, $$

and it is a mapping between the displacement and traction at the inner boundary.

In the real-time domain, this DtN map is written as

$$ f_{I,\Gamma}(t) = \int_0^t \tau(t - s) u_{I,\Gamma}(s) ds. $$

Here $\tau(t) = \mathcal{L}^{-1}\{T(s)\}$ is the inverse Laplace transform of $T(s)$. Fourier transformation versions of the expression (B.4) were discussed in [90, 89, 65].

**Representation 4.** Finally, the fourth expression in Table 3.1 can be obtained by writting,

$$ F_{I,\Gamma}(s) = K(s)(sU_{I,\Gamma}(s) - U_{I,\Gamma}(0)) + T(0)U_{I,\Gamma}(s), $$

and denoting $K(s) = (T(s) - T(0))/s$. Here we have assumed the initial condition $U_{I,\Gamma}(0) = 0$. In the real-time domain, $f_{I,\Gamma}$, accordingly, is expressed in terms of the
velocity of the system. The alternative form of $f_{I,G}$ is

$$f_{I,G}(t) = \int_0^t \kappa(t - s) \dot{u}_{I,G}(s) ds - T(0) u_{I,G}(t).$$

(3.13)

In the time domain, this derivation is equivalent to an integration by parts. In this form, the memory term can be viewed as a damping term, and it makes the stability analysis more straightforward [81].

In this project, we choose the *second* expression of the DtN map, with kernel function $\Theta(s)$, to represent the boundary condition. The main reason is that the kernel function $\Theta(s)$ is symmetric positive definite for any value of $s > 0$, which may not hold in other three cases. Due to this property, some theoretical results can be easily established, and they are quite relevant to the stability of the boundary condition, which will be discussed in section 3.4. For convenience, we denote $\Theta_0 = \Theta(0)$, $\Theta_1 = \Theta(s_1)$, and $\Theta_2 = \Theta(s_2)$ for positive values of $s_1$ and $s_2$.

**Lemma 3.2.1.** For any $s_1 \neq s_2 > 0$,

$$\frac{s_1^2(\Theta_1 - \Theta_0)^{-1} - s_2^2(\Theta_2 - \Theta_0)^{-1}}{s_1 - s_2}$$

is symmetric negative definite.

**Proof.** Let us consider

$$M = \frac{\tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_1) - \tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_2)}{s_1 - s_2},$$

(3.14)

which is symmetric. Now, we show $M$ is also negative definite. In fact, we can write $M$ into a product of two matrices,

$$M = \tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_1) \frac{s_2^2 - s_1^2}{s_1 - s_2} \tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_2)$$

(3.15)

$$= -(s_1 + s_2) \tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_1) \tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_2).$$

Both two matrices $\tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_1)$ and $\tilde{D}_{\mathbb{H},\mathbb{H}}^{-1}(s_2)$ are symmetric positive definite. Since $M$ is symmetric, it follows immediately that $M$ is symmetric negative definite and
$E_\Pi M D_{\Pi,\Pi}^{-1} E_\Pi^T$ is negative definite. Now, we consider the symmetric matrix

$$s_1^2(\Theta_1 - \Theta_0)^{-1} - s_2^2(\Theta_2 - \Theta_0)^{-1}
\frac{s_1 - s_2}{s_1 - s_2}$$

$$=(\Theta_1 - \Theta_0)^{-1} s_1^2(\Theta_2 - \Theta_0) - s_2^2(\Theta_1 - \Theta_0) (\Theta_2 - \Theta_0)^{-1}
\frac{s_1 - s_2}{s_1 - s_2}$$

$$=(\Theta_1 - \Theta_0)^{-1} s_1^2 s_2^2 E_\Pi M D_{\Pi,\Pi}^{-1} E_\Pi^T (\Theta_2 - \Theta_0)^{-1}.$$

Notice $(\Theta_1 - \Theta_0)^{-1}$ and $(\Theta_2 - \Theta_0)^{-1}$ are symmetric negative definite. As a result, $(s_1^2(\Theta_1 - \Theta_0)^{-1} - s_2^2(\Theta_2 - \Theta_0)^{-1})/(s_1 - s_2)$ is symmetric negative definite.

**Lemma 3.2.2.** If $0 < s_1 \neq s_2 < \sqrt{\lambda_{\min}(D_{\Pi,\Pi})}$, then

$$s_1(\Theta_2 - \Theta_0)^{-1} - s_2(\Theta_1 - \Theta_0)^{-1}
\frac{s_1 - s_2}{s_1 - s_2}$$

is positive definite.

**Proof.** We will use the same technique as the proof of the last lemma. Let us denote

$$N = \frac{-s_2 \tilde{D}_{\Pi,\Pi}^{-1}(s_2) + s_1 \tilde{D}_{\Pi,\Pi}^{-1}(s_1)}{s_1 - s_2}$$

which is symmetric.

We factor $\tilde{D}_{\Pi,\Pi}^{-1}(s_1)$ and $\tilde{D}_{\Pi,\Pi}^{-1}(s_2)$ out from $N$ by premultiplying $N$ and postmultiplying the result, and get

$$N = \tilde{D}_{\Pi,\Pi}^{-1}(s_1) s_1 \tilde{D}_{\Pi,\Pi}(s_2) - s_2 \tilde{D}_{\Pi,\Pi}(s_1) \tilde{D}_{\Pi,\Pi}^{-1}(s_2)
\frac{s_1 - s_2}{s_1 - s_2}$$

$$= \tilde{D}_{\Pi,\Pi}(s_1) \frac{(s_1 - s_2)(-s_1 s_2 I + D_{\Pi,\Pi})}{s_1 - s_2} \tilde{D}_{\Pi,\Pi}^{-1}(s_2)$$

$$= \tilde{D}_{\Pi,\Pi}^{-1}(s_1)(-s_1 s_2 I + D_{\Pi,\Pi}) \tilde{D}_{\Pi,\Pi}^{-1}(s_2)$$

Since $s_1 < \sqrt{\lambda_{\min}(D_{\Pi,\Pi})}$ and $s_2 < \sqrt{\lambda_{\min}(D_{\Pi,\Pi})}$, $N$ is symmetric positive definite.
Therefore,

\[
\frac{s_1(\Theta_2 - \Theta_0)^{-1} - s_2(\Theta_1 - \Theta_0)^{-1}}{s_1 - s_2} = (\Theta_1 - \Theta_0)^{-1} s_1(\Theta_2 - \Theta_0) - s_2(\Theta_1 - \Theta_0) (\Theta_2 - \Theta_0)^{-1}
\]

is symmetric positive definite.

3.3 Approximations of the DtN map \(\Theta\)

The direct evaluation of the DtN operator \(\Theta\) is quite challenging. The difficulties of computation lie in two aspects: the inverse of a large matrix and infinitely many evaluations for frequency parameter \(s\). In this section, the exact DtN map will be approximated by rational functions (section 3.3.1). We avoid the inverse of the large matrix by a domain reduction of the system. The domain reduction, in the form of the DtN map in the Laplace domain, will be discussed in section 3.3.2.

3.3.1 Approximation by rational functions

Instead of evaluating the time-dependent memory kernel, rational approximations can be made [55], which leads to dynamics without memory. In fact, the memory is eliminated via the introduction of a new variable. We consider the general form of the rational functions,

\[
R_{n,n}(s) = \left( s^n I - \sum_{i=0}^{n-1} s^{n-1-i} B_i \right)^{-1} \left( \sum_{i=0}^{n-1} s^{n-1-i} A_i \right),
\]

where \(A_i, B_i \in \mathbb{R}^{m \times m}\) for all \(0 \leq i < n\). Notice that the dimension of the matrices \(A_i\) and \(B_i\) is small: \(m \ll n\). The rational functions should satisfy \(R_{n,n}(s) \approx \Theta(s)\).

The form of the rational functions is inspired by the properties of the kernel function \(\Theta(s)\): \(\lim_{s \to \infty} \Theta(s) = 0\), and \(\Theta'(0) = 0\). In our approximation, \(\lim_{s \to \infty} R_{n,n}(0) = 0\) is automatically satisfied. For all following approximations, we always assume \(R_{n,n}(0) = \Theta(0)\). This condition gives us

\textbf{Assumption 1.} \(-B_{n-1}^{-1} A_{n-1} = \Theta_0\).
For higher order approximations, we may assume \( R_{n,n}(0) = \Theta'(0) \) to obtain the better approximation around zero. The first derivative condition leads to

**Assumption 2.** \(-B^{-1}_{n-1}B_{n-2}B^{-1}_{n-1}A_{n-1} + B^{-1}_{n-1}A_{n-2} = 0.\)

In this project, we only show zeroth, first, and second order approximations. It is straightforward to extend the idea to high order cases. We define the approximation order as the degree of the polynomial in the denominator.

**Zeroth order approximation.** The zeroth order approximation is to use a constant matrix, which, according to Assumption 1, becomes \( R_{0,0} = \Theta(0) \). One can also choose \( s = s_0 \) (\( s_0 \) is nonzero) as long as the corresponding dynamics is stable. If we make the intuitive choice \( s = 0 \), the approximate dynamics is reduced to

\[
\ddot{u}_I = -\nabla \Phi(u_I) + E_I^T D_{\Pi,\Gamma} D_{\Pi,\Pi}^{-1} D_{\Pi,\Gamma} u_{1,\Gamma}.
\]

(3.21)

The stability of this approximation is shown in section 3.4. The dynamics can be further simplified by introducing

\[
\bar{\Phi}(u_I) = \Phi(u_I) - \frac{1}{2} u_{1,\Gamma}^T D_{\Pi,\Gamma} D_{\Pi,\Pi}^{-1} D_{\Pi,\Gamma} u_{1,\Gamma}.
\]

(3.22)

The hessian of the potential energy is given by,

\[
\bar{D}_{1,1} = D_{1,1} - E_I^T D_{\Pi,\Gamma} D_{\Pi,\Pi}^{-1} D_{\Pi,\Gamma} E_I,
\]

which is precisely the Schur complement of the matrix \( \bar{D} \). In practice, the interactions in \( \Omega_1 \) are nonlinear, and \( \bar{D}_{1,1} \) never has to be computed. This will be discussed in the next section. Nonetheless, this Schur complement form gives us the insight of the stability of the resulting dynamical system. The zeroth order approximation only involves the displacement of atoms in region \( \Omega_1 \).

**First order approximation.** In this case, we consider the rational function,

\[
R_{1,1}(s) = (sI - B_0)^{-1} A_0,
\]

(3.23)

as the approximation. The coefficients \( A_0 \) and \( B_0 \) are determined by the interpolation at points \((s_0, \Theta(s_0))\) and \((0, \Theta(0))\), in accordance with Assumption 1. The
corresponding approximate DtN map in real-time domain can be written as

$$
\mathbf{u}_{I, \Gamma} = \int_0^t e^{sB_0} A_0 \mathbf{f}_{I, \Gamma}(t - s) ds
$$

which is similar to the alternative form (Eq. (4.16)) of the exact DtN map. We reformulate the approximate DtN map by integration by parts for the purpose of stability analysis in section 3.4. It is worth pointing out that, in this setting, \( \mathbf{u}_{I, \Gamma} \) is expressed in terms of \( \dot{\mathbf{f}}_{I, \Gamma} \). The term \(-B_0^{-1} A_0 \mathbf{f}_{I, \Gamma}\), which according to Assumption 1, coincides with \( \Theta(0) \mathbf{f}_{I, \Gamma} \) that will be moved to the first equation in Eq. (3.2). We denote \( \mathbf{g} = \int_0^t e^{sB_0} B_0^{-1} A_0 \dot{\mathbf{f}}_{I, \Gamma}(t - s) ds \) and append the dynamics of \( \mathbf{g} \) to that of \( \mathbf{u}_1 \). The variable \( \mathbf{g} \) (\( \mathbf{g} \in \mathbb{R}^{m_I \times 1} \)) is coupled with \( \mathbf{v}_{I, \Gamma} \) only. With direct computation, one can verify that the approximate dynamics in this case is expressed as

$$
\begin{align*}
\ddot{\mathbf{u}}_1 &= -\nabla \Phi(\mathbf{u}_1) - D_{I, \Gamma} \mathbf{g}, \\
\dot{\mathbf{g}} &= -B_0^{-1} A_0 D_{I, \Gamma} \mathbf{v}_{I, \Gamma} + B_0 \mathbf{g},
\end{align*}
$$

where \( D_{I, \Gamma} \) has the same definition as the one in the zeroth order approximation.

**Second order approximation.** We express the second order rational approximation as

$$
R_{2,2}(s) = (s^2 I - sB_0 - B_1)^{-1}(sA_0 + A_1).
$$

The coefficients \( A_0, A_1, B_0, \) and \( B_1 \) are determined by the interpolation among the values of \( \Theta(s) \) and \( \Theta'(s) \). In the second order approximation, we take both assumption 1 and assumption 2 into consideration. Two more values of \( \Theta(s) \) will be used, at points \( (s_1, \Theta(s_1)) \) and \( (s_2, \Theta(s_2)) \), to determined those coefficients. In the real time domain, the corresponding approximate dynamics is

$$
\ddot{\mathbf{u}}_{I, \Gamma} = B_0 \dot{\mathbf{u}}_{I, \Gamma} + B_1 \mathbf{u}_{I, \Gamma} + A_0 \dot{\mathbf{f}}_{I, \Gamma} + A_1 \mathbf{f}_{I, \Gamma}.
$$

Equivalently, the above dynamics can be expressed as

$$
\dot{\mathbf{w}} = B \mathbf{w} + A \mathbf{f}_{I, \Gamma},
$$

(3.27)
where \( w = \begin{bmatrix} u^I & \Gamma \\ z \end{bmatrix}, B = \begin{bmatrix} B_0 & I \\ B_1 & 0 \end{bmatrix}, \) and \( A = \begin{bmatrix} A_0 \\ A_1 \end{bmatrix}. \) Employing the same technique in Eq. (B.7), we obtain

\[
w = -B^{-1}A f^I + \int_0^t e^{sB}B^{-1}A f^I(t-s) ds.
\]

We denote \( g = \int_0^t e^{sB}B^{-1}A D^I \dot{v}^I + B g, \) and introduce the matrix \( E_1 \) (different from \( E^I \)) such that \( f^I = E_1 g. \) Then we can write an extended dynamics to represent the ABC:

\[
\begin{aligned}
\ddot{u}_I &= -\nabla \Phi(u_I) - E_1 D^I \dot{v}^I, \\
\dot{v}^I &= -B^{-1}A D^I \dot{v}^I + B g.
\end{aligned}
\]

3.3.2 Evaluation of the DtN map

In practice, the sub-region \( \Omega^I \) contains many atoms, but the region \( \Omega^I \) contains much fewer atoms. As a result, the matrix \( \Theta(s) \in \mathbb{R}^{m^I \times m^I} \) associated with the DtN map does not have a large dimension. However, it involves the inverse of \( \tilde{D}^I(s) \in \mathbb{R}^{n^I \times n^I}. \) The direction computation can be extremely expensive.

Fortunately, it is unnecessary to compute the entire inverse of \( \tilde{D}^I(s). \) We only need to compute the Schur complement of the corresponding block of \( \tilde{D}^I(s) \) for the atoms at the interface \( \Gamma. \) Thanks to the translation invariance of the force constant matrices, this calculation can be done very efficiently. We first consider the problem in the Laplace domain,

\[
\tilde{D}^I(s) U^I(s) = F^I(s), \text{ for given } F^I(s) = -D^I U^I(s).
\]

With the help of the lattice Green’s function (A), the equation can be reduced to the degree of freedoms on the interface \( \Gamma \) by the atomistic-based boundary element method (ABEM) [86, 87]. In the original work, ABEM is implemented for static elasticity. In this project, we extend the idea to dynamics problems where the force constant matrices are shifted by \( s^2 I. \)

Since \( \tilde{D}(s) \) is positive definite, the corresponding lattice Green’s function is well-defined, which follows the relation \( \sum_j \tilde{G}_{nj} \tilde{D}_{ji} = \delta_{ni} I. \) The notation, \( \tilde{\cdot} \), represents the variable in the Laplace domain. As a result, the displacement of atom \( n (n \in \Omega^I) \)
can be trivially expressed as

$$U_n = \sum_{i \in \Omega_\tau} \delta_{ni} U_i = \sum_{i \in \Omega_{\tau}, j} \tilde{G}_{nj} \tilde{D}_{ji} U_i.$$  \hspace{1cm} (3.32)

The key step of the dimensional reduction is applying Abel’s lemma (summation by parts) to Eq. (4.13). In this case, the Abel’s lemma is expressed as

$$\sum_{i \in \Omega_{\tau}, j} \tilde{G}_{nj} \tilde{D}_{ji} U_i = \sum_{i \in \Gamma_1, j \in \Gamma_\tau} \tilde{G}_{ni} D_{ji} U_j - \sum_{i \in \Gamma_1, j \in \Gamma_\tau} \tilde{G}_{nj} D_{ji} U_i + \sum_{j \in \Omega_{\tau}} \tilde{G}_{nj} B_j,$$  \hspace{1cm} (3.33)

where $B_j = \sum_{i \in \Omega} D_{ji} U_i$. In the above equation, the first two summations are over the interface $\Gamma_1$ and $\Gamma_\tau$ because of the locality of $\tilde{D}_{ij}$. When no external force is present, $B_j = 0$. If we choose $n \in \Gamma_\tau$, Eq. (3.33) forms a linear system,

$$U_{\tau, \Gamma} = \tilde{K} U_{\tau, \Gamma} + \tilde{L} F_{\tau, \Gamma},$$  \hspace{1cm} (3.34)

where

$$\begin{cases} \tilde{K}_{nj} = \sum_{i \in \Gamma_1} \tilde{G}_{ni} D_{ji} \\ \tilde{L}_{nj} = \tilde{G}_{nj} \end{cases}$$  \hspace{1cm} (3.35)

The linear system is still closed. This linear system provides an alternative expression of the DtN map, given by

$$U_{\tau, \Gamma}(s) = (I - \tilde{K}(s))^{-1} \tilde{L}(s) F_{\tau, \Gamma}(s).$$  \hspace{1cm} (3.36)

Notice that the matrices in the linear system have dimensions much smaller than $n_{\tau}$. Eq. (4.51), which provides the Schur complement of the corresponding block of the matrix $(s^2 I + D_{\tau, \tau})$, is equivalent to Eq. (4.30). In Eq. (4.51), we do not need to evaluate the inverse of a large matrix.

### 3.4 Stability of absorbing boundary conditions (ABCs)

As a Hamiltonian system, the stability of the MD model after modifications due to the approximate BCs is a very delicate issue [92]. In this section, we will provide
the principles of the approximations in section 3.3.1 to ensure stability. Since the coefficients of the rational approximation are determined by interpolation, our principles will focus on the selections of interpolation points.

**Zeroth order approximation.** The zeroth order approximation is automatically stable when we choose constant matrix $\Theta(0)$ as $R_{0,0}(s)$. In fact,

$$(D_{1,1} - E^T_1 D_{1,1}^{-1} D_{1,1}^{-1} E_1)$$

is the Schur complement of $D_{1,1}$ of symmetric positive definite matrix $D$. Therefore, we have the following stability condition of the dynamics (3.25).

**Theorem 3.4.1 (Zeroth order approximation).** The zeroth-order approximate dynamics (Eq. (3.21)) is stable, provided that the interpolation point is $(0, \Theta(0))$.

**First order approximation.** To establish the linear stability of Eq. (3.25), we introduce the following Lyapunov functional:

$$E(u_1, v_1, g) = \frac{1}{2} v_1^T v_1 + \frac{1}{2} u_1^T \bar{D}_{1,1} u_1 - \frac{1}{2} g^T A_0^{-1} B_0 g.$$  \hspace{1cm} (3.37)

Since $-A_0^{-1} B_0$ (Assumption 1) is symmetric positive definite, $E \geq 0$ for any $v_1, u_1$, and $g$. The derivative of $V$,

$$L_t E = v_1^T \dot{v}_1 + u_1^T \bar{D}_{1,1} \dot{u}_1 - g^T A_0^{-1} B_0 \dot{g}$$

$$= v_1^T (-\bar{D}_{1,1} u_1 - D_{1,1} g) + u_1^T \bar{D}_{1,1} \dot{v}_1$$

$$- g^T A_0^{-1} B_0 (-B_0^{-1} A_0 D_{1,1} v_1 + B_0 g)$$

$$= -g^T A_0^{-1} B_0^2 g.$$  \hspace{1cm} (3.38)

Hence, when $A_0^{-1} B_0^2$ is a positive semi-definite matrix, and $B_0^{-1} A_0$ (Assumption 1) is symmetric negative definite. According to standard ODE theory [92], the first order approximate dynamics (3.25) is stable.

**Theorem 3.4.2 (First order approximation).** The approximate dynamics (3.25) is stable if the coefficients of the rational function (Eq. (3.23)) are determined by $R_{1,1}(0) = \Theta_0$ (Assumption 1) and $R_{1,1}(s_1) = \Theta_1$ with any $s_1 > 0$.\hspace{1cm} 46
Proof. The coefficients $A_0$ and $B_0$ are determined by solving the equations,

\[
\begin{cases}
-B_0^{-1}A_0 = \Theta_0, \\
(s_1 I - B_0)^{-1}A_0 = \Theta_1.
\end{cases}
\]  

(3.39)

We eliminate the coefficient $A_0$ and have

\[
(\Theta_1 - \Theta_0) B_0 = s_1 \Theta_1.
\]  

(3.40)

The matrix

\[
\Theta_1 - \Theta_0 = E \tilde{D}_\Pi^{-1}(s_1) E^T - E \Pi \tilde{D}_{\Pi,\Pi}^{-1} E^T
\]

= $-s_1^2 E \Pi \tilde{D}_{\Pi,\Pi}^{-1}(s_1) D_{\Pi,\Pi}^{-1} E^T,$

(3.41)

is negative definite for any $s_1$. As a result, $B_0 = s_1(\Theta_1 - \Theta_0)^{-1}\Theta_1$ is a negative definite matrix, and $A_0^{-1}B_0^2$ is a positive definite matrix. Therefore, the Lyapunov function defined by Eq. (B.6) is nonnegative, and its derivative $L_t E$ is semi-negative definite.

\[\square\]

**Second order approximation.** The stability of Eq. (3.30) will be analyzed in a similar approach as described in the first order case. The Lyapunov functional for the system (Eq. (3.30)) is defined by

\[
E(u_1, v_1, g) = \frac{1}{2} v_1^T v_1 + \frac{1}{2} u_1^T D_{1,1} u_1 + \frac{1}{2} g^T Q g,
\]  

(3.42)

where

\[
Q = \begin{bmatrix}
-A_{1}^{-1} B_1 & 0 \\
0 & A_{1}^{-1}
\end{bmatrix}.
\]

If $-A_{1}^{-1} B_1$ and $A_{1}^{-1}$ are symmetric positive definite matrices, then $Q$ is positive definite and the Lyapunov function is positive definite. The derivative of $E$ is

\[
L_t E = v_1^T \dot{v}_1 + u_1^T \dot{D}_{1,1} u_1 + g^T Q \dot{g}
\]

\[
= -v_1^T E_1 u_1 g - g^T Q B^{-1} A D_{\Pi,\Pi} v_1 + g^T Q B g
\]

(3.43)

\[\text{\bf 47}\]
Here, $QB$ is explicitly expressed as

$$QB = \begin{bmatrix} -A_1^{-1}B_1B_0 & -A_1^{-1}B_1 \\ A_1^{-1}B_1 & 0 \end{bmatrix}. \quad (3.44)$$

If $QB$ is negative semi-definite, then $L_tE < 0$. $QB$ is negative definite if and only if $-A_1^{-1}B_1B_0$ is negative definite. The stability conditions of dynamics (3.30) are that $A_1^{-1}$ is symmetric positive definite, and $A_1^{-1}B_1B_0$ positive semi-definite.

Actually, these stability conditions are satisfied when we choose the interpolation points properly.

**Theorem 3.4.3** (Second order approximation). *The approximate dynamics (3.30) is stable if the coefficients of the rational function Eq. (B.11) are determined by $R_{2,2}(0) = \Theta(0)$, $R'_{2,2}(0) = \Theta'(0)$, $R_{2,2}(s_0) = \Theta(s_0)$, and $R_{2,2}(s_1) = \Theta(s_1)$ with $0 < s_1 \neq s_2 < \sqrt{\lambda_{\text{min}}(D_{\mathbb{R}^n})}$. 

*Proof.* In fact, the coefficients $A_0$, $A_1$, $B_0$, and $B_1$ are determined by solving a linear system,

$$-B_1^{-1}A_1 = \Theta_0, \quad (3.45a)$$

$$B_1^{-1}B_0B_1^{-1}A_1 - B_1^{-1}A_0 = 0, \quad (3.45b)$$

$$s_1B_0\Theta_1 + B_1\Theta_1 + s_1A_0 + A_1 = s_1^2\Theta_1, \quad (3.45c)$$

$$s_2B_0\Theta_2 + B_1\Theta_2 + s_2A_0 + A_1 = s_2^2\Theta_2, \quad (3.45d)$$

for the coefficients $A_0$, $A_1$, $B_0$, and $B_1$. Eq. (3.45b) (Assumption 2) is reduced to $A_0 = B_0B_1^{-1}A_1$. By solving the linear system for $B_0$ and $B_1$, we have

$$B_0 = \frac{(s_1^2\Theta_1(\Theta_1 - \Theta_0)^{-1} - s_2^2\Theta_2(\Theta_2 - \Theta_0)^{-1})}{s_1 - s_2}, \quad (3.46)$$

and

$$B_1 = \frac{s_1s_2(s_1\Theta_1(\Theta_1 - \Theta_0)^{-1} - s_2\Theta_2(\Theta_2 - \Theta_0)^{-1})}{s_2 - s_1}. \quad (3.47)$$

By Lemma 3.2.1, $B_0$ is positive definite. Since $\Theta_0$ is symmetric positive definite, $A_1^{-1}B_1B_0$ is positive definite. By Lemma 3.2.2, $B_1$ is negative definite. Since
$A_1 = -B_1\Theta_0$, we have that the coefficient,

$$A_1 = s_1s_2\left(\Theta_0 - \Theta_0\frac{(s_1(\Theta_1 - \Theta_0)^{-1} - s_2(\Theta_2 - \Theta_0)^{-1}))}{s_2 - s_1}\Theta_0\right)$$  \hspace{1cm} (3.48)

is symmetric positive definite. Therefore, the dynamics (3.30) is stable. \hfill \Box

### 3.5 Implementation of ABCs and partial-harmonic approximation of MD

For practical applications, the ABCs should be formulated so that the nonlinear interactions in $\Omega_I$ are retained, to properly model defect structure, formation, and migration. This amounts to a partial harmonic approximation of the potential energy $V(u_I, u_{II})$. In this approximation, only the interactions involving the atoms in $\Omega_{II}$ are linearized. From the exact potential, these linear interactions should have coefficients given by

$$D_{I,II} = \frac{\partial^2 V}{\partial u_I\partial u_{II}}(0,0), \quad \text{and} \quad D_{II,II} = \frac{\partial^2 V}{\partial u_{II}^2}(0,0).$$  \hspace{1cm} (3.49)

This is consistent with the notations in section 3.2. In particular, $D_{I,II}$ represents in the coupling between $\Omega_I$ and $\Omega_{II}$.

The key observation is that when the region $\Omega_{II}$ is at mechanical equilibrium, we have $u_{II} = Cu_I$ with $C = -D_{II,II}^{-1}D_{II,I}$, within the linear approximation. Notice that the equilibrium is relative to the displacement of the atoms in $\Omega_I$. With this mechanical equilibrium as the references, we introduce the partial harmonic approximation by defining the following approximate potential energy:

$$\tilde{V}(u_I, u_{II}) = V(u_I, Cu_I) + \frac{1}{2}(u_{II} - Cu_I)^T D_{II,II}(u_{II} - Cu_I).$$  \hspace{1cm} (3.50)

The first part is the potential energy in $\Omega_I$ assuming a mechanical equilibrium in the surrounding area, while the second part is for region $\Omega_{II}$.

We now show that this potential energy $\tilde{V}$ is consistent with the exact model $V$ in the following sense.

1. $\tilde{V}$ is a second order approximation. More specifically, one can easily
verify that,\
\[
\frac{\partial \tilde{V}}{\partial u_i}(0, 0) = 0, \quad \text{for any } i \in \Omega, \quad (3.51)
\]
and
\[
\frac{\partial^2 \tilde{V}}{\partial u_i \partial u_j}(0, 0) = D_{ij} = \frac{\partial^2 V}{\partial u_i \partial u_j}(0, 0), \quad \text{for any } i, j \in \Omega. \quad (3.52)
\]
This of course implies that \( \tilde{V} = V \) if \( V \) is quadratic.

2. **The interactions in the interior of \( \Omega_1 \) is exactly preserved.** To see this property, we notice that most potential energy can be decomposed into site energies,
\[
V = \sum_{i \in \Omega} V_i, \quad (3.53)
\]
and \( V_i \) only depends on the atoms that are within the cut-off radius around the \( i \)-th atom. One can easily verify that, \( V_i = \tilde{V}_i \) for all \( i \in \Omega_1 \setminus \Gamma_1 \).

Applying the Hamilton’s principle, we obtain the corresponding approximate dynamics,
\[
\begin{aligned}
\ddot{u}_I &= -\nabla_{u_I} V(u_I, C u_I) - C^T \nabla_{u_\Sigma} V(u_I, C u_I) \\
&\quad + C^T D_{\Sigma, \Sigma} (u_\Sigma - C u_I), \\
\ddot{u}_\Sigma &= -D_{\Sigma, \Sigma} u_\Sigma - D_{\Sigma, \Sigma} u_I.
\end{aligned}
\quad (3.54)
\]

Now, one can make the observation that the dynamics in \( \Omega_\Sigma \) is identical to that in (3.2). Further more, the first equation is only coupled to \( u_\Sigma \) linearly. These observations show that the DtN map can be formulated as long as the interactions with the bath is linear, as demonstrated in section 3.2. As an example, let us write out the molecular dynamics model in \( \Omega_1 \), supplemented with the first order ABC,
\[
\begin{aligned}
\ddot{u}_I &= -\nabla \Phi(u_I) - D_{1, \Gamma} g, \\
\dot{g} &= -B_0^{-1} A_0 D_{\Sigma, \Gamma} v_{1, \Gamma} + B_0 g, \quad (3.55)
\end{aligned}
\]
where \( \Phi(u_I) \defeq V_I(u_I, C E^T u_{1, \Gamma}) \) is the effective potential energy in \( \Omega_1 \).

It is also straightforward to establish the stability of the dynamics (3.55). We
introduce this Lyapunov functional,

\[ E = \Phi(u_1) + \frac{1}{2} v_1^T v_1 - \frac{1}{2} g^T A_0^{-1} B_0 g. \]  

(3.56)

Its derivative is simply given by,

\[ L_t E = -g^T A_0^{-1} B_0 g. \]

So the stability result still follows.

Since \( \Omega_I \) involves many atoms, it is impracticable to evaluate the second term on the right hand side of the first equation in (4.3). But this term can be neglected. This can be justified by using an expansion,

\[ \nabla_{u_1} V(u_1, C u_1) \approx D_{\Pi,\Pi} C u_1 + D_{\Pi,1} u_1 = 0. \]

The modeling error depends on the deformation of the system in \( \Omega_I \). In this project, we will not provide the detailed proof. In fact,

\[ \nabla_{u_1} V(u_1, C u_1) = D_{\Pi,\Pi} C u_1 + D_{\Pi,1} u_1 + H.O.T. \]

In light of the definition of the matrix \( C \), the leading terms become zero.

### 3.6 Numerical simulations

In this section, we present the results from two molecular simulations with ABCs applied. The standard Verlet method is implemented for the time integration. The ABCs are simply discretized by the forward Euler method with the same time step size as the Verlet method. The time step of the simulations is set to be 76.2 femtoseconds (\( 10^{-15} \) s).

**System setup.** We choose the nonlinear region \( \Omega_I = [-50\text{Å}, 50\text{Å}] \times [-50\text{Å}, 50\text{Å}] \) and the surrounding region to be infinite \( \Omega_R = \mathbb{R}^2 \setminus \Omega_I \). The region \( \Omega_I \) is filled with 3,265 bcc iron atoms. 580 outer atoms around the region \( \Omega_I \) are introduced to help us calculate the DtN map. The presence of the four corners does not impose any computational difficulty in our formulation. The DtN map of the region with corners are exactly evaluated for interpolations, using the atomistic boundary
element methods, which are particularly suited for domains of general geometry. The periodic boundary condition is imposed in the z-direction to mimic a plane strain condition. Among the iron atoms, the interactions are modeled by the EAM potential [93]. As preparations, the force constant matrices are approximated by standard finite difference formulas. Due to the locality of the computed force constant matrices, only 580 atoms in $Ω_{II}$ and 520 atoms in $Ω_{I}$ are involved in the evaluation of the DtN map $T(s)$. The calculation of the lattice Green’s function is discussed in the Appendix. For the initial configuration, the initial velocity is given by

$$v_x = 20 \sin(x/3)e^{-0.1r}, \quad \text{and}$$

$$v_y = 20 \sin(y/3)e^{-0.1r},$$

where $r = \sqrt{x^2 + y^2}$. The displacement of all atoms is zero initially.

**Interpolation points.** In all simulations, we apply zeroth, first, and second order approximate ABCs and monitor the wave reflections. For the zeroth order approximation, the only interpolation point is chosen as $s_0 = 0.1312$ PetaHz. For the first and second approximations, we need to solve a linear system for the coefficients of rational function. In practice, Assumption 1 can be extended to $-B_{n-1}^{-1}A_{n-1} = \Theta(s_0)$, where $s_0$ does not have to be zero. Assumption 2 turns out to be the derivative condition at $s_0$. The proofs of stability still hold.

For the first order approximation, we choose $s_0 = 0.1312$ PetaHz and $s_1 = 0.2624$ PetaHz. For the second order approximation, $s_0 = 0.3936$, $s_1 = 0.01312$ PetaHz, and $s_2 = 0.1312$ PetaHz. One more point at $s_3 = 0.2624$ PetaHz is added to approximate $\Theta'(s_0)$.

**Performance.** In implementing the proposed ABCs, only matrix-vector multiplications are involved in each time step, since the coefficients are determined a priori. Computation times were recorded (Table 3.2) when the three approximate ABCs are imposed on the same problem. We see that the higher order ABCs do not add up the computational cost significantly.

<table>
<thead>
<tr>
<th>Order</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>zeroth order</td>
<td>1979.108 s</td>
</tr>
<tr>
<td>first order</td>
<td>2201.072 s</td>
</tr>
<tr>
<td>second order</td>
<td>2783.020 s</td>
</tr>
</tbody>
</table>

**Table 3.2.** Computational time of the three approximate ABCs imposed on the same problem, same computer, for 200,000 time steps.
3.6.1 Waves in homogeneous systems

![Wave propagations in the homogeneous system. The color indicates the velocity in the x direction.](image)

Figure 3.3. Wave propagations in the homogeneous system. The color indicates the velocity in the x direction.

We observe within a short time period, the resulting velocity fields, under the three ABCs, are almost the identical. However, when the lattice waves arrive at the boundary, a complete reflection is observed under the zeroth order approximation. The reflection is reduced by the first order approximation. The second order approximation exhibited clear improvement: After several reflections, the lattice waves have been almost all absorbed. During the entire process, without any special treatments, the elastic waves are also absorbed at the corners. All of three ABCs are stable in this relatively long time period.

3.6.2 Waves in a system with dislocations

In the second experiment, we implement the ABCs in a system with dislocations. The dislocations are created at \((-20\text{Å}, 0)\) and \((20\text{Å}, 0)\) by analytical solutions \[94\]. The Burgers vectors of the two dislocations are opposite in the same slip plane. In this case, the far-field displacement has fast decays. The reference coordinates of the atoms around the boundaries corresponds to those in a perfect lattice. The boundary conditions in this simulation are exactly the same as the last experiment. As preparations, the system is driven to an equilibrium state by minimizing the total energy. Then the same initial velocity is introduced. An interesting observation in this case is that high-frequency waves are generated.
by the interaction of the initial lattice waves and the dislocations. We observed that the second order approximation still performs the best. The reduction of the reflections is still significant.

![Figure 3.4. Wave propagations in the system with dislocations, the color indicates the value of velocity.](image)

### 3.7 Conclusion

In conclusion, we presented a systematic strategy to represent and approximate the ABCs systematically. It is a robust, efficient and easy-to-implement method to simulate phonons propagation in a large or infinite domain. Under this framework, further extensions can be pursued in various directions.

**Finite temperature.** In this project, we only focused on the wave propagation at low temperature. In practice, the finite-temperature MD is a more widely used tool in chemistry, biology and materials science. Absorbing boundary conditions for the finite-temperature MD are already discussed in [66, 95], following the original idea of Adelman and Doll’s work [90] on generalized Langevin equation (GLE). The proposed ABCs can be extended naturally to the case of finite temperature. The extended approach will be able to exchange heat between truncated atomistic region and the bath.

**Dynamical loading.** Another important application of ABCs is to allow external elastic waves to come through the atomistic regions and interact with local defects, which is similar to [96]. Within the current framework, it means that a physical...
boundary needs to be included into the set $\Gamma$, where a dynamic loading condition is applied. Another approach to include dynamic loading and simulation the propagation of elastic waves is to couple molecular dynamics models to a continuum elastic wave equation [97, 58]. In such a setting, the transparent boundary condition is still an important component.
Chapter 4  
Absorbing boundary conditions in quantum mechanics

4.1 Introduction

Quantum mechanical simulations provide accurate results of physical properties in chemistry and physics [98, 99]. The most challenging problem in quantum mechanical simulation is its limited computational scale. In last five decades, the development of computers and algorithms brought massive computational resources. However, the computational scale of quantum simulations is still under $10,000$ atoms, which is still far away from realistic materials science problems. More numerical techniques are required to extend the applications of the quantum mechanical approach.

The idea of absorbing boundary conditions (ABCs) is one of the approaches which reduce the unbounded domain into a small finite computational domain. There are several different way to design the artificial boundary conditions. Most of them involve the approximation of the DtN map. They are called non-reflecting boundary condition or radiating boundary conditions in different communities. By truncating the far field area, the computational resources are focused on simulating the region of interest. Instead of simply cutting the exterior region off, the absorbing boundary conditions provide a systematic way to mimic the exterior. This idea was originally developed for the wave equation. It is also applied to the molecular dynamics problem and the Schrödinger equation.

**ABCs for Schrödinger equation.** Various techniques [100] are developed
to implement artificial boundary conditions for 1d time-dependent Schrödinger equation (TDSE). Most of these methods follow the procedure: The Dirichlet-to-Neumann (DtN) or Neumann-to-Dirichlet (NtD) maps are constructed based on different discrete versions of TDSE, such as temporally discrete model [101], spatially discrete model [102, 103], and fully discrete model [104]. The time-convolution in the exact DtN map is expensive to evaluate, due to the nonlocality of the kernel function. In these approaches, the exact boundary conditions (DtN or NtD maps) are approximated by finite sums of exponentials in the real-time space [105, 84] or rational functions in the Laplace space or the Fourier space [106, 107, 108]. The convergence, stability, and efficiency of these method are discussed. However, most of these methods are limited in 1d case and suffer from the corner issues in higher dimensional problems. Few methods [82, 109, 83] are extended to 2d or 3d case, but limited only to special geometries of the interior domain. The perfectly matched layer (PML) [56] was applied to the nonlinear Schrödinger equation by Zheng [110].

Many-body problem. For a many-body system, one of the practical numerical methods is to solve the well-known Kohn-Sham equation [111]. In general, there are three empirical approaches to numerically implement ABCs for the Kohn-Sham equation, exterior complex scaling (ECS) [112], mask function [113], and complex absorbing potentials [114]. In those methods, the selections of the scaling radius, mask function, or complex absorbing potentials are quite artificial. More degree of freedoms have to be introduced for two- or three-dimensional simulations. An efficient method is needed to accelerate the time-dependent problems in quantum mechanical simulations. This is another topic we are interested in.

In this project, we apply the formulation of atomistic ABCs in our previous work [115] to the Schrödinger equation and the time-dependent Hartree-Fock model. Our viewpoint is similar to the works by Alonso-Mallo[102, 103]. The DtN map is based on the spatially discrete model in the Laplace space. Typically, these semi-discrete ABCs yield higher absorption qualities than the spatial discretization of the continous ABCs [100]. We employ rational functions to approximate the DtN map. This reduces the exact DtN map to ordinary differential equations. Our contributions are: i) the evaluation of the DtN map in the Laplace space. The exact DtN map is computed by boundary element method for arbitrary geometries. ii) reducing the time-convolution in the DtN map to ODE system. iii) extending the ABC of the Schrödinger equation to the time-dependent Hartree-Fock model.
This chapter is organized as follows: in section 4.2, the reduced problem is formulated. We approximate the transparent boundary condition from Galerkin projection viewpoint in section 4.3. In this section, we provided a choice of subspace such that the approximate dynamics is stable. In section 4.4, both 1d and 3d numerical simulations are performed to verify the stability and effectiveness. Further, we apply the absorbing boundary condition to time-dependent Hartree-Fock model. It turns out that the proposed ABC is also effective to time-dependent Hartree-Fock model.

4.2 Formulation of the DtN map for Schrödinger equation

Let us consider the time-dependent Schrödinger equation in $\Omega \subset \mathbb{R}^d$

$$i \frac{\partial}{\partial t} \psi(x, t) = \hat{H} \psi(x, t)$$

(4.1)

In this equation, we have assumed the reduce Planck constant is 1. $i$ is the imaginary unit. $\psi(x, t)$ is the wave function of the quantum system. The Hamiltonian operator $\hat{H} = -\Delta + V(x)$. $V$ is the potential energy of the system.

Suppose $\Omega_I$ is a subdomain of interest in $\Omega$. We apply the absorbing boundary condition at the boundary of $\Omega_I$, to truncate the remaining region $\Omega_{II}$. Here, $\Omega = \Omega_I \cup \Omega_{II}$. In the exterior region $\Omega_{II}$, we assume that the operator $\hat{H}$ does not depend on $x$. More specifically, $V(x) = 0$. Unlike other continuous absorbing boundary conditions, our approach is based on this spatially discrete model (B.2). Numerically, let $\{x_j\}$ be $n_I$ grid points with a constant spacing of $h$ in the interior $\Omega_I$ and $n_{II}$ grid points in the exterior $\Omega_{II}$. $n_I \ll n_{II}$. The function $\psi(x)$ is approximated by piecewise linear functions, $\psi(x_j) = \psi_j$. The Hamiltonian operator is approximated (C.10) by finite difference formulas (5-point scheme or 9-point scheme), that is,

$$-\Delta \psi \approx \sum_k H_{jk} \psi_k.$$

To simplify the notations, the indices of the nodal points are sorted as $x_1, \ldots, x_{n_I} \in \Omega_I$. 

58
\[ \Omega, \text{ and } x_{n+1}, \ldots, x_{n_\ast} \in \Omega. \] The semi-discrete model is written as a compact form:

\[
\begin{align*}
\frac{\partial}{\partial t} \psi_1(x, t) &= H_{1,1}(t) \psi_1 + H_{1,\ast}(t) \psi_\ast \\
\frac{\partial}{\partial t} \psi_\ast(x, t) &= H_{\ast,1}(t) \psi_1 + H_{\ast,\ast}(t) \psi_\ast
\end{align*}
\] (4.2)

where \( \psi_1 = [\psi_j]_{j \in \Omega} \) and \( \psi_\ast = [\psi_j]_{j \in \Omega_\ast} \). The second equation in 4.2 has a huge size, and should be reduced. We denote the discretization of the Hamiltonian operator

\[ H = \begin{bmatrix} H_{1,1} & H_{1,\ast} \\ H_{\ast,1} & H_{\ast,\ast} \end{bmatrix}. \] (4.3)

\( H \) is a sparse matrix, and has a banded structure. \( H_{1,1} \) and \( H_{\ast,\ast} \) are the discretized Hamiltonian operator in \( \Omega \) and \( \Omega_\ast \). \( H_{1,\ast} \) and \( H_{\ast,1} \) are the off-diagonal blocks due to the interaction between \( \Omega \) and \( \Omega_\ast \). We denote \( \Gamma \) as the boundary of \( \Omega \), such that

\[ \Gamma = \{ j \in \Omega | H_{jk} \neq 0 \text{ for some } \psi_k \in \Omega_\ast \}. \] (4.4)

Correspondingly, \( \psi_\Gamma \) is a vector formed by all \( \psi_j \) for \( j \in \Gamma \), and \( \psi_\Gamma \in \mathbb{R}^{n_\Gamma} \), where \( n_\Gamma \) is the number of nodal points in \( \Gamma \).

Let’s denote, \( \psi_1 = \begin{bmatrix} \psi_\Gamma \\ \psi_{1,\Gamma} \end{bmatrix} \). Similarly, we introduce,

\[ H_{\ast,1} = \begin{bmatrix} H_{\ast,\Gamma} & H_{\ast,1,\Gamma} \end{bmatrix} = \begin{bmatrix} H_{\ast,\Gamma} & 0 \end{bmatrix}. \] (4.5)

It will also be useful to introduce \( E = [I \ 0] \), where \( E \in \mathbb{R}^{n_\Gamma \times n_\ast} \). Using this matrix, we may write \( \psi_\Gamma = E \psi_1 \), and \( H_{\ast,1} = H_{\ast,1}E^T \).

We define an operator \( E \) to extract the desired information at the boundary \( \Gamma \) from a long vector associated with \( \Omega \). For instance, \( \psi_\Gamma = E \psi_1 \). Further, we introduce new notations \( H_{\ast,1} = H_{\ast,1}E^T \). Our starting point is,

\[
\begin{align*}
\frac{\partial}{\partial t} \psi_1(t) &= -iH_{1,1} \psi_1(t) - iH_{1,\ast} \psi_\ast(t) \\
\frac{\partial}{\partial t} \psi_\ast(t) &= -iH_{\ast,1} \psi_1(t) - iH_{\ast,\ast} \psi_\ast(t)
\end{align*}
\] (4.6)

Notice that,

\[ H_{1,\ast} = E^T H_{\Gamma,\ast}. \] (4.7)

59
If we define
\[ f_\Gamma = H_{\Gamma,\Omega} \psi_\Omega, \quad (4.8) \]
then the first equation can be written as,
\[ \frac{\partial}{\partial t} \psi_1(t) = -iH_{1,1} \psi_1(t) - iE^T f_\Gamma(t). \quad (4.9) \]

In the region \( \Omega \), the discretized equation is expressed as
\[ i \frac{d}{dt} \psi_\Omega(t) = H_{\Omega,\Omega} \psi_\Omega(t) + H_{\Omega,1} \psi_1(t) \quad (4.10) \]
where \( H_{jk} \) is the discretization of the Hamiltonian operator. First, we take Laplace transform of the time domain.

\[ is \Psi_\Omega(s) = H_{\Omega,\Omega} \Psi_\Omega(s) + H_{\Omega,1} \Psi_1(s). \quad (4.11) \]

Define \( \tilde{H}_{\Omega,\Omega}(s) = H_{\Omega,\Omega} - isI \). The problem (Eq. (B.3)) turns into a static problem

\[ \tilde{H}_{\Omega,\Omega} \Psi_\Omega = -H_{\Omega,1} \Psi_1. \quad (4.12) \]

Formally, its solution is
\[ \Psi_\Omega = -\tilde{H}_{\Omega,\Omega}^{-1} H_{\Omega,1} \Psi_1. \quad (4.13) \]

Due to the locality of \( H_{\Omega,\Omega} \), \( H_{\Omega,1} \Psi_1 = H_{\Omega,\Gamma} \Psi_\Gamma \). The DtN map \( K(s) \) of the problem (Eq. (B.5)) in the Laplace space is defined as
\[ F_\Gamma(s) = K(s) \Psi_\Gamma(s) \quad (4.14) \]
or in the time domain, we have,
\[ f_\Gamma(t) = \int_0^t \kappa(t - \tau) \Psi_\Gamma(\tau) d\tau \quad (4.15) \]
The kernel \( K(s) \) is expressed as
\[ K(s) = -H_{\Gamma,\Omega}^{-1}(s_0)H_{\Omega,\Gamma} = -H_{\Gamma,\Omega}[H_{\Omega,\Omega} - isI]^{-1}H_{\Omega,\Gamma}. \quad (4.16) \]
As a result, the exact BC can be expressed as follows,

$$\frac{\partial}{\partial t} \Psi_I(t) = -iH_{1,1} \Psi_I(t) - iE^T \int_0^t \kappa(t - \tau) E \Psi_I(\tau) d\tau. \quad (4.17)$$

In some literature, it is preferred to write (B.3) into the alternative form

$$i(s - s_0)(H_{\Pi,\Pi} - is_0I)^{-1} \Psi_{\Pi}(s) = \Psi_{\Pi}(s) + (H_{\Pi,\Pi} - is_0I)^{-1}H_{\Pi,1}\Psi_I(s) \quad (4.18)$$

where $s_0 \in \mathbb{C}$ is a pre-selected scalar. In this case, the kernel function

$$K(s) = -H_{\Gamma,\Pi}(I - i(s - s_0)(H_{\Pi,\Pi} - is_0I)^{-1})^{-1}(H_{\Pi,\Pi} - is_0I)^{-1}H_{\Pi,G} \quad (4.19)$$

If denote $A = i(H_{\Pi,\Pi} - is_0)^{-1}$ and $B = (H_{\Pi,\Pi} - is_0I)^{-1}H_{\Pi,G}$, the Taylor expansion of the kernel function $K(s)$ around $s = s_0$ reads

$$K(s) = -H_{\Gamma,\Pi}(B + AB(s - s_0) + A^2B(s - s_0)^2 + A^3B(s - s_0)^3 + \cdots) \quad (4.20)$$

We denote $M_0 = -H_{\Gamma,\Pi}B$, $M_1 = -H_{\Gamma,\Pi}AB$, $M_2 = -H_{\Gamma,\Pi}A^2B$, and subsequent coefficients in (4.20) as moments. The way to approximate the kernel function $K(s)$ by rational functions with the same moments are called moment matching approach. One may notice that (4.20) is connected to a Krylov space $K(A, B)$.

The direct evaluation of the memory kernel function $\kappa(t)$ is expensive. We will focus on the approximation in the Laplace space. Let us consider the approximation in an abstract manner.

### 4.3 Approximation of the discrete DtN map

In this section, we will present two approaches to approximate the discrete DtN map. Both of the two approaches reduce the model in $\Omega_{\Pi}$ to a ODE system with a much smaller size. One of them is based on Galerkin projection. The other is to approximate the DtN map by rational functions via interpolation. The former turns out to be stable if we choose a proper projection. The later provides the preferable absorbing results. Unfortunately, we are not able to prove its stability.
4.3.1 Galerkin projection

Consider two matrices \( V \in M_{n_{II},m}(\mathbb{R}) \) and \( W \in M_{n_{II},m}(\mathbb{R}) \), where \( m \ll n_{II} \). Let assume \( V \) and \( W \) are full column rank. This is a reasonable assumption for Galerkin projection. Otherwise, we can choose a smaller subspace to approximate the solution

We denote the solution space by \( X = \text{Range}(V) \) and the projection of the residual error is to the subspace \( Y = \text{Range}(W) \). Letting

\[
\psi_{II} = V\mathbf{y} \text{ for any } \mathbf{y} \in Y. \tag{4.21}
\]

The Galerkin projection yields,

\[
W^*V\partial_t \psi = -iW^*H_{II,\Gamma}E\psi_1 - iW^*H_{II,II}V\mathbf{y}. \tag{4.22}
\]

This should be coupled to the first equation, expressed now as

\[
\frac{\partial}{\partial t} \psi_1(t) = -iH_{1,1}\psi_1(t) - iE^T H_{\Gamma,II}V\mathbf{y}. \tag{4.23}
\]

As it turns out, it is more convenient to work with \( z \)

\[
z = W^*V\mathbf{y}. \tag{4.24}
\]

Let us now combined the equations,

\[
\begin{align*}
\partial_t \psi_1 &= -iH_{1,1}\psi_1 - iE^T H_{\Gamma,II}V(W^*V)^{-1}z, \\
\partial_t z &= -iW^*H_{II,\Gamma}E\psi_1 - iW^*H_{II,II}V(W^*V)^{-1}z.
\end{align*} \tag{4.25}
\]

Let us denote

\[
\hat{M} = W^*V, \text{ and } \hat{H} = W^*H_{II,II}(s_0)V. \tag{4.26}
\]

Then the reduced equations are given by,

\[
\begin{aligned}
\partial_t \psi_1 &= -iH_{1,1}\psi_1 - iE^T H_{\Gamma,II}V\hat{M}^{-1}z, \\
\partial_t z &= -iW^*H_{II,\Gamma}E\psi_1 - i\hat{H}\hat{M}^{-1}z + s_0 z.
\end{aligned} \tag{4.27}
\]
To study the stability, we define the Lyapunov functional as follows,

$$U = \psi_1^* \psi_1 + z^* Q z.$$ \hfill (4.28)

Here $Q$ is a positive-definite, Hermitian matrix, and it is to be determined.

Taking derivative, we get,

$$LU = -i \psi_1^* E^T H_{I, I} V \hat{M}^{-1} z + c.c.$$ \hfill (4.29)

This gives rise to two conditions,

$$Q W^* H_{I, I, \Gamma} = \hat{M}^* V^* H_{I, I, \Gamma}, \quad \text{(A)}$$

and

$$-i z^* Q \left[ \hat{H} \hat{M}^{-1} + i s_0 \hat{I} \right] z + c.c \leq 0.$$ \hfill (4.30)

Or, more specifically,

$$\frac{1}{2i} \left[ Q \hat{H} \hat{M}^{-1} - \hat{M}^* \hat{H}^* Q \right] + s_0 Q \leq 0. \quad \text{(B)}$$

The following theorem provides a stable choice of projections.

**Theorem 4.3.1** (Stability of Galerkin projection). For any projections $V$ and $W = H_{I, I}(s_0) V$ with $s_0 > 0$, if $W^* W$ is invertible, that is, 0 is not an eigenvalue of the matrix $W^* W$, the reduced model (4.27) is stable.

**Proof.** In this case, the matrix $Q$ can be defined as $Q = (W^* W)^{-1}$. The first condition (A) is automatically satisfied since

$$(W^* W)^{-1} W^* H_{I, I, \Gamma} = I = (V^* W)^{-1} V^* H_{I, I, \Gamma}$$

For the second condition, we need to verify

$$\text{Im}[z^* (\hat{M}^{-1} + i s_0 \hat{H}^{-1}) z] \leq 0.$$ \hfill (4.30)
Let us consider

\[ \hat{M}^{-1} - \hat{M}_1^{-1} + 2is_0 \hat{H}^{-1} = \hat{M}^{-1}(\hat{M}^* - \hat{M}_1 + 2is_0 \hat{M}^* \hat{H}^{-1} \hat{M})\hat{M}^{-1}, \]  

(4.31)

where

\[ \hat{M}^* - \hat{M} = W^*((H_{\Pi,\Pi} + is_0 I)^{-1} - (H_{\Pi,\Pi} - is_0 I)^{-1})W \]

(4.32)

The last term of eq. (4.31)

\[ 2is_0 \hat{M}^* \hat{H}^{-1} \hat{M} = 2is_0 W^*(H_{\Pi,\Pi} - is_0 I)^{-1} P(H_{\Pi,\Pi} + is_0 I)^{-1} W \]

(4.33)

here we have denoted \( P = W(W^*W)^{-1}W^* \). Obviously, \( P \) is a projection matrix. Overall, the expression inside the bracket in eq. (4.31) can be expressed as

\[ \hat{M}^* - \hat{M} + 2is_0 \hat{M}^* \hat{H}^{-1} \hat{M} = 2is_0 \hat{W}^*(H_{\Pi,\Pi} - is_0 I)^{-1} (P - I)(H_{\Pi,\Pi} + is_0 I)^{-1} \hat{W} \]

(4.34)

The above expression is a pure imaginary matrix, and semi-negative since \( P - I \) is semi-negative definite. As a result, \( \text{Im}(\hat{M}^{-1} + is_0 \hat{H}^{-1}) \) is semi-negative definite. Therefore, the condition (B) is satisfied for any complex vector \( z \).

**Choices of Galerkin projection.** There are many choices of the solution subspace and residual subspace. Our selection of subspaces are based on the following physical observation. Absorbing boundary conditions are highly related to nodal points around the boundary. In this project, we will consider the subspaces spanned by the values of nodal points around the boundary.

One natural choice is that we consider the projections

\[ \hat{V}_1 = H_{\Pi,\Pi}^{-1}(s_0) H_{\Pi,\Gamma} \]

\[ \hat{V}_2 = H_{\Pi,\Pi}^{-2}(s_0) H_{\Pi,\Gamma} \]

\[ \vdots \]

\[ \hat{V}_n = H_{\Pi,\Pi}^{-n}(s_0) H_{\Pi,\Gamma} \]

(4.35)

as the candidates of \( V \). Accordingly, we consider \( \hat{W}_i = H_{\Pi,\Pi}(s_0) \hat{V}_i \) for each \( 1 \leq i \leq n \) as the candidates of \( W \). Unfortunately, \( \hat{W}_i^* \hat{W}_i \) is not necessarily positive definite. These projections may lead to a degenerate dynamical system of eq. (4.27).
But we can select a submatrix of \( \hat{W}_i \) and \( \hat{V}_i \) with linearly independent rows such that \( \text{Rank}(V_i) = \text{Rank}(\hat{V}_i) \) and \( \text{Rank}(W_i) = \text{Rank}(\hat{W}_i) \). Consequently, \( W_i^*W_i \) and \( W_i^*V_i \) are positive definite. By Theorem 4.3.1, the resulting dynamics (4.27) is stable.

**Implementation.** The complex DtN map should be reformulated. The DtN map can be expressed as the conjugate of lattice green’s function and force constant. From computational viewpoint, \( H_{\pi,\pi}^{-1}(s_0) \) is not affordable. At this point, we only are able to evaluate the DtN map and derivatives of the DtN map by finite difference. In this section, we propose a strategy to evaluate the desirable matrix \( \hat{H} \) and \( \hat{M} \) by the DtN map. Let us consider a general form of the blocks of \( \hat{H} \),

\[
\hat{H}_{JK} = H_{\pi,\pi}^{-j}(s_0^*) H_{\pi,\pi}^{-k}(s_0) H_{\pi,\Gamma}
\]

Without loss of generality let us assume that \( j > k \). The matrix \( \hat{H}_{JK} \) can be expressed as a combination of higher order expressions,

\[
\hat{H}_{JK} = 2i s_0 H_{\pi,\pi} \left[ H_{\pi,\pi}^{-j+1}(s_0^*) H_{\pi,\pi}^{-k}(s_0) - H_{\pi,\pi}^{-j}(s_0^*) H_{\pi,\pi}^{-k+1}(s_0) \right] H_{\pi,\Gamma}
\] (4.36)

By the above equation, the order of \( H_{\pi,\pi} \) is increased by 1. We can continue this process until all of the terms are expressed in terms of \( H_{\pi,\pi}(s_0) \) or \( H_{\pi,\pi}(s_0^*) \). Since

\[
K^n(s_0) = -i^n n! H_{\pi,\pi}^{-n-1}(s_0) H_{\pi,\pi}^{-1}(s_0) H_{\pi,\Gamma},
\] (4.37)

\( \hat{H}_{JK} \) can be expressed in terms of derivatives of the DtN map.

**Example.** Let \( W_2 = \left[ H_{\pi,\pi}^{-1}(s_0^*) H_{\pi,\pi}(s_0) \right] \) and \( V_2 = \left[ H_{\pi,\pi}^{-2}(s_0) H_{\pi,\pi}^{-1}(s_0) \right] \).

In this case,

\[
\hat{M} = \begin{bmatrix}
H_{\pi,\pi}^{-1}(s_0^*) H_{\pi,\pi} & H_{\pi,\pi}^{-2}(s_0) H_{\pi,\pi} \\
H_{\pi,\pi}^{-1}(s_0^*) H_{\pi,\pi} & H_{\pi,\pi}^{-2}(s_0) H_{\pi,\pi}
\end{bmatrix}
\] (4.38)

The first three blocks of \( \hat{M} \) can be directly evaluated by the derivatives of the DtN map. The last block

\[
\hat{M}_{22} := H_{\pi,\pi}^{-1}(s_0^*) H_{\pi,\pi}^{-2}(s_0) H_{\pi,\pi} \\
= 2i s_0 H_{\pi,\pi} \left[ H_{\pi,\pi}^{-2}(s_0) - H_{\pi,\pi}^{-1}(s_0^*) H_{\pi,\pi}^{-1}(s_0) \right] H_{\pi,\Gamma}
\] (4.39)
Further, the cross term $H^{-1}_{\Gamma,\Gamma}(s_0^*)H^{-1}_{\Gamma,\Gamma}(s_0)$ is canceled by using (B.8) again, that is,

$$
\hat{M}_{22} = 2is_0H_{\Gamma,\Gamma}H^{-2}_{\Gamma,\Gamma}(s_0)H_{\Gamma,\Gamma} + 4s_0^2H_{\Gamma,\Gamma} \left[ H^{-1}_{\Gamma,\Gamma}(s_0) - H^{-1}_{\Gamma,\Gamma}(s_0^*) \right] H_{\Gamma,\Gamma}
$$

(4.40)

Therefore, the matrix $\hat{M}$ is evaluated by the DtN map. The matrix $\hat{H}$ can be evaluated in the similar manner.

### 4.3.2 Approximation by interpolation

In this approach, the kernel function of the DtN map is approximated by rational functions. In this project, we consider the following rational functions:

$$
R_{n,n}(s) = \left( s^n - s^{n-1}B_0 - s^{n-2}B_1 - \cdots - B_{n-1} \right)^{-1} \left( s^{n-1}A_0 + s^{n-2}A_1 + \cdots + A_{n-1} \right)
$$

(4.41)

$A_0, \ldots, A_{n-1}$ and $B_0, \ldots, B_{n-1}$ are $n_\Gamma \times n_\Gamma$ matrices to be determined. We need $2n$ points of $(s_i, K(s_i))$ to determine these coefficients. The approximate DtN map in the Laplace space is

$$
F_{\Gamma}(s) = R_{n,n}(s) \Psi_{\Gamma}(s)
$$

(4.42)

In real time space, the approximate dynamics is formulated as

$$
f_{\Gamma}^{(n)} = B_0f_{\Gamma}^{(n-1)} + \cdots + B_{n-1}f_{\Gamma} + A_0\psi_{\Gamma}^{(n-1)} + \cdots + A_{n-1}\psi_{\Gamma}
$$

(4.43)

Now, the non-local time-convolution in the DtN map is replaced by a linear ODE system. The higher-order ODE can be reformulated as a larger ODE system for solving numerically. The entire model is approximated by

$$
\begin{cases}
\frac{\partial}{\partial t}\psi_1(t) = -iH_{1,1}\psi_1(t) - iH_{1,\Gamma}\psi_\Gamma(t) \\
f_{\Gamma}^{(n)} = B_0f_{\Gamma}^{(n-1)} + \cdots + B_{n-1}f_{\Gamma} + A_0\psi_{\Gamma}^{(n-1)} + \cdots + A_{n-1}\psi_{\Gamma}
\end{cases}
$$

(4.44)

### 4.4 Applications & numerical experiments

In this section, we apply absorbing boundary conditions to 1d TDSE, 3d TDSE and 3d TDHF models. For each model, we will also present the corresponding numerical simulations. The numerical details are discussed in section 4.4.1, section 4.4.2 and section 4.4.3.
1d TDSE model [100]:

$$i \frac{\partial}{\partial t} \psi(x,t) = \hat{H}\psi(x,t) \text{ in } \mathbb{R}$$

with the initial condition $\Psi^0(x) = \exp(-(x-x_c)^2 + ik_0(x-x_c))$.

3d TDSE model extended from [109]:

$$i \frac{\partial}{\partial t} \Psi(x,t) = \hat{H}\psi(x,t) \text{ in } \mathbb{R}^3$$

with the initial condition $\Phi^0 = \exp\{-x^2 - y^2 - z^2 + ik_0x\}$

3d TDHF model [116]:

$$i \frac{\partial}{\partial t} \psi_j(x,t) = \hat{H}\psi_j(x,t) \text{ in } \mathbb{R}^3, \text{ for } j = 1, \ldots, A$$

with the initial condition $\psi_j^0$. The 3d TDHF model is a system of nonlinear 3d time-dependent Schrödinger equations. The hamiltonian $\hat{H}$ dependents on one-particle wave functions.

**Integrator.** The typical numerical integrators can be formulated as

$$\psi^{(n+1)} = U\psi^{(n)}$$

where $U$ is the operator which varies for different schemes. In the exact integrator, the operator can be expressed as

$$U_E = \exp(-i\Delta t H)$$

The Crank-Nicholson scheme is a widely used method to solve 1d Schrödinger equation, the operator is

$$U_{CN} = (1 + i\Delta t/2H)^{-1}(1 - i\Delta t/2H)$$

For the 3d case, it is impractical to perform the matrix inverse in the Crank-Nicholson scheme. In the TD-DFT community [116], one preferred method is taking
the Taylor expansion of the exact integrator,

\[ U_5 = I - iH\Delta t - \frac{1}{2}H^2(\Delta t)^2 + \frac{1}{6}H^3(\Delta t)^3 - \frac{i}{24}H^4(\Delta t)^4. \]  

(4.49)

### 4.4.1 1d TDSE model

Consider the 1d Schrödinger equation on the interior \( \Omega_I = [-12, 3] \). The exterior domain is \( \Omega_{II} = (0 - \infty, -12) \cup (3, \infty) \). The Laplacian operator is discretized by the five-point scheme with grid spacing of \( h = 0.01 \). We impose Dirichlet boundary condition on the left end and absorbing boundary condition on the right end. The settings of the problem is illustrated in Figure 4.1.

![Figure 4.1. An illustration of the model reduction for 1d Schrödinger equation](image)

We choose \( k_0 = 5 \) and \( x_c = -6 \). This benchmark problem is widely used in many literature, since the analytical solution can be explicitly written as

\[ u^{ex}(x, t) = \sqrt{\frac{i}{i - 4t}} \exp \left( \frac{-k_0(x - x_c) + k_0^2 t - i(x - x_c)^2}{i - 4t} \right). \]  

(4.50)

The DtN map is evaluated by lattice Green’s function. The numerical details of 1d lattice Green’s function are discussed in Appendix B.

**Results by the interpolation.** We select four interpolation points, \( s = 10, 11, 20, 21 \) for the second order approximation and two points \( s = 10, 20 \) for the first order approximation. These points are not optimal. One can find a better choice in terms of the absorbing property.

**Results by the Krylov subspace method.** Due to the degeneracy of the projection \( \hat{V}_i \), the number of the auxiliary variables is not always \( 2i \). For the case of the first order approximation, the number is 2. However, for the second order approximation, the number of the auxiliary variables is 3. Figure 4.4 shows the
Figure 4.2. The solutions by ABC using interpolation and the exact solution.

Figure 4.3. The decay of the norm of the wave function.

comparison between the exact solution and approximate solutions by absorbing boundary conditions. In this simulation, the exterior domain is infinite. The higher

Figure 4.4. The solutions by various absorbing boundary conditions and the exact solution.

order ABC is supposed to be better than the lower order ABCs not only in a short time, but also in a long time period. However, Figure 4.4 gives us a similar result as the finite exterior domain, that is, the higher order ABC is good only in a short
time. The norm of the solution 4.5 confirms this result.

![Graph showing the decay of particle density.](image)

**Figure 4.5.** The decay of the particle density.

### 4.4.2 3d TDSE model

In this section, we will verify the absorbing boundary conditions for the 3d Schrödinger equation. We restrict the computational domain in a box $[-3, 3] \times [-3, 3] \times [-3, 3]$. The 3d Laplace operator is approximated by the 7-point scheme with grid spacing of $h = 0.4$ uniformly. Consequently, there are 31 interior points and 6 exterior points in each axis direction. For each Laplace variable $s$, the DtN map is a $14166 \times 14166$ dense matrix.

Similar to the case in 1d, we still can construct the analytical solution for the system.

$$
\psi^{ex} = \left( \frac{i}{i - 4t} \right)^{3/2} \exp\left( \frac{-i(x^2 + y^2 + z^2) - k_0 x + k_0^2 t}{i - 4t} \right)
$$

with $k_0 = 5$. However, the difference between the analytical solution and the exact solution of the discrete model might not be small due to the large grid spacing. Therefore, we will only use the analytical solution as a reference. We will not compare our results with the analytical solution.

The step size is chosen as 0.001. The number of electrons is almost a constant when we fix the boundary condition (Dirichlet boundary condition). If we impose the absorbing boundary condition on the system, the number of electrons (Figure 4.6) will decay when the wave function propagates to the boundary. When the wave function reaches the boundary for the first time, only 20% of the wave function is reflected. After a few times of reflections, almost all the electrons come out of the
The solutions of 3d tdse with different boundary conditions are shown in Figure 4.7. The fixed boundary condition gives the completely wrong solution. When $t = 0.011$, it does not provide any significant results. The minor reflections are observed in the first order approximation. These errors will be eliminated by the absorbing boundary condition. This experiment also shows the effectiveness of the proposed ABC for the region with corners. The coupled system is stable and relatively accurate even if the corners are involved.

### 4.4.3 3d TDHF model

Let consider the above TDHF model in a large region $\Omega$. Here $\Omega$ can be an infinite region. In practice, the computational domain $\Omega_I$ (usually is a box) is only a small part of the entire $\Omega$. In the typical TDHF simulation, the following assumption is made:

$$\psi_j = 0, \text{ and } \rho = 0 \text{ in } \Omega_{ii} \text{ for } i = 1, \ldots, A$$

The Dirichlet boundary condition or periodic boundary condition is imposed on the boundary for (C.5). Obviously, in this model, the energy and momentum are conserved. When the wave functions propagate to the boundary, they will be reflected back to the computational domain. This phenomenon is not consistent with the physical observation.
Figure 4.7. Solutions of 3d tdse model. The solution by the fixed boundary condition (top). The solution by the first order ABC (middle). The exact solution (bottom). The color indicated the electron density.

Our approach starts from the discrete model. Let denote $\psi^j$ is the discretization of the wave function $\psi^j$ in $\Omega_1$. $H_{I, I}$ is the discretization of the operator $-\frac{\hbar^2}{2m} \nabla^2$. $H_{I, I}$ is still a nonlinear operator. The notations of boundaries and DtN map follow 4.2. In this model, we only assume $\rho = 0$ in $\Omega_1$. The approximate model is expressed as

$$
\begin{cases}
    i\hbar \frac{\partial \psi_I}{\partial t} = H_{I, I}(t) \psi_I + H_{I, I} \psi_{\Gamma} & \text{in } \Omega_1 \\
    \psi_{\Gamma} = \int_0^t k(t-s) f_{\Gamma}(s) ds \text{ and } f_{\Gamma} = H_{I, I} \psi_I & \text{on } \Gamma
\end{cases}
$$

If we use the first order rational function to approximation the kernel function in Laplace space, the approximate model can be further approximated by

$$
\begin{cases}
    i\hbar \frac{\partial \psi_I}{\partial t} = H_{I, I}(t) \psi_I + H_{I, I} \psi_{\Gamma} & \text{in } \Omega_1 \\
    \dot{\psi}_{\Gamma} = B \psi_{\Gamma} + A f_{\Gamma} & \text{on } \Gamma
\end{cases}
$$
In this project, we study the nuclear reaction of the $^{16}O + ^{16}O$ system in the infinite space $\mathbb{R}^3$. The settings of the numerical experiments are mainly from [116]. In this model, we assume the perfect spin-isospin degeneracy for each particle, so that each spatial orbital is occupied by four nucleons. There are 32 nucleons totally in this system. The two particles at ground state are positioned in a box away from each other and the boundary. The ground state is achieved by solving the self-consistent equation for static Hartree-Fock equation. We assume there is no interaction between the two particles at the initial state. The Poisson and Helmholtz problems are solved by preconditioned conjugate gradient method using the same the discretization method as the wave functions.

The initial condition is given by multiplying each orbital by the phase $e^{ik \cdot r}$. Since our goal to simulate the head-on collision, $k$ should be carefully selected to make sure the particles move toward each other. Also, the collision energy should be between certain window, such as two particles pass the Coulomb barrier and do not pass each other. We use the same integrator as the case for three dimensional Schrödinger equation. The time step is set to be $0.001 fm/c$. In each time step, we also need to perform the self-consistent iteration.

In the numerical experiments, $\Omega_I = [-40 fm, 40 fm] \times [-40 fm, 40 fm] \times [-40 fm, 40 fm]$ is discretized with grid spacing of 1 fm. The Laplace operator is approximated by the 7-point scheme in each spatial direction. The energy conservation (Figure 4.8) and mass conservation (Figure 4.8) for the standard TDHF with Dirichlet boundary conditions are verified in our simulations. The system with ABCs released 5 MeV from the total energy, and emitted 0.6 nucleons in the simulating period. More energy and nucleons are expected to be emitted if we run the TDHF a longer time.
Figure 4.9. Contour plot of the nucleon density in time evolution of $^{16}O + ^{16}O$ collision with ABC (top). The difference of the nucleon density in time evolution by ABC and Dirichlet boundary condition.
Chapter 5  |  Conclusion and future work

5.1 Conclusion

In this dissertation, the framework of the model reduction by the DtN map is established. We investigated several classical problems of the model reduction. In the static case, a type of atomistic/continuum coupling method is implemented. By this approach, we are able to handle the simulation of the system with 2 billion atoms on the desktop. In the dynamics problems, we implemented the absorbing boundary conditions for molecular dynamics with only 50% more computational cost. In the other dynamics problem, the absorbing boundary conditions are applied to the Schrödinger equation and time-dependent Hartree-Fock equation.

5.2 Coarse grained MD using ABCs at finite temperature

For the case of molecular dynamics at finite temperature $T$, we still want to develop general boundary conditions based on first-principle, not any empirical assumptions. Especially, we derive the boundary conditions from the equation of motion in the exterior region. The dynamics in the exterior region is reduced to the generalized Langevin equation (GLE) \cite{117, 118} at the boundary

$$\ddot{u}_\Gamma = -\nabla_{x_\Gamma} V(x) - \int_0^t \theta(t-\tau) v_\Gamma(\tau) + R(t)$$
where \( \mathbf{R}(t) \) is the noise due to the finite temperature, and \( \theta(t) \) is related to the DtN map. It satisfies the fluctuation-dissipation theorem

\[
\langle \mathbf{R}(t) \mathbf{R}(t')^T \rangle = k_b T \theta(t - t').
\]

The GLE acts as a heat bath for the region of interest. Generally, it is not practical to solve the GLE because of the expensive computational cost of the time-history kernel. Fortunately, we are able to approximate the DtN map by rational functions [119, 120]. The time-history kernel which is related to the DtN map can also be expressed as a rational function. Therefore, the approximation dynamics is expressed as

\[
\dot{\mathbf{u}}_\Gamma = B \mathbf{u}_\Gamma + A \mathbf{u}_I + \mathbf{\xi}(t)
\]

where the coefficients \( A \) and \( B \) are from rational functions, and \( \mathbf{\xi}(t) \) is the white noise which satisfies the fluctuation-dissipation theorem

\[
\langle \mathbf{\xi}(t) \mathbf{\xi}(t')^T \rangle = k_b T B^{-1} \delta(t - t')
\]

An interesting application of finite temperature ABCs is to study the rare event phenomena in molecular dynamics. The approximate dynamics can be implemented by combining with acceleration methods [121, 122, 123, 124] of MD.

### 5.3 Atomistic-to-continuum coupling for elastic wave interactions

The static atomistic/continuum coupling has raised a lot of interests from mechanical engineering [125, 126] and mathematics communities [127, 128]. In mechanical engineering, another interesting and practical problem is the dynamical coupling. The static coupling aims to eliminate the modeling inconsistency (’ghost’ force). A successful dynamics simulation of concurrent atomistic-continuum methods should not only absorb the phonons generated in atomistic regions, but also allow the elastic waves to pass across the interface. Only a few methods (bridging scale method (BSM) [129, 130, 131], bridging domain method (BDM) [132], and BSM with PML [133, 71]) for the dynamical coupling has been developed. Most of them are limited to the 1D case or a simple geometry in 2D.
Instead of treating phonon reflection issues separately, our concurrent atomistic-continuum method is based on the DtN map. The idea is driven by the fact that the difference between the rational functions used for ABCs and the exact DtN map coincides with a matrix which is responsible for the propagation of low-frequency waves. We approximate the difference by another rational function to get a better approximation of the DtN map. The approximate function is a sum of rational functions. One of the rational functions corresponds to the ABCs we proposed. The implementation of 1d atomic-chain is performed to verify the idea. The result of AtC coupling is compared with the result by full MD simulation. The phonons generated in the MD region is absorbed, while low-frequency waves are able to cross the interface.

![Graph](image)

**Figure 5.1.** One-dimensional simulation of the dynamical atomistic-to-continuum coupling. The Lennard-Jones potential is used in the MD region. The interactions are linearized in the continuum region. The continuum region is discretized for a more accurate approximation of the DtN map. $T = 0, 1 \times 10^4, 2 \times 10^5, 3 \times 10^5$ from top to bottom. The coupling method filters phonons and passing elastic waves in dynamics simulation of concurrent atomistic-continuum method.
Appendix A
Dynamic lattice Green’s function

The calculations of static lattice Green’s functions were discussed in previous works [86, 87]. The integral expression of the lattice Green’s function is numerically approximated by a quadrature formula over k-points. However, for the Green’s function at long-distance, a direct calculation has to rely on a fine quadrature due to the high oscillations. Fortunately, it has been shown that the far-field lattice Green’s function can be approximated by the continuum Green’s function. The detailed proofs were provided in [134, 135]. Another lattice Green’s function in a cylinder domain is discussed in [136]. Due to the finite domain, this lattice Green’s function can be written as a finite sum. In this section, we focus on the calculation of the dynamics Green’s function. An alternate form of the elastodynamic Green’s function in Fourier space is given by C. -Y. Wang [137]. The calculations of the dynamical lattice Green’s functions are discussed in [61, 95].

To explain the connection, let us consider the following 2D Fourier transform in terms of wave number $\xi$:

$$F(\xi) = \mathcal{F}[f(x)] = \int_{\mathbb{R}^2} f(x) e^{-i \xi \cdot x} dx,$$

$$f(x) = \mathcal{F}^{-1}[F(\xi)] = \frac{1}{4\pi^2} \int_{\mathbb{R}^2} F(\xi) e^{i \xi \cdot x} d\xi. \quad (A.1)$$

We are seeking the fundamental solution to the discrete problem,

$$\ddot{u}_i + \sum D_{ik} u_k = f_i. \quad (A.2)$$
The corresponding *continuum* problem is

\[
(c_{ijkl} \partial_j \partial_l - \rho \delta_{jl} \partial_l^2) u_k = f_i, \quad (A.3)
\]

where \(c_{ijkl}\) is the elastic constant. The elastic constant is connected to the force constant matrix, and the density \(\rho\) is related to the volume of unit cell. We may take the Laplace transforms of two problems,

\[
(\Gamma_{ik}(\xi) + \rho s^2 \delta_{ik}) U_k = F_i, \quad (A.4)
\]

and

\[
(D(\xi) + s^2 I) U_k = F_i. \quad (A.5)
\]

Here \(\Gamma_{ik}(\xi) = c_{ijkl} \xi_j \xi_l\), \(D(\xi) = \sum D_R e^{-i \xi \cdot R}\) is the dynamic matrix for the discrete problem. Let us consider the Taylor expansion of \(D(\xi)\),

\[
D(\xi) \approx \sum_R D_R (1 - \frac{1}{2} (\xi \cdot R)^2)
= (-\frac{1}{2} \sum_R D_{i-k} R_j R_l \xi_j \xi_l)_{ik}. \quad (A.6)
\]

The \(\xi^0\) and \(\xi^1\) terms disappear because of the inversion symmetry and the translation invariance. We see from direct comparison that the two problems are consistent with each other if

\[
c_{ijkl} = -\frac{1}{2v_0} \sum_R D_{i-k} R_j R_l, \quad (A.7)
\]

where \(v_0 = 1/\rho\) is the atomic unit volume.

Now, we show the connection between Green’s functions of two above problems. The continuum Green’s function is expressed as a Fourier integral,

\[
G(\mathbf{x}, s) = \frac{1}{4\pi^2} \int_{\mathbb{R}^2} \left[ \rho s^2 I + \Gamma(\xi) \right]^{-1} \cos(\xi \cdot \mathbf{x}) d\xi, \quad (A.8)
\]

and the lattice Green’s function is written as an integral over the first Brillouin zone,

\[
G(\mathbf{R}_j, s) = \frac{1}{|B|} \int_B \left[ s^2 I + D(\xi) \right]^{-1} \cos(\xi \cdot \mathbf{R}_j) d\xi. \quad (A.9)
\]

Unlike static Green’s functions, the matrices \(s^2 I + D(\xi)\) and \(\rho s^2 I + \Gamma(\xi)\) are positive.
definite. Hence, both Green’s functions are uniquely defined. Formally, the lattice Green’s function (A.9) converges to the continuum Green’s function (A.8) when \( x \) and \( R \) are large enough, since only small \( \xi \) will contribute to the integral (A.9) in this regime.

The continuum dynamic Green’s function can be further simplified for numerical evaluation. When we turn it to the polar coordinate, the continuum Green’s function can be written as

\[
G(x, s) = \frac{1}{4\pi^2} \int_0^{2\pi} \int_0^{\infty} \frac{\cos(rn \cdot x)}{r^2 \rho^2 \left( s^2 + r^2 \rho^2 c_i^2(n) \right)} r dr d\theta, \tag{A.10}
\]

where \( n = (\cos \theta, \sin \theta) \). With the eigenvalue decomposition, the above expression of the continuum Green’s function is written as

\[
G(x, s) = \frac{1}{4\pi^2} \sum_i \int_0^{\infty} \int_0^{2\pi} \frac{\cos(rn \cdot x)}{r^2 \rho^2 \left( s^2 + r^2 \rho^2 c_i^2(n) \right)} r dr d\theta P^i(n) d\theta. \tag{A.11}
\]

Here we wrote the \( i \)th eigenvalue of the matrix \( \Gamma(n) \) as \( \rho c_i^2 \). \( w_i(n) \) is the corresponding normalized eigenvector. \( \Gamma(n) = \sum_i \rho c_i^2 P^i(n) \) and \( P^i(n) = w_i(n) \otimes w_i(n) \). The inner integral can be simplified to

\[
\frac{1}{\rho c_i^2} \int_0^{\infty} \frac{\cos(a_i t)}{1 + t^2} dt = -\frac{1}{2 \rho c_i^2} \left[ e^{a_i \text{Ei}(-a_i)} + e^{-a_i \text{Ei}(a_i)} \right] \tag{A.12}
\]

with \( a_i = |n \cdot x|s/c_i \). Let us denote

\[
E(a_i) = \frac{e^{a_i \text{Ei}(-a_i)} + e^{-a_i \text{Ei}(a_i)}}{2}. \tag{A.13}
\]

\( e^{a_i \text{Ei}(-a_i)} \) and \( e^{-a_i \text{Ei}(a_i)} \) go to zero when \( ||x|| \) goes to infinity. \( E(a_i) \) can be evaluated numerically with small round-off errors.

It is interesting that this continuum Green’s function is also connected to Wang’s formula [137], where the dynamic Green’s function in the time domain is given by

\[
g(x, t) = \frac{H(t)}{8\pi^2} \sum_{|n|=1} P^i \left( \frac{1}{c_i t + |n \cdot x|} + \frac{1}{c_i t - |n \cdot x|} \right) dn. \tag{A.14}
\]

where \( H(t) \) is the Heaviside function. Even though our derivation differs from Wang’s, both formulas are the integrals over unit circle. In fact, we take the Laplace
transform of Eq. (A.14) when \(|\mathbf{n} \cdot \mathbf{x}| \neq 0\), and obtain

\[
G(\mathbf{x}, s) = \frac{-1}{4\pi^2} \int_0^{2\pi} \sum_i \frac{P_i}{\rho c_i^2} E(a_i) d\theta.
\]  

(A.15)

Note that there is a singularity when \(\mathbf{n} \cdot \mathbf{x} = 0\).

In the implementation, the singularity can be removed by adding another term inside the integral. More specifically,

\[
G(\mathbf{x}, s) = \frac{-1}{4\pi^2} \int_0^{2\pi} \sum_i \frac{P_i}{\rho c_i^2} (E(a_i) - \ln(|\mathbf{n} \cdot \mathbf{x}|)) d\theta - G(\mathbf{x}, 0),
\]  

(A.16)

where

\[
G(\mathbf{x}, 0) = \frac{-1}{4\pi^2} \int_0^{2\pi} \sum_i \frac{P_i}{\rho c_i^2} \ln(|\mathbf{n} \cdot \mathbf{x}|) d\theta = -\frac{1}{4\pi^2 \rho} \int_0^{2\pi} \Gamma^{-1}(\mathbf{n}) \ln(|\mathbf{n} \cdot \mathbf{x}|) d\theta,
\]  

(A.17)

is the static Green’s function for anisotropic solids. According to the well known Stroh’s formalism, The static Green’s function can be expressed explicitly as,

\[
G(\mathbf{x}, 0) = \frac{1}{\pi} \Im(\ln(z_1) \mathbf{a}_1 \otimes \mathbf{a}_1 + \ln(z_2) \mathbf{a}_2 \otimes \mathbf{a}_2) + C,
\]  

(A.18)

where \(z_1 = x_1 + \mu_1 x_2\) and \(z_2 = x_1 + \mu_2 x_2\). \(\mu_1\) and \(\mu_2\) are the two roots to the sextic equation of elasticity, whose imaginary parts are positive. \(\mathbf{a}_1\) and \(\mathbf{a}_2\) are the two corresponding eigenvalues, and \(C\) can be any constant matrices. Using this subtraction, the integral in (A.16) can be easily evaluated.
Appendix B
Discrete Green’s function for Schrödinger equation

B.1 Discrete Green’s function for 1D Schrödinger equation

Consider the one-dimensional time-dependent Schrödinger equation,

\[
i \frac{\partial \psi(t, x)}{\partial t} + \frac{\partial^2 \psi(t, x)}{\partial x^2} = V(x). \tag{B.1}\]

Take the Laplace-Fourier transform the fundamental solution is given by

\[
si G(s, \omega) - \omega^2 G(s, \omega) = 1, G(s, \omega) = \frac{1}{si - \omega^2}. \tag{B.2}\]

By the inverse Fourier transform, the fundamental solution in the Laplace domain

\[
G(s, x) = -\frac{1}{2\sqrt{-si}}e^{-\sqrt{-si}|x|}. \tag{B.3}\]

\(G(s, x)\) is the Green’s function of the following equation in the Laplace domain,

\[
si \Psi(s, x) + \frac{\partial^2 \Psi(s, x)}{\partial x^2} = V(x) \tag{B.4}\]
On the other hand, we discretize Eq. (B.4) by the five-point scheme,

\[ s_i \Psi_j(s) + \sum_{k=-2}^{2} \frac{c_k \Psi_{j+k}(s)}{h^2} = V(x) \]  

(B.5)

where \( c_{-2} = -1/12, c_{-1} = 4/3, c_0 = -5/2, c_1 = 4/3, \) and \( c_2 = -1/12. \) The characteristic equation of the above equation

\[-\frac{1}{12} u^4 + \frac{4}{3} u^3 + (ish^2 - \frac{5}{2}) u^2 + \frac{4}{3} u - \frac{1}{12} = 0 \]  

(B.6)

Four roots of the characteristic equation are

\[
\begin{align*}
  u_1 &= \sqrt{9 + 3sh^2i} - \sqrt{3sh^2i + 8\sqrt{9+3sh^2i} + 24 + 4}, \\
  u_2 &= -\sqrt{9 + 3sh^2i} + \sqrt{3sh^2i - 8\sqrt{9} + 3sh^2i + 24 + 4}, \\
  u_3 &= -\sqrt{9 + 3sh^2i} - \sqrt{3sh^2i - 8\sqrt{9} + 3sh^2i + 24 + 4}, \\
  u_4 &= \sqrt{9 + 3sh^2i} + \sqrt{3sh^2i + 8\sqrt{9} + 3sh^2i + 24 + 4},
\end{align*}
\]  

(B.7)

where \( \text{Re}(u_1) < 1 \) and \( \text{Re}(u_3) < 1 \) for a small \( s. \)

The analytical form of the discrete Green’s function is expressed as

\[ G_j(s) = c_1 u_1^{[j]} + c_2 u_3^{[j]} \]  

(B.8)

where

\[
\begin{align*}
  c_1 &= \frac{h^2}{2} \sqrt{\frac{3}{(3 + sh^2i)(24 + 3sh^2i + 8\sqrt{9} + 3sh^2i)}} \\
  c_2 &= \frac{h^2}{2} \sqrt{\frac{3}{(3 + sh^2i)(24 + 3sh^2i - 8\sqrt{9} + 3sh^2i)}}
\end{align*}
\]  

(B.9)

The coefficients \( c_1 \) and \( c_2 \) are determined by

\[ \sum_j D_{0j} u_j = 0 \]

and

\[ \sum_j D_{1j} u_j = 1. \]
The comparison between the continuum Green’s function and analytical discrete Green’s function is shown by the following figure.

![Figure B.1. 1D discrete Green’s function vs 1D continuum Green’s function, s=1, h=1](image)

### B.2 Discrete Green’s function for 3D Schrödinger equation

Consider the three-dimensional time-dependent Schrödinger equation,

\[ i\partial_t \phi(t, \mathbf{x}) + \Delta \phi(t, \mathbf{x}) = V(\mathbf{x}) \]  

\[ \text{(B.10)} \]

The fundamental solution in the Laplace space is given by

\[ G(\mathbf{x}) = -\frac{1}{4\pi r} e^{-\sqrt{s}r} \]  

\[ \text{(B.11)} \]

where \( r = \sqrt{x^2 + y^2 + z^2} \).

We discretize the operator by 9-point scheme in each direction.

\[ \frac{\partial^2 u}{\partial x^2} \approx \sum_{k=-4}^{4} \frac{c_k u_{j+k}}{h^2}. \]  

\[ \text{(B.12)} \]

where \( c_{-4} = -1/560, c_{-3} = 8/315, c_{-2} = -1/5, c_{-1} = 8/5, c_0 = 205/72, c_1 = 8/5, c_2 = -1/5, c_3 = 8/315, \) and \( c_4 = -1/560. \)
The discrete Green’s function can be expressed as

$$G_{nj} = \frac{1}{|B|} \int_B D(\xi)^{-1} e^{(R_n - R_j) \cdot \xi} d\xi.$$  \hspace{1cm} (B.13)

The approximate discrete Green’s function is obtained by the quadrature over $100 \times 100 \times 100$ k-points in Brillouin zone.

**Figure B.2.** 3D discrete Green’s function vs 3D continuum Green’s function, $h=0.01$, $s=10$
Appendix C
Derivation of the time-dependent
Hartree-Fock equation for the
nucleon system

Let us start with an $A$-nucleon system.

\[ i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi(t) \]  

(C.1)

where $\Psi(t)$ is the wave function of the system. $\hat{H}$ is the many-body Hamiltonian, which generally can be written as

\[ \hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} V_{ij}. \]  

(C.2)

The wave function $\Psi(r_1, r_2, \cdots, r_A)$ is in the so-called Fock space. The dimension of the wave function is $3A$. It is impractical to solve the many-body Schrödinger equation directly. The simplest approximation of the many-body system is Hartree-Fock approximation. According to the Hartree-Fock theory, the wave function takes the form of a Slater determinant

\[ \Psi(r_1, r_2, \cdots, r_A) = \frac{1}{\sqrt{A!}} \begin{vmatrix} \psi_1(r_1) & \cdots & \psi_A(r_A) \\ \vdots & \ddots & \vdots \\ \psi_1(r_A) & \cdots & \psi_A(r_A) \end{vmatrix} \]  

(C.3)
ψ_j, j = 1, ..., A are orthonormal three-dimensional wave functions. They are also called the nucleon orbitals. The Hartree-Fock model can be achieved from a variational principle which makes the "action"

\[ S[t_0, t_1; \Psi(t)] = \int_{t_0}^{t_1} dt \langle \Psi | i\hbar \frac{\partial}{\partial t} - \hat{H} | \Psi \rangle \]  

(C.4)

stationary with respect to the variation of these wave functions. The variation gives the coupled TDHF equations

\[ i\hbar \frac{\partial \psi_j}{\partial t} = H(t)\psi_j, \quad j = 1, \ldots, A \]  

(C.5)

where \( H \) is the time-dependent one-body HF Hamiltonian. This one-body HF hamiltonian can be explicitly written as

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{3}{4} t_0 \rho + \frac{3}{16} t_3 \rho^2 + W_y + W_C \]  

(C.6)

here \( t_0 \) and \( t_3 \) are the coefficients of the Skyrme interactions. All the terms of the one-body hamiltonian depend on the nucleon density, which is given by

\[ \rho(r) = \sum_{j=1}^{A} |\psi_j(r)|^2 \]  

(C.7)

Among five terms in the one-body Hamiltonian, the first term is from the kinetic energy. The following two terms are the expectation value of the zero-range density-dependent two-body effective interaction. \( W_y \) is the Yukawa potential

\[ W_y(r) = V_0 \int dr \frac{\exp\{-|r - r'|/a\}}{|r - r'|/a} \rho(r') \]  

(C.8)

and \( W_C \) is the Coulomb potential given by

\[ W_C(r) = e^2 \int dr' \frac{1}{|r - r'|} \rho_p(r') \]  

(C.9)

where \( V_0 \) and \( a \) are the coefficients of Yukawa interactions. \( \rho_p \) is the proton density. In practice, the Yukawa and Coulomb potentials are calculated by solving the
corresponding Poisson and Helmholtz problems.

\[
\begin{align*}
\nabla^2 W_c &= -2\pi e^2 \rho \\
(\nabla^2 - 1/a^2)W_Y &= -4\pi V_0 a \rho 
\end{align*}
\]  
(C.10)
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100


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