



**POLITECNICO
DI TORINO**

UNIVERSITÀ
DEGLI STUDI
DI TORINO



Doctoral Dissertation

Doctoral Program in Pure and Applied Mathematics (33rd cycle)

Time-Reversal Symmetry and Charge Transport in External Fields: Theoretical Features and Simulation Techniques

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Monday 10th May, 2021

Declaration

I hereby declare that, the contents and organization of this dissertation constitute my own original work and does not compromise in any way the rights of third parties, including those relating to the security of personal data.

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* This dissertation is presented in partial fulfillment of the requirements for the degree of *Philosophiæ Diploma* (PhD degree) in **Pure and Applied Mathematics**.

To my parents.

Acknowledgments

Abstract

Time-reversal symmetries of systems of charged classical particles are reconsidered in this thesis. It is noted how under fairly common assumptions on the interaction potential the inversion of momenta does not represent the only valid time-reversal symmetry for these systems. A first very important consequence of this statement is that the lacking of invariance of the equations of motion under the “standard” time-reversal transformation is not enough to define a system as non-time-reversal invariant. As a major example, systems under constant magnetic field are reconsidered in light of this property and it is shown how it is possible to recover standard relations of equilibrium and nonequilibrium statistical mechanics, such as Kubo, Onsager and fluctuation relations even in presence of magnetic fields, without the necessity of inverting it, as commonly done in the literature. Molecular dynamics simulations are used to corroborate these results.

A new algorithm for the numerical solution of the dynamics of adiabatically separated systems, called mass-zero constrained dynamics (MaZe), is also introduced. The method, based on constrained molecular dynamics, allows the simulations of systems where two or more sets of degrees of freedom are adiabatically separated. MaZe is shown to be symplectic and time reversible and to sample the correct probability distribution in physical space. The algorithm is tested on simulations of realistic systems in different areas of molecular dynamics, from the force-field based simulations of supercapacitor to first principles molecular dynamics of metals. In all cases, the method proved to be accurate and stable and more efficient than most of the state-of-the-art alternatives.

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List of Symbols

Matrices

$\mathbb{M}$	Metric matrix
$\mathbb{M}^{-1}$	Inverse of $\mathbb{M}$
$\mathbb{A}, \mathbb{B}, \mathbb{\Gamma}$	Sub-blocks of $\mathbb{M}$
$\mathbb{\Delta}, \mathbb{E}, \mathbb{Z}$	Sub-blocks of $\mathbb{M}^{-1}$
$\widetilde{\mathbb{A}}, \widetilde{\mathbb{B}}, \widetilde{\mathbb{\Gamma}}$	Sub-blocks of $\mathbb{M}$ evaluated for $\sigma = 0$ and $\dot{\sigma} = 0$
$\widetilde{\mathbb{\Delta}}, \widetilde{\mathbb{E}}, \widetilde{\mathbb{Z}}$	Sub-blocks of $\mathbb{M}^{-1}$ evaluated for $\sigma = 0$ and $\dot{\sigma} = 0$
$\mathbb{J}$	Symplectic matrix
$\mathbb{S}$	Shake matrix
$\mathbb{S}_{\mathbf{GG}}, \mathbb{S}_{\mathbf{GG}}^*$	Sub-blocks of $\mathbb{S}$ in complex space
$\mathbb{S}_{\mathbf{GG}}^*, (\mathbb{S}^*)_{\mathbf{GG}}^*$	Complex sub-blocks of $\mathbb{S}$ in complex space

Numerical Sets / Elements

$\mathbb{R}$	Real line
$\mathbb{R}^*$	Dual space of $\mathbb{R}$
$T\mathbb{R}_x$	Tangent space of $\mathbb{R}$ in the point x
$T\mathbb{R}$	Tangent bundle of $\mathbb{R}$
(a, b)	Subset of $\mathbb{R}$ between a, b

$(A)_\delta$	Subset of $\mathbb{R}$ of width δ around A
$\mathfrak{M}$	Classical phase space
Γ	Point in phase space
$\rho_0(\Gamma)$	Probability density in phase space at time $t = 0$ (usually equilibrium)
μ_0	Probability measure in phase space at time $t = 0$ (usually equilibrium)
Λ	Phase-space expansion rate
$\Omega^{(0)}$	Dissipation function
$\mathfrak{O}$	Space of classical observables
Φ, Ψ	Classical observables in phase-space
$\{\Psi\}_{(a,b)}$	Set of phase-space points such that Ψ takes values in (a,b)
X	Point in Nosé-Hoover extended dynamical phase space

Operators / Transformations

$\mathbb{1}$	Identity operator
$\mathcal{O}$	Generic operator on the space of classical observables
$\eta_\Psi^{\mathcal{O}}$	Signature of Ψ under the action of the operator $\mathcal{O}$
$\mathcal{M}$	Time-reversal transformation on points in phase space
$\mathcal{M}_s$	Standard time-reversal transformation, <i>i.e.</i> inversion of momenta
$\widetilde{\mathcal{M}}_s$	Standard time-reversal transformation when a magnetic field is present, <i>i.e.</i> inversion of momenta together with the inversion of the magnetic field
$\mathbf{M}$	Time-reversal operator on the space of classical observables
$\mathbf{M}^\dagger$	Adjoint of the operator $\mathbf{M}$

$\mathcal{U}_t$	Time-evolution transformation for a time t on points in phase space
U_t	Time-evolution operator for a time t on the space of classical observables
iL	Classical Liouvillian operator

Simulation parameters

N	Number of particles in the system
N_{el}	Number of electrons in the system
N_{I}	Number of ions
N_{D}	Direct space grid size
N_{R}	Reciprocal space grid size
$\mathcal{V}$	Volume of the system or of the simulation box
Ω	Volume of the cell
$\Omega_{\mathbf{G}}$	Volume prefactor: Ω if $\mathbf{G} = 0$, 2Ω if $\mathbf{G} > 0$
L	Lagrangian function
H	Classical Hamiltonian of the system
H_{NH}	Nosé-Hoover conserved quantity
K	Kinetic energy of the system
$K(\Gamma)$	Microscopic estimator of the kinetic energy
K^*	Thermostats target value of kinetic energy
V	Potential energy of the system
W	Extended potential energy
U	Interaction energy when supercapacitors are discussed
E_{K}	Kinetic energy of the electrons

E_{PS}	Pseudopotential energy
E_{ES}	Electrostatic energy of the valence electrons and the nuclei
E_{XC}	Exchange-correlation energy
E_{H}	Hartree energy
$E_{\text{K}}^{\text{TF}}, E_{\text{K}}^{\text{vW}}, E_{\text{K}}^{\text{P}}$	Thomas-Fermi, von Weizsäcker and Perrot kinetic energy functionals
χ^{vW}, χ^0	Von Weizsäcker and Lindhard screened susceptibilities
G	Degrees of freedom of the system
$\mathbf{r}$	The set of all coordinates of an N -particles system, <i>i.e.</i> $\mathbf{r} = \{\mathbf{r}_i\}_{i=1}^N$
$\mathbf{p}$	The set of all conjugate momenta of an N -particles system, <i>i.e.</i> $\mathbf{p} = \{\mathbf{p}_i\}_{i=1}^N$
$n(\mathbf{r})$	Electronic density in real space
$n^{\text{c}}(\mathbf{r})$	Electronic density of the atomic cores in real space
$n^{\text{t}}(\mathbf{r})$	Total electronic density in real space
$\varsigma(\mathbf{r})$	Modulus squared of the gradient of the density in real space
ϵ_{KXC}	Kinetic-Exchange-Correlation energy kernel per particle
ε_{KXC}	Kinetic-Exchange-Correlation energy kernel per unit volume
$v_{\text{KXC}}^n, v_{\text{KXC}}^{\varsigma}$	Kinetic-Exchange-Correlation energy gradient kernels per unit volume
$f_{\text{KXC}}^{nn}, f_{\text{KXC}}^{n\varsigma}, f_{\text{KXC}}^{\varsigma\varsigma}$	Kinetic-Exchange-Correlation energy hessian kernels per unit volume
$\Xi(\mathbf{r}), \Phi_{\alpha}(\mathbf{r}), \Psi_{\alpha\beta}(\mathbf{r})$	Contractions of different Hessians and gradients of KXC energy in real space
$\mathbf{G}$	Reciprocal space vectors

$\mathbf{G}_{\max}$	Maximum value of $\mathbf{G}$ given the cutoff
$S_I(\mathbf{G})$	Structure factor
$\xi(\mathbf{G})$	Homogeneous limit factor in plane-waves expansion
k_F	Fermi wavevector for a uniform system of N_{el} electrons
m_i	Mass of particle i
q_i	Charge of particle i
Q, χ, Z	Core, shell and ionic charge in the Shell Model
r_{ij}	Distance between two particles, <i>i.e.</i> $r_{ij} = \mathbf{r}_i - \mathbf{r}_j $
δt	Simulation timestep
α_{IK}	Isokinetic thermostat parameter
τ_{NH}	Characteristic time of Nosé-Hoover thermostat
$\mathbf{B}$	Magnetic field
$\mathbf{A}(\mathbf{r})$	Vector potential associated to magnetic field
ω_i	Cyclotron frequency of particle i
$\mathbf{E}$	Electric field
$\mathbf{J}$	Microscopic estimator of the electric current
v_d	Drift velocity
$\Omega_{\pm}$	Region of space occupied by positive/negative electrode
$\Psi_{\Omega_{\pm}}$	Electric potential associated to the region of positive/negative electrode
$\Psi_{\pm}$	Electric potential associated to the atomic sites of positive/negative electrode
Other Symbols	
$\delta^{\alpha\beta}, \delta^{ij}$	Kronecker delta

$\delta(x - x_0)$	1D Dirac's delta function centred on x_0
$\mathcal{Z}$	Partition function
$\mu_0(\{\Psi\}_{(a,b)})$	Probability to find Ψ in (a, b) at time $t = 0$
$\mathcal{C}_0(A, \delta)$	Correlation term in the derivation of the steady-state Ω -FR
$\mathbf{R}$	Physical variables in Mass-Zero constrained dynamics
s	Additional variables in Mass-Zero constrained dynamics
μ	Fictitious mass initially associated to the s variables
$\sigma(\mathbf{R}, s)$	Set of holonomic constraints enforced by MaZe dynamics
$\hat{s}$	Values of s that satisfy the adiabatic condition
λ	Lagrange multipliers before taking the limit of $\mu \rightarrow 0$
γ	Lagrange multipliers divided by μ in the $\mu \rightarrow 0$ limit
$f(s)$	Additional kinematic conditions enforced on s
$\mathbf{v}$	Lagrange multipliers treated as additional variables used to enforce additional kinematic conditions
κ	Homogeneity parameter for the homogeneous mass-zero limit
$J(\gamma; t)$	Constraint acceleration at time t as a function of γ
$\gamma^{(n)}$	Value of γ at iteration n
η	Over-relaxation parameter
$\tilde{n}^P, \mathbf{v}^P$	Provisional values of the additional variables
Operations	
$\Re$	Real part of a complex number
$\Im$	Imaginary part of a complex number
$ J $	Jacobian of a transformation

$\wedge$	Wedge product
$\tilde{f}(\mathbf{G})$	Fourier transform of the function $f(\mathbf{r})$
$\tilde{f}^*(\mathbf{G})$	Complex conjugate of the function $\tilde{f}(\mathbf{G})$
$\partial_{xy}^2 \mathcal{F}_{ij}^t$	Derivative of the function $\mathcal{F}$ with respect to variables x and y computed at indexes i and j at time t
$\langle \Phi, \Psi \rangle$	Scalar product between the observables Φ and Ψ
$\langle \Phi(0) \Psi(t) \rangle$	Time-correlation function of the observables Φ and Ψ
$\Psi_{t,t+\tau}(\Gamma)$	Time integral of the observable Ψ in the time interval $t, t + \tau$
$\overline{\Psi}_{t,t+\tau}(\Gamma)$	Time average of the observable Ψ in the time interval $t, t + \tau$
$\langle \Phi \rangle_{\{\overline{\Psi}_{0,\tau}\}_{(A)_\delta}}^{(0)}$	Conditional phase-space average of Φ with respect to the measure μ_0 , over the set of initial conditions Γ such that $\overline{\Psi}_{0,\tau} \in (A)_\delta$

Chapter 1

Introduction

The general goal of this thesis is to study transport in charged systems. The theoretical framework adopted is that of equilibrium and nonequilibrium classical statistical mechanics, complemented with molecular dynamics simulations. The work reported here contains two main original contributions. The first is the study of the time-reversal properties of charged systems, in particular when subjected to a constant and homogeneous external magnetic field, and the consequences of these properties on the analytical and numerical calculation of relevant observables, such as diffusion or conductivity. We begin by discussing in detail the conditions for which a classical system of particles is time-reversal invariant together with the necessary hypotheses for such a definition to hold. The study highlights that the concept of time-reversal invariance is indeed much wider than commonly thought. For a large class of systems which are central in classical and statistical mechanics, the definition of time-reversal invariance is, in fact, not limited to the invariance of the equations of motion of the system under the transformation that inverts the momenta together with the arrow of time, the so-called *standard* time-reversal symmetry. When particles interact through distance-dependent potentials, different transformations can be found satisfying the definition of time-reversal symmetry. The combination of the invariance of the equations of motion with respect to these transformations allows the theoretical prediction of the null value of some of the cross-component of transport tensors, such as diffusion or conductivity.

The presence of more than one time-reversal invariance also allows a reexamination of those systems in which time-reversal invariance was considered absent.

It is shown that the lack of symmetry with respect to the standard time-reversal transformation, is not a sufficient condition to define the system non-time-reversal invariant. In particular, it turns out that the statement “An external magnetic field breaks the time-reversal symmetry of the dynamics” is false for several physically interesting situations. It is shown in detail in this work that, for example, a system of charged particles interacting through Coulomb interactions in constant external magnetic field is still time-reversal invariant. This work will be focused on charge transport in external electromagnetic fields, but it is easy to show that other situations in which time-reversal invariance is considered absent are formally equivalent to this case. For example, it has already been noticed in the literature that systems in external magnetic field, systems in rotating frames and particles subject to shear are formally equivalent [1, 2].

These results indicate that a revision of many of the conclusions presented in the literature about non-time-reversal invariant systems is appropriate, at least when the magnetic field is constant. In facts, many key references in equilibrium and nonequilibrium statistical mechanics have described these systems in very broad terms, rising arguments and concerns which most of the times were not necessary for real-world applications. A celebrated example is certainly Casimir’s correction to Onsager reciprocal relations [3]. The same is true for Kubo’s relations between correlation functions [4, 5] and for transient and steady-state fluctuation relations [6].

All the above-mentioned results are derived mathematically in this work and are supported by numerical simulations. Since the early days of electronic computers, numerical simulations have been a major tool for filling the gap between experimentalists and theoreticians. Molecular dynamics simulations in particular have been regarded as the reference tool when dynamical properties were to be investigated. In the study of equilibrium and nonequilibrium charge transport, many successful examples can be found where the use of simulations have been central in the proof of theories and hypotheses (see, for example, Ref. [7] and references therein).

The accuracy of a molecular dynamics experiment for the study of a system of charged particles depends mainly on two things: The modelization of the interaction and the algorithm for the numerical solution of the equations of motion. The second main contribution presented in this thesis is the formal and algorithmic development of an original method to integrate the evolving equations for polarizable and electronic-structure representations of charged particles. These models are

commonly adopted in classical and first principles simulations of charge transport and both rely on introducing, in addition to the physical degrees of freedom, a set of auxiliary variables that mimic given properties of the quantum electronic density. Consistent with their representing electron's properties, these auxiliary variables are assumed to have much smaller mass than the physical degrees of freedom. In these systems, then, two separated scales of motion are present, due to the difference of the masses of the variables involved in the motion. The consequence of this separation is that the auxiliary variables (evolving much faster than the physical ones) are always found at the minimum of the interaction potential (*i.e.* have time to “equilibrate” at each step along the physical motion), and no exchange of energy happens between the two sets. For this reason the sets are said to be adiabatically separated. Available algorithms for solving the coupled evolution of adiabatically separated sets of variables are expensive or unstable.

In this thesis we propose to solve the dynamics of the adiabatically separated degrees of freedom with a completely original approach in which the minimum condition is treated as a holonomic constraint [8–10] and rigorous adiabatic separation is achieved by assigning a zero mass to the auxiliary degrees of freedom. This dynamical scheme is indicated as mass-zero constrained dynamics. This approach allows to derive dynamical equations for every degrees of freedom, meaning that all variables are governed by mechanical equations of motion. A very important consequence is that all the properties of the underlying mechanics are conserved by the numerical solution of the equations of motion, ensuring very good stability features of the overall dynamics. The dynamics is also proven to sample the correct probability density in phase space. The algorithm is versatile and can be applied to different areas of theoretical physics and computational chemistry, whenever adiabatic separation is present. In this thesis, we produced proof-of-principles calculations in which the algorithm is successfully applied to force-field-based and *ab initio* simulations. For the former category we chose the simulations of supercapacitors, particular technological devices complementary to batteries, whose study is of growing interest in the scientific community due to their very interesting technological applications [11–14]. For the latter, we chose the framework of orbital-free density functional theory, an approach for first-principles molecular dynamics which allows to solve the dynamics of condensed-matter systems in a linear-scaling fashion, representing in many technologically interesting and physically relevant situations

a valid and efficient alternative to the more expensive Kohn-Sham orbital-based density functional theory [15–18].

The thesis is organized as follows: In Chapter 2 the state of the art of time-reversal symmetry of classical mechanics is discussed. The most important theorems and relations based on the symmetries of the dynamics with respect to time reversal are presented. The chapter is also used to lay down the notation, highlighting the difference between time-reversal transformations and time-reversal operators (some of the discussions reported in this chapter have already been published in Ref. [19]). Based on the work already published in Ref. [20], Chapter 3 deals with systems of particles interacting through an isotropic potential. New time-reversal transformations are derived that allow to predict the cancellation of cross-coefficients of transport tensors such as diffusion and conductivity. The presence of constant external electromagnetic fields is also considered. It is shown how a magnetic and an electric field, under the above-mentioned hypotheses on the interaction potential, do not behave much differently from each other, as commonly believed. In fact, they break the same number of time-reversal symmetries, which are all restored once the field is inverted. Furthermore, systems subject to either fields are shown to maintain a certain number of valid time-reversal symmetries. Standard statistical mechanics relations known and widely used in the absence of external fields (magnetic in particular) are derived in the presence of magnetic (and electric) field, lifting prescriptions on systems long considered as exceptions. Finally it is shown how the simultaneous presence of electric and magnetic fields, while reducing the number of symmetry transformations available, still leaves the system time-reversal invariant. This result is used and developed in Chapter 4 where transient and steady-state fluctuation relations for dissipative systems in magnetic fields are examined and theoretically proven with two examples of deterministic thermostats, the isokinetic and the generalized Nosé-Hoover. The transient fluctuation relation is also demonstrated numerically on a realistic system of Sodium Chloride in presence of external magnetic field, yielding results in very good agreement with the theoretical predictions. Most of the content of this chapter is also published in Refs. [21, 22].

The discussion is then moved to the simulations of adiabatically separated systems. Based on the theoretical discussions in Refs. [23, 24], in Chapter 6 the mass-zero constrained dynamics is introduced in general and its properties are discussed together with methods for numerically solving the equations of motion stemming from it. The statistical mechanics of the dynamical system is discussed and it is

proven that the equations of motion sample the correct probability distribution in physical space. The algorithm is proven to be symplectic and time reversible. In Chapter 7 the method is applied to the simulation of realistic models of supercapacitors in force-field-based approach. The method is shown to be more robust and more efficient of some of the most used and widely spread iterative alternatives. Results and discussions in this chapter are based on the work published in Refs. [23, 25]. Finally in Chapter 8 the mass-zero constrained algorithm is applied, for the first time, to *ab initio* simulations, in the particular case of orbital-free density functional theory. The equations of the method are derived in complex space and it is shown how it is possible to obtain a method whose computational complexity scales linearly with the dimensionality of the system. Simulation results on a simple model of solid Sodium are presented from the published results in Ref. [24]. Again, the mass-zero constrained algorithm is compared with available alternatives, showing to be, once again, more robust and more efficient of other iterative methods used for electronic density minimizations. In Chapter 9 conclusions are drawn and possible future developments are discussed.

Part I

Time-Reversal Symmetries

Chapter 2

Setting the stage

2.1 Time-Reversal Symmetry in Classical Dynamical Systems

The concept of time-reversal symmetry has been part of fundamental physics and, more in particular, of classical mechanics since its very first formulation. Most of the differential equations describing physics laws are symmetric in time. Among these, the celebrated Newton's second law of motion is likely to be the one that influenced the most the common view on this particular subject. Considering a unidimensional system with given initial conditions, the differential equation $m\ddot{x} = F$, where $F = -\nabla V(x)$,¹ is clearly time-symmetric, in the sense that the transformation $t \rightarrow -t$ leaves the equation — and its solution due to the existence and uniqueness theorem — invariant. For example, let us consider the trajectory generated by the equation for a time interval $[0, \tau]$. Given the initial conditions $x(0)$, $\dot{x}(0)$, the solution for a time τ is given by a curve $x(t)$, $t \in [0, \tau]$. The inversion of time $t \rightarrow -t$ has no effect on the evolution equation, being it of second order in time. On the other hand, the final state will be transformed as $x(\tau) \rightarrow x(\tau)$ and $\dot{x}(\tau) \rightarrow -\dot{x}(\tau)$. Considering the transformed final state as the initial state of a new evolution regulated again by Newton's second law, the solution will be given by the same trajectory $x(t)$, $t \in [\tau, 0]$ now traced backwards — *i.e.* with inverted velocities — and the evolution after a time interval τ will leave the system in the position $x(0)$ with velocity $-\dot{x}(0)$. This is probably the main reason why in classical mechanics the transformation commonly associated with time reversal always inverts the sign of the velocities of the components of the system together with the arrow of time. This concept, described with an intuitive picture in the previous lines, will be central in the development of this work so let us formalise it in mathematical terms and introduce the notation that will be necessary for a quantitative treatment.

Let us consider a dynamical system

$$\dot{\Gamma} = G(\Gamma) \tag{2.1}$$

where $\Gamma \in \mathfrak{M}$ is a point in the phase space $\mathfrak{M}$ and $G : \mathfrak{M} \rightarrow \mathfrak{M}$ is a vector field. Given an initial time $t_0 \in \mathbb{R}$ and the initial conditions $\Gamma(t_0) \equiv \Gamma_0 \in \mathfrak{M}$ (in the following we set $t_0 = 0$), the state of the system at any time $t \in \mathbb{R}$ is the solution $\Gamma_t = \Gamma(t; \Gamma_0) \in \mathfrak{M}$

¹as it will become more clear in the following of this work, it is crucial for the truthfulness of this proposition that forces do not depend on velocities.

of the system of ODEs in Eq. (2.1). This solution can be formally expressed as the action of the nonlinear time-evolution transformation $\mathcal{U}_t : \mathfrak{M} \rightarrow \mathfrak{M}$ on the initial state: $\mathcal{U}_t \Gamma_0 = \Gamma_t$. $\mathcal{U}_0$ is the identity $\mathbb{1}$, and the transformation obeys the time-composition property $\mathcal{U}_{t_1+t_2} = \mathcal{U}_{t_1} \mathcal{U}_{t_2}$. From these properties (considering $\mathcal{U}_{t_1+t_2} = \mathcal{U}_{t_1} \mathcal{U}_{t_2}$ with $t = t_1 = -t_2$) it follows that $\mathcal{U}_t^{-1} = \mathcal{U}_{-t}$, *i.e.* the inverse transformation generates evolution backwards in time.

For a dynamical system in the form of (2.1) we have the following

Definition 2.1 (Time-reversal transformation). *A time-reversal transformation is an involution of phase space $\mathcal{M} : \mathfrak{M} \rightarrow \mathfrak{M}$ such that*

$$\mathcal{U}_{-t} \Gamma = \mathcal{M} \mathcal{U}_t \mathcal{M} \Gamma \quad \forall t \in \mathbb{R}, \forall \Gamma \in \mathfrak{M} \quad (2.2)$$

Note that, from the definition of an involution $\mathcal{M}^2 = \mathbb{1}$ and therefore $\mathcal{M} = \mathcal{M}^{-1}$. Together with the property of the inverse of the time-evolution transformation, this enables to write the relationship above as $\mathcal{M} \mathcal{U}_t = \mathcal{U}_{-t} \mathcal{M} = \mathcal{U}_t^{-1} \mathcal{M}$, or

$$\mathcal{M}^{-1} \mathcal{U}_t \mathcal{M} = \mathcal{U}_t^{-1} \quad (2.3)$$

which can be read as the statement that the transformation $\mathcal{M}$ generates the inverse evolution for any value of the parameter t .

The concept of time-reversal transformation on phase space induces an analogous notion on the space of observables. To illustrate this, let us consider the space $\mathfrak{O}$ of classical observables (smooth functions defined on the phase space), endowed with the scalar product

$$\langle \Phi, \Psi \rangle = \int d\Gamma \rho_0(\Gamma) \Phi(\Gamma) \Psi(\Gamma) \quad (2.4)$$

where $\mathfrak{O} \ni \Phi, \Psi : \mathfrak{M} \rightarrow \mathbb{R}$ are two classical observables,² and $\rho_0(\Gamma) : \mathfrak{M} \rightarrow (0, 1]$ is the equilibrium probability density of the system. For the moment we restrict the discussion to Hamiltonian systems where the Hamiltonian $H(\Gamma) \in \mathfrak{O}$ does not depend on time. In this situation, the evolution equation for an arbitrary observable Ψ , can be written as

$$\dot{\Psi} = iL\Psi \quad (2.5)$$

²We restrict, for simplicity, our discussion to real observables. The considerations in the following can however be generalized trivially to complex functions $\Phi, \Psi : \mathfrak{M} \rightarrow \mathbb{C}$ by adding a complex conjugate to Φ in the definition of the scalar product, Eq. (2.4).

where the Liouvillian operator $iL : \mathfrak{D} \rightarrow \mathfrak{D}$ is defined as the Poisson bracket of the observable with the Hamiltonian: $iL\Psi = \{\Psi, H\}$. The solution of Eq. (2.5) at time t can be expressed evaluating the function Ψ at the phase-space point of the system at time t , *i.e.* $\Psi_t(\Gamma) = \Psi(\Gamma_t) = \Psi(\mathcal{U}_t\Gamma)$. This can be expressed conveniently defining the time-evolution operator³ $U_t : \mathfrak{D} \rightarrow \mathfrak{D}$ on the space of observables as:

$$U_t\Psi(\Gamma) := \Psi(\mathcal{U}_t\Gamma) \quad (2.6)$$

To summarize, U_t is a linear operator which acts transforming the function Ψ in another function Ψ_t of phase space. $\mathcal{U}_t$, on the other hand, acts on phase-space points mapping the point Γ to the point Γ_t , its explicit form depends on the equations of motion and the transformation is, in general, nonlinear. Eq. (2.6) makes the connection between the two symbols explicit. Note that, in analogy with its counterpart on phase space, $U_{t=0}$ is the identity, it satisfies the time composition property for any t , and $U_t^{-1} = U_{-t}$.

In analogy with Eq. (2.3), we have the following

Definition 2.2 (Time-reversal operator). *A time-reversal operator in the space of the observables $M : \mathfrak{D} \rightarrow \mathfrak{D}$ is defined by*

$$M^\dagger U_t M = U_t^{-1} = U_{-t} \quad \forall t \in \mathbb{R} \quad (2.7)$$

where $M^\dagger$ is the adjoint of M with respect to the scalar product in Eq. (2.4).

Note that, since U_0 is the identity, Eq. (2.7) directly implies $M^\dagger M = \mathbb{1}$ or $M^\dagger = M^{-1}$. As for the time evolution, the action of M on observables is defined through a transformation of the underlying phase space. In particular,

$$M\Psi(\Gamma) := \Psi(\mathcal{M}\Gamma) \quad (2.8)$$

Eq. (2.8), together with Definition 2.2 also implies the following

Lemma 2.1. *The operator M is Hermitian.*

³In what follows we will keep this nomenclature, indicating by the word *operator* the linear operators acting on observables and by the word *transformation* the (in general) nonlinear operators acting on phase-space points.

Proof. Applying Definition 2.2 to the adjoint of the time-reversal operator $M^\dagger$ we obtain

$$M^\dagger \Psi(\Gamma) = M^{-1} \Psi(\Gamma) = \Psi(\mathcal{M}^{-1} \Gamma) = \Psi(\mathcal{M} \Gamma) = M \Psi(\Gamma) \quad (2.9)$$

where the relations $M^\dagger = M^{-1}$ and $\mathcal{M} = \mathcal{M}^{-1}$ (the latter derived by Definition 2.1) have been used. This proves the Lemma. $\square$

Summarizing, the operator M is Hermitian and $M^2 = \mathbb{1}$ so a time-reversal operator is an involution in the space of observables. Since the concepts of time-reversal transformation and time-reversal operator are intimately connected, in the following we will use the expression *time-reversal symmetry* to refer to the invariance of a system under the action of either mathematical entity.

2.1.1 Consequences of Time-Reversal Symmetry on Time-Correlation Functions

As observed by Kubo [4, 5], time-reversal symmetry of the dynamics implies interesting relationships for time-correlation functions of observables. To discuss them we need the following

Definition 2.3 (Signature). *The signature of an observable $\Psi \in \mathfrak{D}$ under the operator $O : \mathfrak{D} \rightarrow \mathfrak{D}$, when it exists, is the real eigenvalue of module one $\mathbb{R} \ni \eta_\Psi^O = \pm 1$ associated to the operator O whose eigenvector is Ψ , i.e.*

$$O\Psi = \eta_\Psi^O \Psi \quad (2.10)$$

Let us now consider two operators Φ and Ψ such that they have a well-defined signature under the time-reversal operator M , i.e.

$$M\Phi(\Gamma) = \Phi(\mathcal{M}\Gamma) = \eta_\Phi^M \Phi(\Gamma) \quad (2.11a)$$

$$M\Psi(\Gamma) = \Psi(\mathcal{M}\Gamma) = \eta_\Psi^M \Psi(\Gamma) \quad (2.11b)$$

Then we have the following theorem by Kubo:

Theorem 2.1 (Kubo). *The time-correlation function $\langle \Phi(0)\Psi(t) \rangle$ of the two observables Φ and Ψ defined by*

$$\langle \Phi(0)\Psi(t) \rangle = \int d\Gamma \rho_0(\Gamma) \Phi(\Gamma) [U_t \Psi(\Gamma)] \quad (2.12)$$

satisfies the relation

$$\langle \Phi(0)\Psi(t) \rangle = \eta_\Phi^M \eta_\Psi^M \langle \Phi(t)\Psi(0) \rangle \quad (2.13)$$

where η_Φ^M and η_Ψ^M are the signatures of Φ and Ψ under the time-reversal operator M , if the equilibrium distribution ρ_0 has even parity under the action of M .

Proof. Using Eq. (2.7), Eq. (2.12) can also be written as

$$\begin{aligned} \langle \Phi(0)\Psi(t) \rangle &= \int d\Gamma \rho_0(\Gamma) \Phi(\Gamma) [M U_{-t} M \Psi(\Gamma)] \\ &= \int d\Gamma [M \rho_0(\Gamma)] [M \Phi(\Gamma)] [U_{-t} M \Psi(\Gamma)] \end{aligned} \quad (2.14)$$

where, in the second equality, we have multiplied the expression from the left by $M^\dagger$ and we have used the fact that M is Hermitian (Lemma 2.1). Using Eqs. (2.11), the time-correlation function can be further simplified as

$$\langle \Phi(0)\Psi(t) \rangle = \eta_\Phi^M \eta_\Psi^M \int d\Gamma \rho_0(\Gamma) \Phi(\Gamma) [U_{-t} \Psi(\Gamma)] = \eta_\Phi^M \eta_\Psi^M \langle \Phi(0)\Psi(-t) \rangle \quad (2.15)$$

where we have also assumed the even parity of the equilibrium distribution under the time-reversal operator, *i.e.* $M\rho_0 = \rho_0$. Finally, from the time-translation invariance of the Hamiltonian, the result

$$\langle \Phi(0)\Psi(t) \rangle = \eta_\Phi^M \eta_\Psi^M \langle \Phi(0)\Psi(-t) \rangle = \eta_\Phi^M \eta_\Psi^M \langle \Phi(t)\Psi(0) \rangle \quad (2.16)$$

is obtained. □

2.2 The Fluctuation Relations

Statistical mechanics has traditionally investigated macroscopic systems at or near thermodynamic equilibrium, where fluctuations of observables are negligible com-

pared to their mean value. More recently, however, nano and biosciences have called attention to mesoscopic scales, in which fluctuations are considerably more relevant [26, 27] and the notion of thermodynamic equilibrium becomes problematic. Consequently, theories of fluctuations and of far-from-equilibrium response, have become a major chapter of contemporary statistical mechanics. In particular, a fruitful line of research on nonequilibrium fluctuations originated from Refs. [28–31], where a class of relations, now known as Fluctuation Relations (FRs), was introduced, relating the probabilities of opposite energy dissipations of driven system. Close to equilibrium, FRs reproduce the Green-Kubo and Onsager relations [32, 33]. Moreover, FRs are among the few exact results valid almost arbitrarily far from equilibrium and have therefore attracted considerable interest [34–37]. Related relations have, in fact, been determined, for observables such as work heat and energy dissipation, in diverse frameworks [2, 36–47], including dynamical systems and stochastic processes, classical and quantum systems, transient, steady-states and aging systems, for both global and local quantities, and for steady and time-dependent states. FRs have also been experimentally verified in gravitational wave detectors [27].

In what follows we summarize the derivation of two important examples of FRs, the transient and steady-state FRs for deterministic systems, stressing the role of time-reversal symmetry. General discussions about the FRs can be found, for example, in Refs. [34, 41, 48–50].

Consider again a point $\Gamma \in \mathfrak{M}$, evolving under the generic dynamical equation (2.1). For any observable $\Psi \in \mathfrak{O}$ and time interval $[t, t + \tau]$ with $\tau > 0$ we define

$$\Psi_{t,t+\tau}(\Gamma) := \int_t^{t+\tau} ds \Psi(\mathcal{U}_s \Gamma) \quad (2.17)$$

which is also an observable. The time average over a time τ of Ψ is given by $\bar{\Psi}_{t,t+\tau}(\Gamma) := \tau^{-1} \Psi_{t,t+\tau}(\Gamma)$. For any interval $(a, b) \subset \mathbb{R}$ we denote by $\{\Psi\}_{(a,b)}$ the set of phase-space points such that Ψ takes values in (a, b) :

$$\mathfrak{M} \supset \{\Psi\}_{(a,b)} := \{\Gamma \in \mathfrak{M} : \Psi(\Gamma) \in (a, b)\} \quad (2.18)$$

Let $\mathfrak{M}$ be endowed with a probability measure μ_0 of density ρ_0 , at time $t = 0$, so that $d\mu_0(\Gamma) = \rho_0(\Gamma)d\Gamma$ is the probability of an infinitesimal volume element around Γ . The probability of finding the value of Ψ in a given interval (a, b) at time $t = 0$ is

given by

$$\mu_0(\{\Psi\}_{(a,b)}) = \int_{\{\Psi\}_{(a,b)}} d\mu_0(\Gamma) = \int_{\{\Psi\}_{(a,b)}} \rho_0(\Gamma) d\Gamma$$

We now introduce the dissipation function, a quantity which will be central in the development of the theory:

Definition 2.4 (Dissipation function). *Assuming $\rho_0 \neq 0$ in $\mathfrak{M}$, the dissipation function $\Omega^{(0)}$ is*

$$\Omega^{(0)}(\Gamma) := -\nabla_{\Gamma} \ln \rho_0 \cdot G(\Gamma) - \Lambda(\Gamma) \quad (2.19)$$

where $\Lambda = \nabla \cdot \dot{\Gamma}$ is the phase-space expansion rate.

A corollary of Definition 2.4 is

Corollary 2.1. *Assuming ρ_0 even under the action of a time-reversal transformation $\mathcal{M}$, i.e. $\rho_0(\mathcal{M}\Gamma) = \rho_0(\Gamma)$, the dissipation function is odd under the same transformation: $\Omega^{(0)}(\mathcal{M}\Gamma) = -\Omega^{(0)}(\Gamma)$.*

Proof. The proof is trivial once it is realized that the parity of the dissipation function is determined by $\dot{\Gamma} = G(\Gamma)$ — odd under time reversal — in both terms of Eq. (2.19). $\square$

We have now introduced all the necessary notation to prove the FRs. The proof will make use of the two following lemmas:

Lemma 2.2. *The Jacobian $|J|$ of the phase-space coordinate transformation $\Gamma' = \mathcal{M}\mathcal{U}_t\Gamma$ is given by*

$$|J| = \left| \frac{d\Gamma'}{d\Gamma} \right| = \exp \left[\int_0^t ds \Lambda(\mathcal{U}_s\Gamma) \right] = \exp[\Lambda_{0,t}(\Gamma)] \quad (2.20)$$

Proof. The proof for $\mathcal{M}$ equal to the identity can be found in *e.g.* Ref. [51]. When $\mathcal{M}$ is a time-reversal transformation satisfying the Definition 2.1, the proof is not substantially modified as $\mathcal{M}$ preserves phase-space volumes, hence

$$\left| \frac{d\mathcal{M}\mathcal{U}_t\Gamma}{d\Gamma} \right| = \left| \frac{d\mathcal{U}_t\Gamma}{d\Gamma} \right| \quad (2.21)$$

$\square$

Lemma 2.3. *For any pair of intervals $(\pm A)_\delta = (\pm A - \delta, \pm A + \delta) \subset \mathbb{R}$ with $\delta > 0$ and for any τ , the following relation between subsets of $\mathfrak{M}$ holds*

$$\{\bar{\Psi}_{0,\tau}\}_{(-A)_\delta} = \mathcal{M}\mathcal{U}_\tau\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}$$

where Ψ is any observable that is odd under the chosen time reversal symmetry $\mathcal{M}$, i.e. $\Psi(\mathcal{M}\Gamma) = -\Psi(\Gamma)$.

Proof. Let us begin by establishing the action of $\mathcal{M}\mathcal{U}_\tau$ on a subset of phase space. We have that for any interval $(a, b) \subset \mathbb{R}$ (see Eq. (2.18))

$$\begin{aligned} \mathcal{M}\mathcal{U}_\tau\{\Psi\}_{(a,b)} &= \mathcal{M}\mathcal{U}_\tau\{\Gamma \in \mathfrak{M} : \Psi(\Gamma) \in (a, b)\} = \\ &= \{(\Gamma' = \mathcal{M}\mathcal{U}_\tau\Gamma) \in \mathfrak{M} : \Psi(\Gamma) \in (a, b)\} = \\ &= \{\Gamma' \in \mathfrak{M} : \Psi(\Gamma = (\mathcal{M}\mathcal{U}_\tau)^{-1}\Gamma') \in (a, b)\} = \\ &= \{\Gamma' \in \mathfrak{M} : \Psi(\mathcal{U}_{-\tau}\mathcal{M}\Gamma') \in (a, b)\} \end{aligned} \quad (2.22)$$

In the last equality, we used the properties $\mathcal{U}_\tau^{-1} = \mathcal{U}_{-\tau}$ and $\mathcal{M}^{-1} = \mathcal{M}$.

We will now show that, for any $\Gamma \in \{\bar{\Psi}_{0,\tau}\}_{(-A)_\delta}$, then $\mathcal{M}\mathcal{U}_\tau\Gamma \in \{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}$. Let us consider the expression for the $\bar{\Psi}_{0,\tau}(\mathcal{U}_{-\tau}\mathcal{M}\Gamma)$ that, based on Eqs. (2.17) and (2.22), is the value of the time-averaged observable on a point of the transformed phase-space subset. We have

$$\bar{\Psi}_{0,\tau}(\mathcal{U}_{-\tau}\mathcal{M}\Gamma) = \frac{1}{\tau} \int_0^\tau ds \Psi(\mathcal{U}_s \mathcal{U}_{-\tau} \mathcal{M}\Gamma) = \frac{1}{\tau} \int_0^\tau ds \Psi(\mathcal{U}_{s-\tau} \mathcal{M}\Gamma)$$

where, in the last equality, the time-composition property of the propagator was employed. Performing the change of variable $t = s - \tau$, the integral becomes

$$\bar{\Psi}_{0,\tau}(\mathcal{U}_{-\tau}\mathcal{M}\Gamma) = \frac{1}{\tau} \int_{-\tau}^0 dt \Psi(\mathcal{U}_t \mathcal{M}\Gamma) \quad (2.23)$$

Using the definition of time-reversal transformation, Eq. (2.2), we have that $\mathcal{U}_t \mathcal{M} = \mathcal{M}\mathcal{U}_{-t}$ and Eq. (2.23) can be written as

$$\bar{\Psi}_{0,\tau}(\mathcal{U}_{-\tau}\mathcal{M}\Gamma) = \frac{1}{\tau} \int_{-\tau}^0 dt \Psi(\mathcal{M}\mathcal{U}_{-t}\Gamma)$$

Another change of the integration variable $u = -t$ and the exchange of the integration extrema now yield

$$\overline{\Psi}_{0,\tau}(\mathcal{U}_{-\tau}\mathcal{M}\Gamma) = \frac{1}{\tau} \int_0^\tau du \Psi(\mathcal{M}\mathcal{U}_u\Gamma) = -\frac{1}{\tau} \int_0^\tau du \Psi(\mathcal{U}_u\Gamma) = -\overline{\Psi}_{0,\tau}(\Gamma) \quad (2.24)$$

In going from the second to the third equality, the odd parity of the observable was used, while the last equality recognizes the definition of Eq. (2.17). From Eq. (2.24), it immediately follows that if $\overline{\Psi}_{0,\tau}(\mathcal{U}_{-\tau}\mathcal{M}\Gamma) \in [-A - \delta, -A + \delta]$ then $\overline{\Psi}_{0,\tau}(\Gamma) \in [A - \delta, A + \delta]$ and *viceversa* for any phase-space point Γ , which completes the proof. $\square$

The proof shows that the lemma is a direct consequence of time-reversal invariance of the dynamical system under $\mathcal{M}$. We can now derive the following:

Theorem 2.2 (Transient Ω -FR). *For any pair of intervals $(\pm A)_\delta = (\pm A - \delta, \pm A + \delta) \subset \mathbb{R}$ with $\delta > 0$ and for any τ , there exists $\varepsilon(\delta, A, \tau)$ such that*

$$\frac{\mu_0(\{\overline{\Omega}^{(0)}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\overline{\Omega}^{(0)}_{0,\tau}\}_{(A)_\delta})} = \exp\left[-\tau[A + \varepsilon(\delta, A, \tau)]\right] \quad (2.25)$$

with $|\varepsilon(\delta, A, \tau)| \leq \delta$.

Proof. We start again by considering an observable Ψ which is odd under the time-reversal transformation $\mathcal{M}$, i.e. $\Psi(\mathcal{M}\Gamma) = -\Psi(\Gamma)$. We then consider the ratio between the probabilities to find the value of the time average for a time τ of the observable in a neighborhood of size δ of certain values A and $-A$. The ratio between the two probabilities can be written as

$$\frac{\mu_0(\{\overline{\Psi}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\overline{\Psi}_{0,\tau}\}_{(A)_\delta})} = \frac{\int_{\{\overline{\Psi}_{0,\tau}\}_{(-A)_\delta}} \rho_0(\Gamma) d\Gamma}{\int_{\{\overline{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\Gamma) d\Gamma} \quad (2.26)$$

We now make use of Lemma 2.3

$$\{\overline{\Psi}_{0,\tau}\}_{(-A)_\delta} = \mathcal{M}\mathcal{U}_\tau\{\overline{\Psi}_{0,\tau}\}_{(A)_\delta} \quad (2.27)$$

so that the numerator of the RHS of Eq. (2.26) can be recast in the form

$$\int_{\{\bar{\Psi}_{0,\tau}\}_{(-A)_\delta}} \rho_0(\Gamma) d\Gamma = \int_{\mathcal{M}\mathcal{U}_\tau\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\Gamma) d\Gamma \quad (2.28)$$

The application of the transformations $\mathcal{M}$ and $\mathcal{U}_\tau$ in the integration domain allows the recast of the ratio in Eq. (2.26) as

$$\frac{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta})} = \frac{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\mathcal{M}\mathcal{U}_\tau\Gamma) d(\mathcal{M}\mathcal{U}_\tau\Gamma)}{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\Gamma) d\Gamma} \quad (2.29)$$

It is now possible to recognize in the integral in the numerator of the RHS of Eq. (2.29) a change of variables of the kind $\Gamma' = \mathcal{M}\mathcal{U}_\tau\Gamma$. We can then apply Lemma 2.2 so that Eq. (2.26) takes the form

$$\frac{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta})} = \frac{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\mathcal{M}\mathcal{U}_\tau\Gamma) \exp[\Lambda_{0,\tau}(\Gamma)] d\Gamma}{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\Gamma) d\Gamma} \quad (2.30)$$

Assuming now that the equilibrium density ρ_0 is even under the time-reversal transformation $\mathcal{M}$, *i.e.* $\rho_0(\mathcal{M}\Gamma) = \rho_0(\Gamma)$, the final expression of the ratio of the probabilities is given by

$$\frac{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta})} = \frac{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\mathcal{U}_\tau\Gamma) \exp[\Lambda_{0,\tau}(\Gamma)] d\Gamma}{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\Gamma) d\Gamma} \quad (2.31)$$

Computing the time integral of $\Omega^{(0)}$ from Definition 2.4 in the interval $0, \tau$

$$\Omega_{0,\tau}^{(0)}(\Gamma) = \ln \left[\frac{\rho_0(\Gamma)}{\rho_0(\mathcal{U}_\tau\Gamma)} \right] - \Lambda_{0,\tau}(\Gamma) \quad (2.32)$$

we see that, multiplying and dividing the integrand in the numerator by $\rho_0(\Gamma)$, Eq. (2.26) can be recast in the form

$$\frac{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta})} = \frac{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\Gamma) \exp[-\Omega_{0,\tau}^{(0)}] d\Gamma}{\int_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}} \rho_0(\Gamma) d\Gamma} := \left\langle \exp[-\Omega_{0,\tau}^{(0)}] \right\rangle_{\{\bar{\Psi}_{0,\tau}\}_{(A)_\delta}}^{(0)} \quad (2.33)$$

where the last equality defines the conditional phase-space average of $\exp[-\Omega_{0,\tau}^{(0)}]$ with respect to the measure μ_0 , over the set of initial conditions Γ such that $\bar{\Psi}_{0,\tau} \in$

$(A)_\delta$. Recalling that the width of the interval $(+A)_\delta$ is 2δ , the average $\overline{\Psi}_{0,\tau}$ is almost constant in the set $\{\overline{\Psi}_{0,\tau}\}_{(+A)_\delta}$ if δ is small. In the case in which we identify Ψ with $\Omega^{(0)}$ we obtain the transient Ω -FR

$$\frac{\mu_0(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta})}{\mu_0(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta})} = \left\langle \exp[-\Omega_{0,\tau}^{(0)}] \right\rangle_{\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta}}^{(0)} = \exp[-[A + \varepsilon(\delta, A, \tau)]\tau] \quad (2.34)$$

where the correction term ε is not larger than δ because $\overline{\Omega^{(0)}}_{0,\tau}$ is bound to take values in $(+A)_\delta = (A - \delta, A + \delta)$. $\square$

From the proof, it appears clear that time-reversal invariance of the dynamics and of ρ_0 are the only requirements for the derivation of the transient Ω -FR: the specific form of $\mathcal{M}$ is irrelevant, as long as Eq. (2.2) is satisfied.

Introducing the evolved probability measure μ_t , defined by the conservation of probability $\mu_t(E) = \mu_0(\mathcal{U}_{-t}E)$, $E \subset \mathfrak{M}$, and taking the $t \rightarrow \infty$ limit followed by the $\tau \rightarrow \infty$ limit of Eq. (2.25), one may write [34, 40]:

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \lim_{t \rightarrow \infty} \ln \frac{\mu_t(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta})}{\mu_t(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta})} = -[A + \varepsilon(A, \delta) - \mathcal{C}_0(A, \delta)], \quad (2.35)$$

where

$$\mathcal{C}_0(A, \delta) := \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \lim_{t \rightarrow \infty} \left\langle e^{-\Omega_{0,t}^{(0)} - \Omega_{t+\tau, 2t+\tau}^{(0)}} \right\rangle_{\{\overline{\Omega^{(0)}}_{t,t+\tau}\}_{(A)_\delta}}^{(0)} \quad (2.36)$$

with $\langle \cdot \rangle_{\{\overline{\Omega^{(0)}}_{t,t+\tau}\}_{(A)_\delta}}^{(0)}$ denoting, once again, an average with respect to μ_0 , under the condition $\overline{\Omega^{(0)}}_{t,t+\tau}(\Gamma) \in (A)_\delta$. Under the additional hypothesis that $\mathcal{C}_0(A, \delta)$ vanishes, Eq. (2.35) defines

Theorem 2.3 (Steady-State Ω -FR). *For any pair of intervals $(\pm A)_\delta = (\pm A - \delta, \pm A + \delta) \subset \mathbb{R}$ with $\delta > 0$ and for any large τ , there exists $\varepsilon(\delta, A, \tau)$ such that*

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \ln \frac{\mu_\infty(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(-A)_\delta})}{\mu_\infty(\{\overline{\Omega^{(0)}}_{0,\tau}\}_{(A)_\delta})} = -[A + \varepsilon(A, \delta)] \quad (2.37)$$

where $\mu_\infty(E) = \lim_{t \rightarrow \infty} \mu_t(E)$ and $|\varepsilon(A, \delta)| \leq \delta$.

That correlations behave in such a way that $\mathcal{C}_0(A, \delta)$ vanishes is a nontrivial requirement. There are indeed systems that remain indefinitely trapped and do not reach a steady state. Eq. (2.35) and Theorem 2.3 are left without proof, but an extensive treatment and derivation of these two results can be found, *e.g.* in Refs. [40, 48, 50]

2.3 Current Paradigm when Magnetic Fields are Present

It is well known that the evolution equations of charged systems subject to an external magnetic field are not invariant under the standard time-reversal transformation defined *via* inversion of the momenta

$$\mathcal{M}_s(\mathbf{r}, \mathbf{p}) = (\mathbf{r}, -\mathbf{p}) \quad (2.38)$$

combined with the change $t \rightarrow -t$. The reason are the Lorentz forces, which are velocity dependent and that make the RHS term of Newton's second law not invariant under the standard time-reversal transformation. This fact originated the idea that these systems require special treatment when discussing properties based on time reversibility. The usual approach extends the system to include the electric currents generating the magnetic field. Currents, and hence the magnetic field, are reversed under time reversal and so the symmetry is restored, in the nonextended problem, by considering two systems subject to opposite external magnetic fields. In conclusion the common view on system subject to external magnetic field is that they are time-reversal invariant under the transformation

$$\widetilde{\mathcal{M}}_s(\mathbf{r}, \mathbf{p}, \mathbf{B}) = (\mathbf{r}, -\mathbf{p}, -\mathbf{B}) \quad (2.39)$$

This point of view is widespread in the literature on the subject. For example, it led Casimir [3] to modify the Onsager reciprocal relations, so that, unlike the original ones, they do not concern the properties of a given physical system, but relate cross-transport coefficients of pairs of systems with identical interparticle interactions but under magnetic fields of opposite signs, without specifying what such coefficients should actually be for the system of interest.

Since in presence of a magnetic field the transformation $\mathcal{M}_s$ does not correspond to a temporal symmetry anymore, numerous authors have viewed the Casimir modification of Onsager relations as necessary. For instance:

- in Ref. [3], Casimir states: “*If a magnetic field is present, the Eqs. (8), (10), and (12) are no longer valid, but **must** be replaced by [...]*”;
- “*This equation of symmetry will hold for an arbitrary fourpole, **as long as no magnetic field is present***” [3];
- more explicitly, Landau and Lifshitz [52], writing about the derivation of the Onsager Reciprocal Relations, state: “*proof depends on the symmetry of the equations of motion with respect to time, and the formulation of this symmetry is somewhat altered for fluctuations in a uniformly rotating body and for bodies in an external magnetic field: in these cases the symmetry under time reversal holds **only** if the sign of the angular velocity of rotation $\mathbf{D}$ or of the magnetic field $\mathbf{H}$ is simultaneously changed*”;
- Kubo, in his fundamental paper on linear response [5] further explains that: “*The time-reversal operation **means** the transformation*

$$t \rightarrow -t, p \rightarrow -p, \boldsymbol{\sigma} \rightarrow -\boldsymbol{\sigma}, \mathbf{B} \rightarrow -\mathbf{B}$$

...”. Therefore, no other notion of time reversibility should be considered, within Kubo’s vast framework;

- and finally De Groot and Mazur [53] explain why: “*particles only retrace former paths if both momenta and the magnetic field are reversed. Similar situation arises for Coriolis forces where angular velocity **must** be reversed*”.

As recently pointed out [1, 19, 20], this approach yields correct relations in presence of magnetic fields, drastically departing, however, from the meaning, predictive power and experimental relevance of Onsager theory, which refers to material properties of a given physical system. Interestingly, neither experiments nor simulations of systems in a magnetic field have revealed any violation of the Onsager Reciprocal Relations [54, 55].

This “state-of-the-art” interpretation is therefore unsatisfactory for two main reasons. The first one is conceptual: the introduction of a second system, while phys-

ically correct, blurs the distinction between the system and its external environment. Indeed, in the evolution equations of the system, the magnetic field appears as an external agent whose physical origin (*e.g.* moving charges originating a current) is not associated to active degrees of freedom in the dynamical system. Its inversion then implicitly implies an extension of the system to include the sources of the magnetic field, applying $\widetilde{\mathcal{M}}_s$ to the extended system, and then forgetting again about the additional degrees of freedom. The second reason is practical: this commonly adopted approach reduces the predictive power of the statistical relationships mentioned above. For example, within linear response theory, null values of transport coefficients in experiments concerning a single system in a given magnetic field cannot be predicted based on symmetry properties of the time-correlation functions. Similarly, in the context of nonlinear response, null cumulants of the dissipation cannot be identified *via* symmetry.

As a matter of fact, while the time-reversal symmetry expressed by $\mathcal{M}_s$ allows particles to “retrace former paths”, this is but sufficient for the existence of initial conditions in $\mathfrak{M}$ leading to opposite values of particular classical observables (*e.g.* currents) under the forward evolution. As observed in [19, 20, 56–59] and discussed in the next sections, such a strong condition as time-reversal invariance under $\mathcal{M}_s$, is not necessary for the validity of macroscopic properties such as the Kubo, Onsager or the fluctuation relations. For instance, concerning linear response, Kreuzer [60] apparently maintains the view expressed by Casimir and others reported above, but states something quite different:

microscopic reversibility (detailed balance) is a consequence of the invariance of Hamilton equations of motion under time reversal.

In other words, while attributing microscopic reversibility to time-reversal invariance in phase space, Kreuzer identifies it with detailed balance, *i.e.* a statistical rather than a microscopic temporal symmetry [60].

The fact is that macroscopic properties arise from sums and averages of many microscopic quantities, and may thus be obtained from different microscopic mechanisms: many details of the microscopic dynamics are irrelevant [61].

In the next chapter it will be shown how to overcome these limitations in the current state-of-the-art in the interpretation of the time-reversal invariance in pres-

ence of external fields, with particular reference to charged systems in constant electromagnetic fields.

Chapter 3

New Symmetries: Isotropic Systems and Constant External Fields

The most common statement of the time-reversal symmetry of classical dynamics is that the dynamical system determining the evolution is invariant under the combined action of a transformation of the phase-space variables and the inversion of time. As discussed in Section 2.1, the time-reversal symmetry induces interesting properties on the time-correlation of observables, which can be related in turn, *via* linear response theory, to predictions on measurable quantities such as spectra or transport coefficients. For particle systems, these results are usually based on a single, specific, phase-space transformation that changes the sign of the momenta of the system while leaving the coordinate untouched.¹ This “standard” time-reversal transformation has been defined in Eq. (2.38) of Chapter 2. Indeed, the literature often states that classical dynamical systems that are not invariant under this transformation require special treatment. The most notable case is that of systems subject to an external magnetic field as discussed in Section 2.3 together with other examples of the same kind.

Recently [1, 19, 20], it was shown that, under rather common assumptions for the interaction potential, these generalizations are in fact unnecessary for magnetic fields constant in space and time. This case has considerable interest because it is often employed in theoretical and experimental works [64, 65]. Furthermore, the corresponding dynamical system can be easily transformed into that of other interesting problems, such as systems in a uniformly rotating frame (substituting the magnetic field intensity with the modulus of the angular velocity) or subject to constant shear (where the viscosity plays the role of the magnetic field). The key observation to describe these systems on the same footings as those governed by standard Hamiltonians is that alternative transformations of the phase space exist that, upon inversion of time, leave their dynamics invariant. These transformations satisfy all the formal properties associated to time-reversal symmetry and enable to derive, following the same proofs available for the standard case, all the results mentioned above. Moreover, for a given orientation of the magnetic field, more than one transformation can be defined and, as discussed more in general in the following, this allows one to predict analytically that some elements of the diffusion and conductivity tensors must be zero. These elements are difficult to measure in experiments and simulations, so the theory has practical use.

¹Other time-reversal transformations are sometimes discussed in the general framework of dynamical and stochastic systems [62, 63], but the consequences of their existence are never discussed for many-particles, deterministic systems.

In this chapter, we develop further these ideas by identifying new sets of time-reversal symmetries for systems of physical interest and showing how their combined use enables predictions on time-correlation functions. The work is organized as follows. In Sections 3.1 and following we consider different interaction potentials with given, physically common and relevant invariance properties and show new time-reversal symmetries that hold for them. Notably, for point particles interacting *via* distance dependent potentials, eight time-reversal transformations exist that leave the system invariant and we demonstrate that this implies, for example, zero values of all off-diagonal components of some transport tensors. We then consider the case of the constant external magnetic field to show that four time-reversal transformations are preserved in this dynamical system. We also show that a classical dynamical system subject to a constant electric field also preserves four time-reversal symmetries. Finally, we consider the simultaneous action of constant external electric and magnetic fields in three relevant geometries and describe the impact of these set ups on the symmetries. Whenever appropriate, we connect the time symmetries with properties of the transport coefficients.

3.1 Time-Reversal Symmetries for Isotropic Interactions

In this section, we specialize the discussion to a system of N point particles not subject to external potentials. The state of this dynamical system is identified by a point $\Gamma = (\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)$ in the $6N$ -dimensional phase space of coordinates, $\mathbf{r} = \{\mathbf{r}_i\}_{i=1}^N$, and conjugate momenta, $\mathbf{p} = \{\mathbf{p}_i\}_{i=1}^N$. We consider first a system described by a Hamiltonian of standard form $H(\Gamma) = K(\mathbf{p}) + V(\mathbf{r})$, in which the kinetic energy K is a function of the momenta alone, and the potential V is a completely general function only of the coordinates. The dynamics is determined by Hamilton's system of linear differential equations

$$\begin{aligned} \frac{dx_i}{dt} &= \frac{p_i^x}{m_i} & \frac{dp_i^x}{dt} &= -\frac{\partial V(\mathbf{r})}{\partial x_i} \\ \frac{dy_i}{dt} &= \frac{p_i^y}{m_i} & \frac{dp_i^y}{dt} &= -\frac{\partial V(\mathbf{r})}{\partial y_i} \\ \frac{dz_i}{dt} &= \frac{p_i^z}{m_i} & \frac{dp_i^z}{dt} &= -\frac{\partial V(\mathbf{r})}{\partial z_i} \end{aligned} \quad (3.1)$$

where $i = 1, \dots, N$, $\mathbf{r}_i = x_i, y_i, z_i$, $\mathbf{p}_i = p_i^x, p_i^y, p_i^z$ are the Cartesian components of the coordinates and momenta, respectively and m_i is the mass of particle i .

To discuss, in particular, noninteracting particles, it proves notationally convenient to introduce “single-particle” time-reversal transformations, *i.e.* transformations acting on the phase-space coordinates of particle i , and define the total transformation of the system as a block diagonal transformation with the single-particle transformation acting on particle i on the i -th block. We adopt the symbol $\mathcal{M}_i^{(\alpha)}$ to indicate transformation α acting on particle i , and $\mathcal{M}^{(\alpha)}$ to indicate the transformation on the whole phase-space point Γ .

3.1.1 Ideal Gas and Separable Hamiltonian

The simplest possible Hamiltonian of the kind considered in this section describes a system of N noninteracting particles of mass m_i subject to no external fields:

$$H(\Gamma) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} \quad (3.2)$$

The corresponding dynamical system is given by Eqs. (3.1) with $V(\mathbf{r}) = 0$.

Proposition 3.1. *For noninteracting systems of particles, every operator transforming a coordinate and its associated conjugate momentum with opposite parity does not change the evolution equations upon inversion of time.*

Proof. Proposition 3.1 is proven by direct inspection of the equations of motion (3.1) with $V(\mathbf{r}) = 0$. □

More explicitly, the following single-particle transformations

$$\mathcal{M}_i^{(1)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (x_i, y_i, z_i, -p_i^x, -p_i^y, -p_i^z) \quad (3.3a)$$

$$\mathcal{M}_i^{(2)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (-x_i, -y_i, -z_i, p_i^x, p_i^y, p_i^z) \quad (3.3b)$$

$$\mathcal{M}_i^{(3)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (-x_i, y_i, z_i, p_i^x, -p_i^y, -p_i^z) \quad (3.3c)$$

$$\mathcal{M}_i^{(4)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (x_i, -y_i, z_i, -p_i^x, p_i^y, -p_i^z) \quad (3.3d)$$

$$\mathcal{M}_i^{(5)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (x_i, y_i, -z_i, -p_i^x, -p_i^y, p_i^z) \quad (3.3e)$$

$$\mathcal{M}_i^{(6)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (x_i, -y_i, -z_i, -p_i^x, p_i^y, p_i^z) \quad (3.3f)$$

$$\mathcal{M}_i^{(7)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (-x_i, y_i, -z_i, p_i^x, -p_i^y, p_i^z) \quad (3.3g)$$

$$\mathcal{M}_i^{(8)}(x_i, y_i, z_i, p_i^x, p_i^y, p_i^z) = (-x_i, -y_i, z_i, p_i^x, p_i^y, -p_i^z) \quad (3.3h)$$

leave the dynamical system invariant in combination with the inversion of the sign of time. A pictorial representation of the effect of the transformations $\mathcal{M}^{(1)}$ and $\mathcal{M}^{(2)}$ on a point in a 2-dimensional phase space is represented in Figure 3.1. It is readily

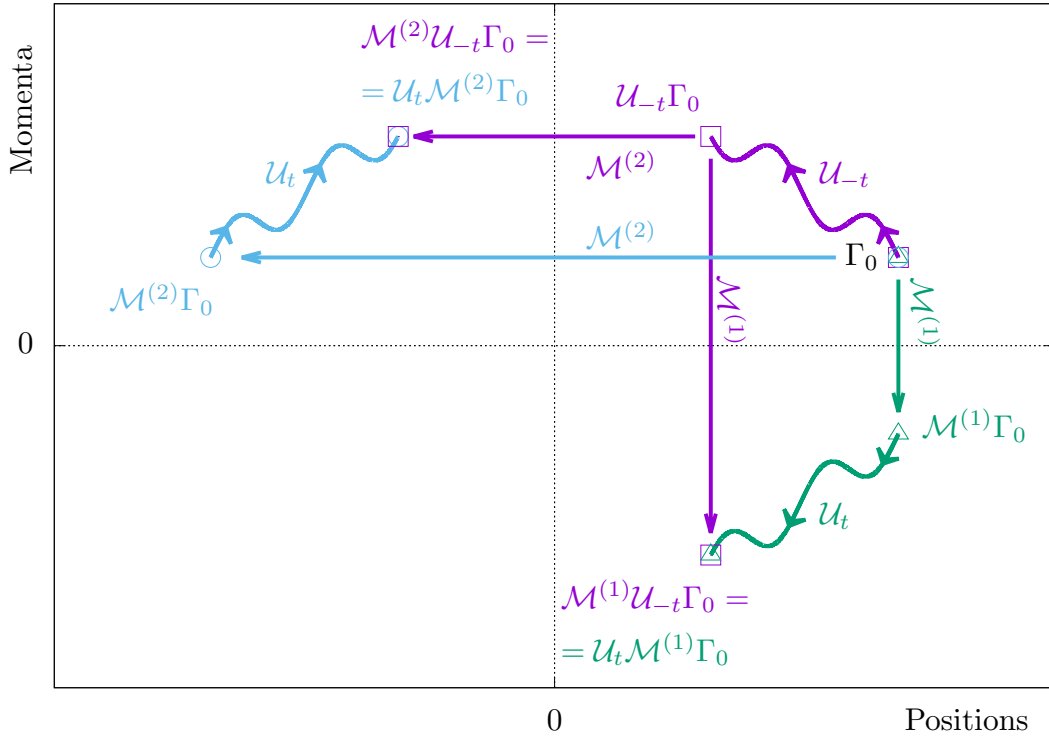


Fig. 3.1 A pictorial representation of the effect of two time-reversal symmetries (defined by the analogous of Eqs. (3.3a) and (3.3b)) on the point Γ_0 (in black) in a 2-dimensional phase space.

seen that $\mathcal{M}_i^{(1)} = \mathcal{M}_s$ is the standard time-reversal transformation for particle i .

Remark 3.1. *In general, for a d -dimensional system, 2^d time-reversal transformations per particle exist. Thanks to the separability of the Hamiltonian, any combination of N of these operations is a valid global time-reversal symmetry for a noninteracting system of particles subject to no external fields. Thus, a three-dimensional ideal gas admits 8^N time-reversal transformations.*

As first pointed out in [19], the simultaneous existence of more than one time-reversal symmetry can be used to determine null values of time-correlation functions of observables. To illustrate this, let us begin by specifying the eight global symmetries on phase space obtained by combinations of the equations above in which all single particles are subject to the same transformation. Thus, $\mathcal{M}^{(\kappa)}$ ($\kappa = 1, \dots, 8$) is the block diagonal transformation with $\mathcal{M}_i^{(\kappa)}$ on the i -th block. These transformations induce eight time-reversal operators on the space of classical observables via the definition, see Eq. (2.8), $M^{(\kappa)}\Psi(\Gamma) := \Psi(\mathcal{M}^{(\kappa)}\Gamma)$. Substituting $\mathcal{M}^{(\kappa)}$ and $M^{(\kappa)}$ to the standard time-reversal operators in the definitions in Eqs. (2.11) and retracing the steps from Eq. (2.12) to Eq. (2.16) with these symmetries, it can be easily shown that the signature property of the time-correlation functions holds for them. Thus, indicating with $\eta_{\Psi}^{M^{(\kappa)}}$ the signature of observable Ψ under $M^{(\kappa)}$ (with an analogous definition for other observables), we have

$$\langle \Phi(0)\Psi(t) \rangle = \eta_{\Phi}^{M^{(\kappa)}} \eta_{\Psi}^{M^{(\kappa)}} \langle \Phi(t)\Psi(0) \rangle \quad (3.4)$$

The relationship above expresses eight conditions that must be simultaneously fulfilled by the time-correlation function of the two observables. From this, we have the following

Theorem 3.1. *The time correlations of observables for which the product of the signatures has a different sign under two different time-reversal operators must be zero at all times.*

Proof. Let us consider two observables, $\Psi(\Gamma)$ and $\Phi(\Gamma)$ with signatures $\eta_{\Psi, \Phi}^{M^{(\kappa_1)}}$ and $\eta_{\Psi, \Phi}^{M^{(\kappa_2)}}$ under two different time-reversal transformations $M^{(\kappa_1)}$ and $M^{(\kappa_2)}$ ($\kappa_1 \neq \kappa_2$), respectively. Then, by comparing

$$\begin{aligned} \langle \Psi(t)\Phi(0) \rangle &= \eta_{\Psi}^{M^{(\kappa_1)}} \eta_{\Phi}^{M^{(\kappa_1)}} \langle \Psi(0)\Phi(t) \rangle \\ \langle \Psi(t)\Phi(0) \rangle &= \eta_{\Psi}^{M^{(\kappa_2)}} \eta_{\Phi}^{M^{(\kappa_2)}} \langle \Psi(0)\Phi(t) \rangle \end{aligned} \quad (3.5)$$

the following cases can present themselves: First, the product of the signatures in the first and second line has different sign. In this case, since the relationships above imply that the function has to be always equal to its opposite, the correlation function must be zero for all times. Second, the sign of the product of the signatures in the two lines is the same and positive. In this case, only the less stringent statement that the function must be even in time can be made. Third, the sign of the product of the signatures in the two lines is different. In this case, only the less stringent statement that the function must be odd in time can be made. $\square$

Example 3.1. *As an example, consider the time-correlation of the functions $\Psi(\Gamma) \equiv v_i^\alpha(\Gamma) = p_i^\alpha/m_i$ where $i = 1, \dots, N$ and $\alpha \in \{x, y, z\}$. Using the symmetries $M^{(1)}$ and $M^{(3)}$, for example, we have*

$$\langle v_i^x(0)v_i^y(t) \rangle = \eta_{v_i^x}^{M^{(1)}} \eta_{v_i^y}^{M^{(1)}} \langle v_i^y(0)v_i^x(t) \rangle = \langle v_i^y(0)v_i^x(t) \rangle \quad (3.6a)$$

$$\langle v_i^x(0)v_i^y(t) \rangle = \eta_{v_i^x}^{M^{(3)}} \eta_{v_i^y}^{M^{(3)}} \langle v_i^y(0)v_i^x(t) \rangle = -\langle v_i^y(0)v_i^x(t) \rangle \quad (3.6b)$$

which yields $\langle v_i^x(0)v_i^y(t) \rangle = 0 \forall t$.

More in general, by appropriate combinations of the single particle symmetries, it can be shown that the only nonzero velocity correlation functions are of the form $\langle v_i^\alpha(0)v_i^\alpha(t) \rangle$. For example, using $M^{(1)}$ and $M^{(8)}$ ($M^{(1)}$ and $M^{(4)}$), it can be shown that $\langle v_i^x(0)v_i^z(t) \rangle = 0 \forall t$ ($\langle v_i^y(0)v_i^z(t) \rangle = 0 \forall t$). Furthermore, as noted above, any combination of the single-particle symmetries in Eqs. (3.3) can be used to obtain a valid global symmetry for the system. We can then construct, for example, a global transformation in which the phase-space coordinates of one of the particles, say particle j , transforms according to $\mathcal{M}_j^{(3)}$ while those all other particles transform according to $\mathcal{M}_i^{(1)}$ ($i \neq j$). This new global symmetry, in combination with $M^{(1)}$, enables to prove that $\langle v_j^x(0)v_i^y(t) \rangle = 0 \forall t$. These results, together with the invariance of the Hamiltonian under rotations and permutations of the particle indexes, implies that the diffusion tensor of the system, given by the time integral of the velocity correlations, is a multiple of the identity.

More in general, the considerations in this subsection apply to separable Hamiltonians $H(\Gamma) = \sum_{i=1}^N h_i(\Gamma_i)$ as long as the single particle contribution $h_i(\Gamma_i)$ is symmetric under the transformations defined by eqs. (3.3). This applies, for example, to a central potential problem with $h_i(\Gamma_i) = \mathbf{p}_i^2/2m_i + V(|\mathbf{r}_i|)$.

3.1.2 Interacting Hamiltonian

Let us now consider a system of N point particles of mass m_i interacting through a pair potential that only depends on the distance between particles. The Hamiltonian can then be written as

$$H(\Gamma) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i \neq j}^N V(r_{ij}) \quad (3.7)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. This is a considerably more interesting model than the ideal gas since it describes a large number of condensed phase systems commonly encountered in simulations. Examples range from the Coulomb potential to the Lennard-Jones potential for simple fluids, to the Tosi-Fumi potential for molten salts, to the Parrinello-Rahman potential for superionic conductors. The dynamics of system is still given by Eqs. (3.1), where now $\frac{dp_i^\alpha}{dt} = F_i^\alpha$, with

$$F_i^\alpha = \sum_{j \neq i}^N f_{ij}^\alpha = \sum_{j \neq i}^N \left(-\frac{\partial V(r_{ij})}{\partial \alpha_i} \right) = \sum_{j \neq i}^N \frac{\alpha_j - \alpha_i}{r_{ij}} \frac{\partial V(r_{ij})}{\partial r_{ij}} \quad (3.8)$$

The coupling between the particles' coordinates in the potential now prevents the definition of global symmetries built using different $\mathcal{M}_i^{(\alpha)}$. Thus, these systems obey only the eight transformations of the form $\mathcal{M}^{(\alpha)}$ defined in the previous subsection. When looking at time-correlation functions, we consider again the example of the correlation of the velocities, the property

$$\langle v_i^\alpha(0) v_i^\beta(t) \rangle = \delta^{\alpha\beta} \langle v_i(0) v_i(t) \rangle \quad (3.9)$$

is then still valid, but we can no longer make statements about correlations referring to different particles, $\langle v_i^\alpha(0) v_j^\beta(t) \rangle$ with $i \neq j$.

Using similar considerations, the signature of the observables under the different time-reversal operations can be used, for example, to establish the following

Proposition 3.2. *The imaginary part of the intermediate scattering function*

$$F(\mathbf{k}, t) = \frac{1}{N} \left\langle \sum_{i,j}^N e^{-i\mathbf{k} \cdot \mathbf{r}_i(0)} e^{i\mathbf{k} \cdot \mathbf{r}_j(t)} \right\rangle \quad (3.10)$$

for systems with distance-dependent potentials must be zero and the real part is an even function of time.

Proof. Repeat the steps of Example 3.1 acting with $M^{(1)}$ and $M^{(2)}$ on the real and imaginary part of $F(\mathbf{k}, t)$. $\square$

For charged systems, indicating the particle charge by q_i , the same idea proves that the conductivity tensor, proportional to the time integral of the current-current time-correlation functions, where the Cartesian components of the microscopic estimator of the electric current are defined as $J^\alpha = \mathcal{V}^{-1} \sum_{i=1}^N q_i v_i^\alpha$ must be diagonal (the same symmetry operations used for the diffusion tensor lead to the result), where $\mathcal{V}$ is the volume of the system.

3.2 The Effect of Applied Fields

The observations in the previous sections provide interesting results also for systems subject to one or more external fields that break, in part, the symmetry of the Hamiltonian in space. In the following, we shall consider, in particular, the effect of magnetic and electric fields, individually or in combination. The case of the magnetic field has considerable interest since, as mentioned in Section 2.3, in commonly adopted reference literature these systems are not considered time reversible and they require special treatment. While this statement is true for completely anisotropic interactions we shall show that in conceptually and experimentally interesting set ups more than one time symmetry survives. This enables, in particular, to obtain standard symmetry features of the correlation functions and basic statistical properties such as the Kubo and Onsager relationships without the need to invert the direction of the magnetic field, as commonly done. This inversion is instead necessary when considering the standard time-reversal $\mathcal{M}^{(1)}$, leading in fact to statements that connect the statistical properties of two different systems (each associated with a specific orientation of the magnetic field). The case of the electric field, on the other hand, is interesting both conceptually and in view of the importance of charge transport phenomena. Given that the electric field performs work on the system, the definition of time-correlation functions is more delicate than in the other cases considered in this chapter, and requires the field to allow for a stationary probability density. To simplify the discussion, in this case we restrict our considerations to the

time-reversal properties of the Hamiltonian dynamics. In particular, we consider first the effect of an electric field constant in space to illustrate the analogies with the case of the constant magnetic field. We then consider the case, relevant for example when studying the Hall effect or the fluctuation relations, of the simultaneous presence of external electric and magnetic fields and discuss how different relative orientations of these fields affect time-reversal properties.

3.2.1 Magnetic Field

The Hamiltonian of N particles of mass m_i and charge q_i subject to an external magnetic field can be written as

$$H(\Gamma) = \sum_{i=1}^N \frac{(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i))^2}{2m_i} + \frac{1}{2} \sum_{i \neq j}^N V(r_{ij}) \quad (3.11)$$

where $\mathbf{A}(\mathbf{r})$ is the vector potential associated to the magnetic field $\mathbf{B} = \nabla_{\mathbf{r}} \times \mathbf{A}(\mathbf{r})$. We assume the magnetic field to be constant in time and space, and orient our reference system so that the magnetic field is directed along the z -axis, *i.e.* $\mathbf{B} = (0, 0, B^z)$. With this set up, the vector potential can be defined as

$$\mathbf{A}(\mathbf{r}) = \frac{B^z}{2} \begin{pmatrix} -y \\ x \\ 0 \end{pmatrix} \quad (3.12)$$

In writing the Hamiltonian, we have also maintained the assumption that the interparticle potential is pairwise additive and depends only on the distance of the particles. The equations of motion take the form

$$\begin{aligned} \frac{dx_i}{dt} &= \frac{p_i^x}{m_i} + \omega_i y_i & \frac{dp_i^x}{dt} &= F_i^x + \omega_i(p_i^y - m_i \omega_i x_i) \\ \frac{dy_i}{dt} &= \frac{p_i^y}{m_i} - \omega_i x_i & \frac{dp_i^y}{dt} &= F_i^y - \omega_i(p_i^x + m_i \omega_i y_i) \\ \frac{dz_i}{dt} &= \frac{p_i^z}{m_i} & \frac{dp_i^z}{dt} &= F_i^z \end{aligned} \quad (3.13)$$

where F_i^α is given as in Eq. (3.8), and $\omega_i = \frac{B^z q_i}{2m_i}$ is the cyclotron frequency of particle i .

Proposition 3.3. *The equations of motion (3.13) are left invariant by any time-reversal transformation that, for each particle, changes the sign of the products xp^x and yp^y .*

Proof. The proposition is again proved by direct inspection of the equations of motion. $\square$

Examining Eqs. (3.3), it follows that the global transformations $\mathcal{M}^{(3)}$, $\mathcal{M}^{(4)}$, $\mathcal{M}^{(6)}$, and $\mathcal{M}^{(7)}$ satisfy this condition. Note, in particular, that standard time-reversal, $\mathcal{M}^{(1)}$ is no longer a symmetry. In spite of that, the existence of four time-reversal transformations makes it still possible to derive relevant properties of time-correlation functions and transport coefficients. In fact, the most interesting consequence of the loss of the first four symmetry operations is that it is no longer possible to state that the cross-correlations of the components of the velocity in the x - y plane must be zero. This property, in fact, was obtained by combining the action of $M^{(3)}$ — still valid — and of the standard time-reversal which is no longer available. Using the symmetries $M^{(3)}$ and $M^{(4)}$, we can only obtain the weaker result

$$\begin{aligned}\langle v^x(0)v^y(t) \rangle &= \eta_{v_i^x}^{M^{(3)}} \eta_{v_i^y}^{M^{(3)}} \langle v^x(t)v^y(0) \rangle = -\langle v^x(t)v^y(0) \rangle \\ \langle v^x(0)v^y(t) \rangle &= \eta_{v_i^x}^{M^{(4)}} \eta_{v_i^y}^{M^{(4)}} \langle v^x(t)v^y(0) \rangle = -\langle v^x(t)v^y(0) \rangle\end{aligned}\quad (3.14)$$

i.e. the correlation is an odd function of time.

Remark 3.2. *Eqs. (3.14) imply that the diffusion and conductivity tensors are antisymmetric in the x - y plane (the plane orthogonal to the magnetic field), but the off-diagonal components in this plane are no longer necessarily zero.*

In fact, nonzero components of these tensors in the plane orthogonal to $\mathbf{B}$ are indicators of the onset of the Hall effect in the system. Molecular dynamics simulations illustrating these analytical results were presented in Refs. [19, 66, 67] *via* the calculation of the charge transport properties of NaCl, AgI and CaF₂ in the presence of an external magnetic field.

It may be worth to stress that a given observable may have a well defined signature only under some of the available symmetry operations. A typical example is the intermediate scattering function $F(\mathbf{k}, t)$ which, for generic wave vectors, has signature only when transformed via $M^{(1)}$ (standard time-reversal) and $M^{(2)}$. Thus,

for this observable, the concept of signature is meaningful only in the absence of magnetic field.²

3.2.2 Electric Field

In the presence of an external electric field $\mathbf{E}$, the Hamiltonian is given by

$$H(\Gamma) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i \neq j}^N V(r_{ij}) - \sum_{i=1}^N q_i \mathbf{E} \cdot \mathbf{r}_i \quad (3.15)$$

As in the previous subsection, we consider a system described by pairwise, distance dependent, internal interactions and subject to an external field constant in time and space. To fix the notation, in this case we set the x -axis parallel to the field, $\mathbf{E} = (E^x, 0, 0)$. The evolution equations are then given by

$$\begin{aligned} \frac{dx_i}{dt} &= \frac{p_i^x}{m_i} & \frac{dp_i^x}{dt} &= F_i^x + q_i E^x \\ \frac{dy_i}{dt} &= \frac{p_i^y}{m_i} & \frac{dp_i^y}{dt} &= F_i^y \\ \frac{dz_i}{dt} &= \frac{p_i^z}{m_i} & \frac{dp_i^z}{dt} &= F_i^z \end{aligned} \quad (3.16)$$

Upon inversion of time, the dynamical system above is invariant under the phase-space transformations $\mathcal{M}^{(1)}$, $\mathcal{M}^{(4)}$, $\mathcal{M}^{(5)}$ and $\mathcal{M}^{(6)}$ which are then valid time-reversal symmetries for the system. More in general, the following holds:

Proposition 3.4. *The electric field breaks in the same way all symmetries in which the sign of the coordinate parallel to the field is changed.*

Proof. The proposition is again proved by direct inspection of the equations of motion. $\square$

With the current geometry, these are $\mathcal{M}^{(2)}$, $\mathcal{M}^{(3)}$, $\mathcal{M}^{(7)}$, $\mathcal{M}^{(8)}$.

Remark 3.3. *Inverting the sign of the electric field then restores all the time-reversal symmetries, in analogy with the usual statement that inverting the sign of the external magnetic field restores the standard time-reversal invariance.*

²Null components of the wave vector make it possible to recover signature in particular cases.

Example 3.2. *Let us consider $\mathcal{M}^{(3)}$. Direct inspection shows that this transformation fails to leave the system invariant because it results in*

$$-\frac{dp_i^x}{dt} = -F_i^x + q_i E^x \quad (3.17)$$

(all other equations remain unchanged). The overall symmetry can be restored if, in addition to the phase-space transformation, the direction of the external electric field is inverted.

To conclude, note that orienting the field along a different axis simply moves the term due to the electric field to the evolution equation for the corresponding component of the momenta. The results discussed above can then be adapted quite easily to the new geometry.

3.2.3 Simultaneous Action of Electric and Magnetic Field

We conclude our survey by considering a system subject, at the same time, to a magnetic and to an electric field. In this case, violation of the time-reversal symmetries introduced in Section 3.1.1 arises both from direct breaking of the invariance of space, and from the nonstandard form of the kinetic energy. The Hamiltonian for this system is

$$H(\Gamma) = \sum_{i=1}^N \frac{(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i))^2}{2m_i} + \frac{1}{2} \sum_{i \neq j}^N V(r_{ij}) - \sum_{i=1}^N q_i \mathbf{E} \cdot \mathbf{r}_i \quad (3.18)$$

Let us consider different possible situations. For $\mathbf{B}$ and $\mathbf{E}$ parallel, and parallel to the z -axis, the equations of motion are

$$\begin{aligned} \frac{dx_i}{dt} &= \frac{p_i^x}{m_i} + \omega_i y_i & \frac{dp_i^x}{dt} &= F_i^x + \omega_i (p_i^y - m_i \omega_i x_i) \\ \frac{dy_i}{dt} &= \frac{p_i^y}{m_i} - \omega_i x_i & \frac{dp_i^y}{dt} &= F_i^y - \omega_i (p_i^x + m_i \omega_i y_i) \\ \frac{dz_i}{dt} &= \frac{p_i^z}{m_i} & \frac{dp_i^z}{dt} &= F_i^z + q_i E^z \end{aligned} \quad (3.19)$$

The only transformations that leave the dynamics invariant upon time reversal are $\mathcal{M}^{(3)}$ and $\mathcal{M}^{(4)}$. The system has then lost, due to the presence of the magnetic field,

the standard time-reversal symmetry and, in addition, two of the four symmetries ($\mathcal{M}^{(6)}$ and $\mathcal{M}^{(7)}$) previously identified as valid in the presence of the magnetic field alone.

On the other hand, if $\mathbf{B} \perp \mathbf{E}$, with the magnetic field parallel to the z -axis and the electric field aligned to the x -axis, the dynamical system becomes

$$\begin{aligned} \frac{dx_i}{dt} &= \frac{p_i^x}{m_i} + \omega_i y_i & \frac{dp_i^x}{dt} &= F_i^x + \omega_i(p_i^y - m_i \omega_i x_i) + q_i E^x \\ \frac{dy_i}{dt} &= \frac{p_i^y}{m_i} - \omega_i x_i & \frac{dp_i^y}{dt} &= F_i^y - \omega_i(p_i^x + m_i \omega_i y_i) \\ \frac{dz_i}{dt} &= \frac{p_i^z}{m_i} & \frac{dp_i^z}{dt} &= F_i^z \end{aligned} \quad (3.20)$$

The presence of $\mathbf{E}$ invalidates the time-reversal operations in which the sign of the x coordinate (more in general, the direction of the electric field) is changed. In this case then, $\mathcal{M}^{(4)}$ and $\mathcal{M}^{(6)}$ are the only two possible transformations. As in the previous case, two of the four transformations present when only the magnetic or only the electric fields are active are now lost.

Remark 3.4. *The two symmetries surviving for parallel or perpendicular electro-magnetic fields preserve the time-reversibility of the dynamics in these set-ups.*

If the magnetic and electric fields are at an arbitrary angle, it is still possible to find a reference frame such that both fields have at least one null component. In particular, aligning the z -axis with the magnetic field, *i.e.* $\mathbf{B} = (0, 0, B^z)$, two situations are possible: $\mathbf{E} = (E^x, 0, E^z)$, in which case the phase-space transformation $\mathcal{M}^{(4)}$ is a time-reversal symmetry, or $\mathbf{E} = (0, E^y, E^z)$, in which case $\mathcal{M}^{(3)}$ is a time-reversal symmetry. In either case, then, the system is time-reversal invariant. This makes it possible, for example, to extend to these cases nonequilibrium relationships such as the Onsager reciprocity relations. Indeed, only the addition of another field, not parallel to $\mathbf{B}$ or $\mathbf{E}$ and thus breaking the residual space isotropy of the system, would destroy all time-reversal symmetries.

3.3 Summary

The time-reversal symmetry of classical dynamics was reconsidered in this chapter. We noted that, under fairly general assumptions for the interactions among the

particles in isolated system, new time-reversal operations can be defined in addition to the standard one. Combining the signature properties of time-correlation functions under these different symmetries, null components of measurable quantities such as the diffusion tensor can be identified analytically. We have then extended the analysis to systems in external potentials and focused on the notable case of an applied constant magnetic field. These systems violate standard time-reversal invariance and are treated in the literature as a somewhat special case. Starting from the observation that four of the newly defined symmetry operations are preserved by the evolution equations, we showed that — for systems with distance dependent pairwise interactions — the usual procedure of considering relationships between time-correlation functions of systems with opposite orientations of the field is, in fact, unnecessary. In view of applications to charge transport, and in particular to simulations of the Hall effect beyond linear response theory and of the study of the fluctuation relations, the effect on time-reversal of a constant external electric field (alone and in combination with a magnetic field) was also considered.

Chapter 4

Fluctuation Relations in Constant Magnetic Field

The discussion in Section 2.2 shown that the main ingredient to prove Fluctuation Relations (FRs) is some kind of time reversibility. For deterministic dynamics this typically means the standard reversibility defined by the momentum inversion operator $\mathcal{M}^{(1)}$:

$$\mathcal{M}^{(1)}(\mathbf{r}, \mathbf{p}) = (\mathbf{r}, -\mathbf{p}), \quad \forall (\mathbf{r}, \mathbf{p}) := \Gamma \in \mathfrak{M} \quad (4.1)$$

where we recall that Γ is a point in the phase space $\mathfrak{M}$ of an N -particle system, with positions $\mathbf{r} = \{\mathbf{r}_i\}_{i=1}^N$ and momenta $\mathbf{p} = \{\mathbf{p}_i\}_{i=1}^N$. As discussed in Section 2.3, the symmetry $\mathcal{M}^{(1)}$ is broken by an external magnetic field $\mathbf{B}$. This has consolidated, also in the domain of FRs, the idea that statistical properties of charged systems in external magnetic field necessitate special treatment.

However, observing that invariance of the Hamiltonian under Eq. (4.1) is a sufficient but not necessary condition for the properties mentioned above, it was demonstrated in Chapter 3 that a more general approach is possible. There exist, in fact, alternative time-reversal operators that, together with the change $t \rightarrow -t$, leave the evolving equations invariant without changing the sign of the magnetic field, *i.e.* considering properties of a single system. Exploiting them, standard statistical relations can be immediately reinstated. Chapter 3, together with Refs. [19, 20], demonstrate this for time-correlation functions, illustrating the result with numerical simulations [19]. Here, we extend this single-system description, to transient and steady-state FRs and to their corollaries, such as relations linking cumulants of currents to driving dissipative forces.

To this end, let us consider a three-dimensional system of N particles of charge q_i and mass m_i , subject to uniform and static electric and magnetic fields, in a volume $\mathcal{V}$. The Hamiltonian is

$$\begin{aligned} H(\Gamma) &= H_0(\Gamma) - \sum_{i=1}^N q_i \mathbf{E} \cdot \mathbf{r}_i = \\ &= \sum_{i=1}^N \frac{(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i))^2}{2m_i} + \sum_{i,j < i}^N V(r_{ij}) - \sum_{i=1}^N q_i \mathbf{E} \cdot \mathbf{r}_i \end{aligned} \quad (4.2)$$

where $\mathbf{A}(\mathbf{r})$ is the vector potential associated to the magnetic field $\mathbf{B} = \nabla_{\mathbf{r}} \times \mathbf{A}(\mathbf{r})$, $\mathbf{E}$ is the electric field and $V(r_{ij})$ is a pairwise additive interaction potential, depending only on the modulus of the distance between particles: $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. We orient

the magnetic field as $\mathbf{B} = (0, 0, B^z)$. A compatible vector potential, enforcing the Coulomb gauge $\nabla_{\mathbf{r}} \cdot \mathbf{A}(\mathbf{r}) = 0$, is $\mathbf{A}(\mathbf{r}) = B^z/2(-y, x, 0)$. This setting, while not completely general, includes the majority of physically interesting cases and is usually adopted to discuss the time-reversal properties of systems in external magnetic fields [64, 65, 68, 69].

We now consider deterministic thermostats coupled to this system with different orientations of the electric field. We present first time-reversal symmetries that make the proof of FRs applicable, then we obtain explicit expressions for $\Omega^{(0)}$ and for the FRs.

4.1 The Isokinetic Nonequilibrium Ensemble

The isokinetic thermostat is often used in connection with FRs [34, 70]. Orienting the electric field along the x -axis, *i.e.* $\mathbf{E} = (E^x, 0, 0)$, the isokinetic evolution associated to Eq. (4.2) is

$$\begin{aligned} \frac{dx_i}{dt} &= \frac{p_i^x}{m_i} + \omega_i y_i & \frac{dp_i^x}{dt} &= F_i^x + \omega_i(p_i^y - m_i \omega_i x_i) + q_i E^x - \frac{\alpha_{\text{IK}}}{2}(p_i^x + m_i \omega_i y_i) \\ \frac{dy_i}{dt} &= \frac{p_i^y}{m_i} - \omega_i x_i & \frac{dp_i^y}{dt} &= F_i^y - \omega_i(p_i^x + m_i \omega_i y_i) - \frac{\alpha_{\text{IK}}}{2}(p_i^y - m_i \omega_i x_i) \\ \frac{dz_i}{dt} &= \frac{p_i^z}{m_i} & \frac{dp_i^z}{dt} &= F_i^z - \frac{\alpha_{\text{IK}}}{2} p_i^z \end{aligned} \quad (4.3)$$

where F_i^λ and $\omega_i = \frac{B^z q_i}{2m_i}$ are the λ Cartesian component of the interparticle force and the cyclotron frequency for particle i , respectively. The thermostat parameter α_{IK} can be obtained using Gauss' principle of least constraint.

Gauss Principle (1829). *Consider N point particles of mass m_i , subjected to frictionless bilateral constraints and to active forces Φ . Among all motions allowed by the constraints, the natural one minimizes the “curvature” Q defined by*

$$Q = \sum_{i=1}^N m_i \left[\ddot{\mathbf{r}}_i - \frac{\Phi_i}{m_i} \right]^2 \quad (4.4)$$

where the $\ddot{\mathbf{r}}_i$ represent the accelerations subject to the selected constraint(s).

The active forces $\Phi_i = -\nabla_{\mathbf{r}_i} H$ are given by the RHS of the unconstrained (nonequilibrium) dynamics expressed in Newtonian form

$$\begin{aligned} m_i \ddot{x}_i &= F_i^x + 2m_i \omega_i \dot{y}_i + q_i E^x \\ m_i \ddot{y}_i &= F_i^y - 2m_i \omega_i \dot{x}_i \\ m_i \ddot{z}_i &= F_i^z \end{aligned}$$

while the isokinetic constraint is given by

$$g(\mathbf{r}, \dot{\mathbf{r}}) = K(\Gamma) - K^* = \frac{1}{2} \sum_{i=1}^N m_i |\dot{\mathbf{r}}_i|^2 - K^* = 0 \quad (4.5)$$

where $K(\Gamma)$ is the standard microscopic estimator of the kinetic energy and K^* indicates the specific value of the kinetic energy set by the initial state.

To obtain an explicit expression for the constraint as a function of the variables $\ddot{\mathbf{r}}$ we take the derivative with respect to time of Eq. (4.5)

$$\dot{g}(\mathbf{r}, \dot{\mathbf{r}}) = \sum_{i=1}^N \nabla_{\dot{\mathbf{r}}_i} g(\mathbf{r}, \dot{\mathbf{r}}) \cdot \ddot{\mathbf{r}}_i = \sum_{i=1}^N m_i \dot{\mathbf{r}}_i \cdot \ddot{\mathbf{r}}_i = 0 \quad (4.6)$$

and then we minimize the curvature subject to the constraint, with respect to $\ddot{\mathbf{r}}_j$, leading to:

$$\frac{d}{d\ddot{\mathbf{r}}_j} \left\{ \sum_{i=1}^N m_i \left[\dot{\mathbf{r}}_i - \frac{\Phi_i}{m_i} \right]^2 - \alpha \sum_{i=1}^N m_i \dot{\mathbf{r}}_i \cdot \ddot{\mathbf{r}}_i \right\} = 0 \quad j = 1, \dots, N$$

where α is a Lagrange multiplier to be determined in order to satisfy the constraint. This yields the equations of motion for the constrained system

$$m_i \ddot{\mathbf{r}}_i = \Phi_i - \alpha \frac{m_i}{2} \dot{\mathbf{r}}_i \quad (4.7)$$

The Lagrange multiplier α is determined *via* Eq. (4.6) multiplying Eq. (4.7) by $\dot{\mathbf{r}}_i$ and summing over $i = 1, \dots, N$

$$\sum_{i=1}^N m_i \dot{\mathbf{r}}_i \ddot{\mathbf{r}}_i = \dot{g}(\mathbf{r}, \dot{\mathbf{r}}) = 0 = \sum_{i=1}^N \left[\Phi_i \cdot \dot{\mathbf{r}}_i - \alpha \frac{m_i}{2} \dot{\mathbf{r}}_i \cdot \dot{\mathbf{r}}_i \right]$$

to obtain

$$\alpha_{\text{IK}} = \frac{\sum_{i=1}^N \boldsymbol{\Phi}_i \cdot \dot{\mathbf{r}}_i}{\frac{1}{2} \sum_{i=1}^N m_i |\dot{\mathbf{r}}_i|^2} = \frac{\sum_{i=1}^N \boldsymbol{\Phi}_i \cdot (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) / m_i}{\sum_{i=1}^N |\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)|^2 / 2m_i} \quad (4.8)$$

Substituting in Eq. (4.7) and formulating the evolution in Hamiltonian form we obtain the dynamical system in Eq. (4.3).

Proposition 4.1. *The equilibrium distribution for the dynamical system (4.3) is given by*

$$\rho_0(\Gamma) = \frac{\exp[-\beta H_0(\Gamma)] \delta(K(\Gamma) - K^*)}{\int_{\mathcal{M}} d\Gamma \exp[-\beta H_0(\Gamma)] \delta(K(\Gamma) - K^*)} \quad (4.9)$$

where $H_0(\Gamma)$ is defined in Eq. (4.2) and $\beta = 1/k_B T$.

Proof. We show that Eq. (4.9) is the equilibrium distribution for the nondissipative isokinetic dynamics (*i.e.* Eqs. (4.3) with $\mathbf{E} = 0$) by verifying, *via* direct substitution, that it satisfies the generalized Liouville equation specialized to the equilibrium isokinetic dynamical system, Eq. (4.3) with $\mathbf{E} = 0$. At equilibrium, the generalized Liouville equation reads

$$(\nabla_{\Gamma} \rho) \cdot \dot{\Gamma} + \rho (\nabla_{\Gamma} \cdot \dot{\Gamma}) = 0 \quad (4.10)$$

Let us consider first the compressibility of the system $\Lambda = \nabla_{\Gamma} \cdot \dot{\Gamma}$. To set the stage, we write the dynamical system in the form

$$\begin{aligned} \dot{\mathbf{r}}_i &= \nabla_{\mathbf{p}_i} H_0 \\ \dot{\mathbf{p}}_i &= -\nabla_{\mathbf{r}_i} H_0 - \frac{\alpha_{\text{IK}}^0}{2} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \end{aligned}$$

with

$$\alpha_{\text{IK}}^0 = \frac{\sum_{i=1}^N \boldsymbol{\Phi}_i^0 \cdot (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) / m_i}{\sum_{i=1}^N |\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)|^2 / 2m_i} = \frac{1}{K} \sum_{i=1}^N \boldsymbol{\Phi}_i^0 \cdot \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i}$$

where $\boldsymbol{\Phi}_i^0 = -\nabla_{\mathbf{r}_i} H_0$. The superscript/subscript “0” indicates in the following that we are considering the equilibrium situation with $\mathbf{E} = 0$. The compressibility can then be computed as

$$\nabla_{\Gamma} \cdot \dot{\Gamma} = \sum_{i=1}^N \left\{ -\nabla_{\mathbf{p}_i} \cdot \frac{\sum_{j=1}^N \boldsymbol{\Phi}_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j}{\sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j} \cdot (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \right\} \quad (4.11)$$

Calculating the gradient in $\mathbf{p}_i$ yields

$$\begin{aligned} \nabla_{\Gamma} \cdot \dot{\Gamma} = & -3N \frac{\sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j}{\sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j} + \\ & - \sum_{i=1}^N (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \cdot \nabla_{\mathbf{p}_i} \frac{\sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j}{\sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j} \end{aligned} \quad (4.12)$$

The gradient in the last term of the equation above can be written as

$$\begin{aligned} \nabla_{\mathbf{p}_i} \frac{\sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j}{\sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j} &= \frac{1}{4K^2} \left[2K \nabla_{\mathbf{p}_i} \sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j + \right. \\ & \left. - \sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j \nabla_{\mathbf{p}_i} \sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j \right] = \\ &= \frac{1}{4K^2} \left[2K \Phi_i^0 / m_i - 2(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) / m_i \sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j \right] \end{aligned}$$

where the notation $K \equiv K(\Gamma) = K^*$ has been used. Note, in fact, that the presence of the thermostat parameter α_{IK} in the dynamical system Eqs. (4.3) enforces at all time the exact equality of the instantaneous kinetic energy $K(\Gamma)$ and K^* , fixed by the initial conditions. Substituting in Eq. (4.12) yields

$$\begin{aligned} \nabla_{\Gamma} \cdot \dot{\Gamma} = & -3N \frac{\sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j}{\sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j} - \frac{1}{4K^2} \sum_{i=1}^N (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \cdot \\ & \cdot \left[2K \Phi_i^0 / m_i - 2(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) / m_i \sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j \right] = \\ &= -3N \frac{\sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j}{\sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j} + \\ & - \frac{1}{2K} \left[\sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j - 2 \sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j \right] = \\ &= - \frac{\sum_{j=1}^N \Phi_j^0 \cdot (\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)) / m_j}{\sum_{j=1}^N |\mathbf{p}_j - q_j \mathbf{A}(\mathbf{r}_j)|^2 / m_j} (3N - 1) = - \frac{\alpha_{\text{IK}}^0}{2} (3N - 1) \end{aligned}$$

From the equipartition theorem for a system of N particles in three dimensions with a frozen degree of freedom due to the isokinetic constraint we can write

$$\frac{3N-1}{2}k_B T = K \implies \beta = \frac{3N-1}{2K}$$

so that, finally,

$$\nabla_\Gamma \cdot \dot{\Gamma} = -\beta K \alpha_{\text{IK}}^0 \quad (4.13)$$

Next, we compute the gradient of the distribution

$$\begin{aligned} \nabla_\Gamma \rho_0 &= \nabla_\Gamma \mathcal{Z}^{-1} \exp[-\beta H_0] \delta(K - K^*) \\ &= \mathcal{Z}^{-1} \left[\delta(K - K^*) \nabla_\Gamma \exp[-\beta H_0] + \exp[-\beta H_0] \nabla_\Gamma \delta(K - K^*) \right] \end{aligned} \quad (4.14)$$

where $\mathcal{Z} = \int d\Gamma \exp[-\beta H_0] \delta(K - K^*)$ is the partition function. The first term in the last line above is easily computed as

$$\begin{aligned} \mathcal{Z}^{-1} \delta(K - K^*) \nabla_\Gamma \exp[-\beta H_0] &= \\ &= \mathcal{Z}^{-1} \delta(K - K^*) (-\beta \exp[-\beta H_0] \nabla_\Gamma H_0) = -\beta \rho_0 \nabla_\Gamma H_0 \end{aligned} \quad (4.15)$$

Scalar product of this term with the flux on the phase space (see first term in Eq. (4.10)) gives

$$\begin{aligned} -\beta \rho_0 \nabla_\Gamma H_0 \cdot \dot{\Gamma} &= \frac{\beta}{2} \rho_0 \sum_{i=1}^N \nabla_{\mathbf{p}_i} H_0 \cdot \alpha_{\text{IK}}^0(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) = \\ &= \frac{\beta}{2} \rho_0 \sum_{i=1}^N \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i} \cdot \alpha_{\text{IK}}^0(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) = \beta \rho_0 K \alpha_{\text{IK}}^0 \end{aligned} \quad (4.16)$$

We shall now show that second term of the RHS of Eq. (4.14) vanishes. We have

$$\mathcal{Z}^{-1} \exp[-\beta H_0] \nabla_\Gamma \delta(K - K^*) = \mathcal{Z}^{-1} \exp[-\beta H_0] \delta'(K - K^*) \nabla_\Gamma K \quad (4.17)$$

where we introduced the quantity

$$\frac{d}{dx} \delta(x - x_0) = \delta'(x - x_0)$$

The chain rule for the Dirac's delta function can be easily obtained in the framework of the generalized functions [71]. The scalar product of the derivative above with the

phase-space flux is given by

$$\nabla_{\Gamma} K \cdot \dot{\Gamma} = \sum_{i=1}^N \left[\nabla_{\mathbf{r}_i} K \nabla_{\mathbf{p}_i} H_0 - \nabla_{\mathbf{p}_i} K \nabla_{\mathbf{r}_i} H_0 - \nabla_{\mathbf{p}_i} K \cdot \frac{\alpha_{\text{IK}}^0}{2} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \right]$$

The first term of the RHS is null since $\nabla_{\mathbf{r}_i} K = 0$ as easily verified remembering that, in the adopted Coulomb gauge, $\nabla_{\mathbf{r}_i} \cdot \mathbf{A}(\mathbf{r}_i) = 0$. The other two terms in square parenthesis are equal and opposite. Indeed

$$-\sum_{i=1}^N \nabla_{\mathbf{p}_i} K \nabla_{\mathbf{r}_i} H_0 = \sum_{i=1}^N \Phi_i^0 \cdot \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i}$$

and

$$\begin{aligned} -\sum_{i=1}^N \nabla_{\mathbf{p}_i} K \cdot \frac{\alpha_{\text{IK}}^0}{2} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) &= -\alpha_{\text{IK}}^0 \sum_{i=1}^N \frac{|\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)|^2}{2m_i} = \\ &= -\sum_{i=1}^N \Phi_i^0 \cdot \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i} \end{aligned} \quad (4.18)$$

Summarizing, the calculations above show that the nonzero contributions to the generalized Liouville equation arise from the compressibility, Eq. (4.13), and from Eq. (4.16). Substituting in Eq. (4.10) then completes the proof since

$$(\nabla_{\Gamma} \rho_0) \cdot \dot{\Gamma} + \rho_0 (\nabla_{\Gamma} \cdot \dot{\Gamma}) = \beta \rho_0 K \alpha_{\text{IK}}^0 - \beta \rho_0 K \alpha_{\text{IK}}^0 = 0$$

□

Remark 4.1. *Note that in presence of an external magnetic field, the total momentum is conserved on average, not instantaneously, explaining the lack of the delta function on momentum usually present in the isokinetic density (see, for example, Ref. [70]).*

The discussion carried on in Section 3.2.3 and direct inspection of Eq. (4.3) and Eq. (4.8) shows that the dynamical system is invariant under two of the eight time-reversal transformations introduced by Eq. (3.3), in particular:

$$\mathcal{M}^{(4)} \Gamma = (x, -y, z, -p^x, p^y, -p^z) \quad (4.19a)$$

$$\mathcal{M}^{(6)} \Gamma = (x, -y, -z, -p^x, p^y, p^z) \quad (4.19b)$$

Inspection of Eq. (4.9), shows that the initial probability density is even. The hypotheses introduced in Section 2.2 to derive of Eqs. (2.25) and (2.35) are then satisfied and we can establish the explicit expression of the FRs for this system. Note that the validity of the time-reversal symmetries $\mathcal{M}^{(4)}$ and $\mathcal{M}^{(6)}$ depends on the orientation of the magnetic and electric fields. In Section 3.2.3, however, it was shown that at least one time symmetry remains for arbitrary orientations of the fields, as long as the interparticle potential is isotropic.

4.1.1 Dissipation Function and Fluctuation Relations

The dissipation function, defined in Eq. (2.19), is computed for the particular system by direct substitution of the equilibrium density ρ_0 , Eq. (4.9) and of the dissipative phase-space flux, Eq. (4.3) with $\mathbf{E} \neq 0$. The relevant dynamical system is thus

$$\begin{aligned}\dot{\mathbf{r}}_i &= \nabla_{\mathbf{p}_i} H \\ \dot{\mathbf{p}}_i &= -\nabla_{\mathbf{r}_i} H - \frac{\alpha_{\text{IK}}}{2} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i))\end{aligned}\tag{4.20}$$

where the Hamiltonian and α_{IK} are defined in Eq. (4.2) and (4.8), respectively. For this dynamical system we have the following

Proposition 4.2. *The instantaneous dissipation function $\Omega^{(0)}(\Gamma)$ is given by*

$$\Omega^{(0)}(\Gamma) = \beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E}$$

where $\mathcal{V}$ is the volume of the system and $\mathbf{J}(\Gamma)$ is the microscopic estimator of the electric current.

Proof. The compressibility, $\Lambda = \nabla_{\Gamma} \cdot \dot{\Gamma}$, is computed repeating the steps in Eqs. (4.11)-(4.13) of the previous section for the nonequilibrium phase-space flux and is given by

$$\nabla_{\Gamma} \cdot \dot{\Gamma} = -\beta K \alpha_{\text{IK}}$$

As for the term $\nabla_{\Gamma} \rho_0 \cdot \dot{\Gamma}$, the gradient of the initial-state distribution is the same of the equilibrium case (see previous section).

$$\nabla_{\Gamma} \rho_0 = -\beta \rho_0 \nabla_{\Gamma} H_0 + \mathcal{Z}^{-1} \exp[-\beta H_0] \delta'(K - K_0) \nabla_{\Gamma} K \tag{4.21}$$

The phase-space flux of the dynamical system, on the other hand, now corresponds to Eq. (4.20). Multiplication of the first term of Eq. (4.21) by the phase-space flux yields

$$\begin{aligned}
 -\beta\rho_0\nabla_\Gamma H_0 \cdot \dot{\Gamma} &= \beta\rho_0 \sum_{i=1}^N \nabla_{\mathbf{p}_i} H_0 \cdot \left(-q_i \mathbf{E} + \frac{\alpha_{\text{IK}}}{2} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \right) = \\
 &= \beta\rho_0 \sum_{i=1}^N \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i} \cdot \left(-q_i \mathbf{E} + \frac{\alpha_{\text{IK}}}{2} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \right) = \\
 &= \beta\rho_0 \left(K\alpha_{\text{IK}} - \sum_{i=1}^N \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i} \cdot q_i \mathbf{E} \right)
 \end{aligned}$$

The scalar product of the second term of Eq. (4.21) with the phase-space flux yields again a null contribution as it can be easily shown retracing the steps of the previous section (Eqs. (4.17)-(4.18)).

The expression for the dissipation function for the isokinetic system in the chosen external magnetic and electric field is then given by

$$\begin{aligned}
 \Omega^{(0)}(\Gamma) &= -\frac{1}{\rho_0} \nabla_\Gamma \rho_0 \cdot \dot{\Gamma} - \nabla_\Gamma \cdot \dot{\Gamma} = \\
 &= -\beta \left(K\alpha_{\text{IK}} - \sum_{i=1}^N q_i \mathbf{E} \cdot \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i} \right) + \beta K\alpha_{\text{IK}} = \\
 &= \beta \sum_{i=1}^N q_i \mathbf{E} \cdot \frac{\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)}{m_i}
 \end{aligned}$$

which can be written in a more concise form as

$$\Omega^{(0)}(\Gamma) = \beta \sum_{i=1}^N q_i \mathbf{E} \cdot \dot{\mathbf{r}}_i = \beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E}$$

where the last equality recognizes the microscopic estimator for the electric current $\mathbf{J} = \mathcal{V}^{-1} \sum_{i=1}^N q_i \dot{\mathbf{r}}_i$. $\square$

The time-averaged dissipation function is obtained, from Eq. (2.17), as $\overline{\Omega^{(0)}}_{0,\tau} = \beta \mathcal{V} \bar{\mathbf{J}}_{0,\tau}(\Gamma) \cdot \mathbf{E}$. The dissipation function is proportional to the dissipative flux, hence to the dissipated energy. Moreover, as expected, $\Omega^{(0)}$ is odd under $\mathcal{M}^{(4)}$ and $\mathcal{M}^{(6)}$.

The transient FR is obtained substituting in Eq. (2.25):

$$\frac{\mu_0(\{\beta \mathcal{V} \bar{\mathbf{J}}_{0,\tau} \cdot \mathbf{E}\}_{(-A)_\delta})}{\mu_0(\{\beta \mathcal{V} \bar{\mathbf{J}}_{0,\tau} \cdot \mathbf{E}\}_{(A)_\delta})} = \exp \left[-\tau [A + \varepsilon(\delta, A, \tau)] \right] \quad (4.22)$$

For the steady-state FR to hold, $\mathcal{C}_0(A, \delta)$ of Eq. (2.36) must vanish. Numerical findings show that the steady-state FR typically holds in chaotic particle systems, characterized by fast decay of correlations [40, 41]. In Ref. [70], the test is explicitly performed for color diffusion, but it has never been done for systems in a magnetic field. While interparticle interactions promote disorder, hence decay of correlations, the Lorentz force tends to induce ordered circular motions that may hinder the decay of $\mathcal{C}_0(A, \delta)$. However, such an ordering effect may not be critical, as illustrated by the following example.

Example 4.1. *We consider the function $\mathcal{C}_0(A, \delta)$ for a system of noninteracting particles in external magnetic and electric fields with an isokinetic thermostat. To set the stage, we start by studying the evolution of the system in the absence of the thermostat, an exactly solvable model. The equations of motion of N noninteracting particles in external magnetic and electric field, $\mathbf{B} = (0, 0, B^z)$ and $\mathbf{E} = (E^x, 0, 0)$ are given by*

$$\begin{aligned} m_i \ddot{x}_i &= q_i E^x + q_i B^z \dot{y}_i \\ m_i \ddot{y}_i &= -q_i B^z \dot{x}_i \\ m_i \ddot{z}_i &= 0 \end{aligned} \quad (4.23)$$

The system is separable in its single components and the motion on the z -axis is trivial. Furthermore, the single-particle solution of Eq. (4.23) on the xy -plane is [72]

$$\begin{aligned} x(t) &= x(0) + \frac{v^\perp}{\omega} \cos(\phi) - \frac{v^\perp}{\omega} \cos(\omega t + \phi) \\ y(t) &= y(0) - \frac{v^\perp}{\omega} \sin(\phi) + \frac{v^\perp}{\omega} \sin(\omega t + \phi) - v_d t \end{aligned} \quad (4.24)$$

where we have dropped the subscript i for notational convenience and introduced the cyclotron frequency $\omega = \frac{qB^z}{m}$ and the drift velocity $v_d = \frac{E^x}{B^z}$. The constants $v^\perp$

and ϕ are fixed by the initial conditions

$$\begin{aligned} v^\perp &= \sqrt{(v^x(0))^2 + (v^y(0) + v_d)^2} \\ \phi &= \arctan \left[\frac{v^x(0)}{v^y(0) + v_d} \right] \end{aligned} \quad (4.25)$$

where $v^x(0)$ and $v^y(0)$ are the x and y component of the initial velocity, respectively. The trajectory in Eq. (4.24) is a cycloid on the xy -plane. For the noninteracting system, the correlation term in Eq. (2.36) can also be computed analytically. First note that the single-particle instantaneous dissipation is given by $\Omega^{(0)}(t) = \beta q E^x \dot{x}(t)$. Then

$$\begin{aligned} \Omega_{0,t}^{(0)} &= \int_0^t dt \Omega^{(0)}(t) = \beta E^x q \int_0^t dt \dot{x}(t) = \beta E^x q [x(t) - x(0)] \\ \Omega_{t+\tau, 2t+\tau}^{(0)} &= \int_{t+\tau}^{2t+\tau} dt \Omega^{(0)}(t) = \beta E^x q \int_{t+\tau}^{2t+\tau} dt \dot{x}(t) = \beta E^x q [x(2t+\tau) - x(t+\tau)] \end{aligned} \quad (4.26)$$

Substitution of Eqs. (4.24) and some trigonometry yield

$$\begin{aligned} -\Omega_{0,t}^{(0)} - \Omega_{t+\tau, 2t+\tau}^{(0)} &= \\ &= -\frac{\beta E^x q v^\perp}{\omega} \left\{ \Upsilon(t) + 2 \sin\left(\frac{1}{2}\omega t\right) \left[\Theta(t) \cos(\omega\tau) + \Xi(t) \sin(\omega\tau) \right] \right\} \end{aligned} \quad (4.27)$$

with

$$\begin{aligned} \Upsilon(t) &= \cos(\phi) [1 - \cos(\omega t)] + \sin(\omega t) \sin(\phi) \\ \Theta(t) &= \cos(\phi) \sin\left(\frac{3}{2}\omega t\right) + \sin(\phi) \cos\left(\frac{3}{2}\omega t\right) \\ \Xi(t) &= \cos(\phi) \cos\left(\frac{3}{2}\omega t\right) - \sin(\phi) \sin\left(\frac{3}{2}\omega t\right) \end{aligned} \quad (4.28)$$

The integrated N -particle dissipation functions for the separable system, Eq. (4.23), are given by the sum of the single-particle quantities computed above. Substituting in Eq. (2.36) results in

$$\begin{aligned} \mathcal{C}_0(A, \delta) &= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \lim_{t \rightarrow \infty} \left\langle \exp \left[-\beta \sum_i^N \frac{E^x q_i v_i^\perp}{\omega_i} \left\{ \Upsilon_i(t) + \right. \right. \right. \\ &\quad \left. \left. \left. + 2 \sin\left(\frac{\omega_i t}{2}\right) \left[\Theta_i(t) \cos(\omega_i \tau) + \Xi_i(t) \sin(\omega_i \tau) \right] \right\} \right] \right\rangle_{\{\overline{\Omega^{(0)}}_{t,t+\tau}\}_{(A)} \delta}^{(0)} \end{aligned} \quad (4.29)$$

The exponent of the expression above remains bounded for all values of t and τ , ensuring that the function $\mathcal{C}_0(A, \delta)$ is null.

This result remains qualitatively true also for the thermostatted system. The evolution of the isokinetic noninteracting model is still separable and trivial along the z -axis, with the single-particle evolution on the xy -plane (see Eq. (4.3)) given by

$$\begin{aligned}\ddot{x} &= \omega(v_d + \dot{y}) - \frac{m\omega v_d}{2K^*} \dot{x}^2 \\ \ddot{y} &= -\omega\dot{x} - \frac{m\omega v_d}{2K^*} \dot{x}\dot{y}\end{aligned}\tag{4.30}$$

where (see Eq. (4.8))

$$\alpha_{\text{IK}} = \frac{m\omega v_d}{K^*} \dot{x}\tag{4.31}$$

with $K^* = \frac{1}{2m} \left[(v^x(0))^2 + (v^y(0))^2 \right]$. The system (4.30) cannot be solved analytically, but its properties can be determined combining analysis of its equilibrium solutions, $\ddot{x} = \ddot{y} = 0$, with numerical integration. The study of the equilibrium solutions shows that for $|v_d| > \sqrt{2K^*/m}$, the thermostat dominates the motion leading to a nonphysical constant-velocity diffusion in the plane. Figure 4.1 shows the x -component of the trajectory numerically obtained for different drift velocities in the interval $-\sqrt{2K^*/m} < v_d < \sqrt{2K^*/m}$ (the y -component does not enter in the evaluation of the single-particle dissipation). In the figure, the numerical results are compared with nonthermostatted evolution for each value of the drift velocity. As it can be seen, the motion remains bounded along the x -direction also in the presence of the thermostat, implying — as for the noninteracting case — decay of $\mathcal{C}_0(A, \delta)$.

The numerical study described above shows that, for appropriate relative intensities of the fields, the motion remains bounded in the direction parallel to the electric field, cancelling the correlation term also for a noninteracting isokinetic model. This analysis holds in general for the components of the electric field orthogonal to the magnetic field. If the fields have a parallel component, the magnetic field, which only influences the orthogonal motion, does not affect directly dissipation in the parallel direction. Since interactions should further reduce correlation times, this argument suggests that the steady-state condition can be verified.

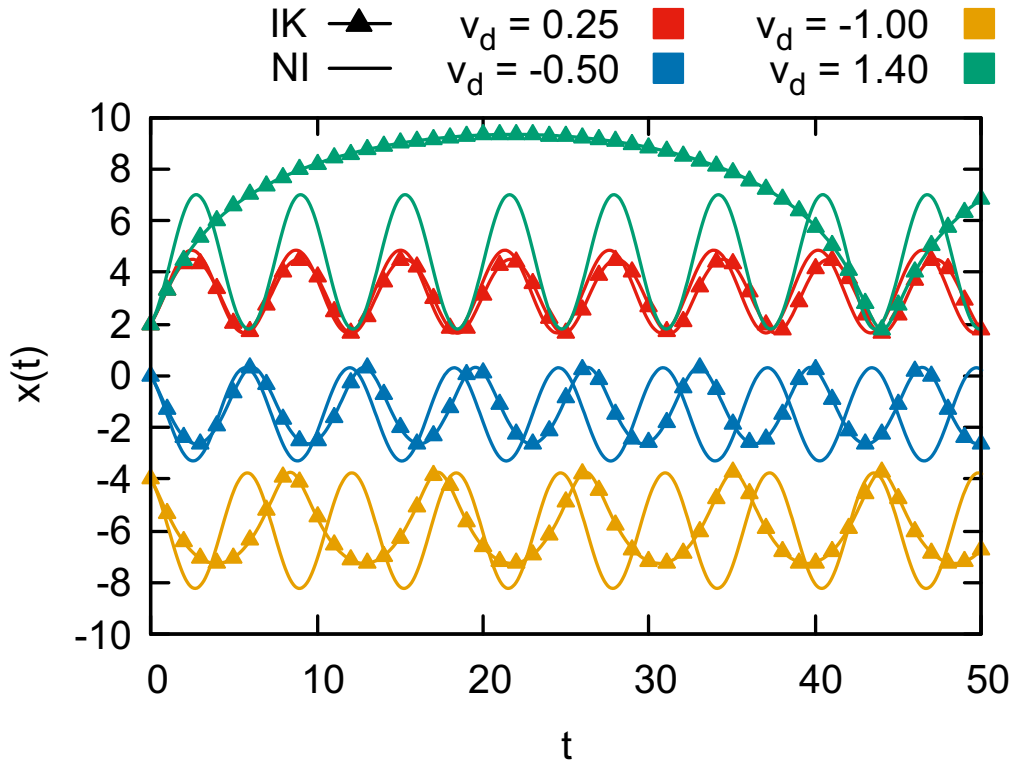


Fig. 4.1 Single-particle motion parallel to the electric field for noninteracting (NI, solid curves) and isokinetic (IK, curves with triangles). Color coding refers to evolution for different v_d in the physical regime, with NI and IK solution with the same initial conditions and same drift velocity plotted in the same color. We set $\omega = m = 1$ in arbitrary units. Different initial conditions (leading to $K^* = 1$) are used for different runs and the qualitative behaviour of the trajectory does not change with different (physical) initial conditions. For the thermostatted systems, the physical regime corresponds to $|v_d| < \sqrt{2}$. Noninteracting solutions are analytical, isokinetic evolution is computed numerically using Mathematica [73].

Assuming convergence of Eq. (2.36) and apart for an error $O(\tau^0)$ in the exponential, the steady-state FR can be written as

$$\frac{\mu_\infty(\{\beta \mathcal{V} \bar{\mathbf{J}}_{0,\tau} \cdot \mathbf{E}\}_{(-A)_\delta})}{\mu_\infty(\{\beta \mathcal{V} \bar{\mathbf{J}}_{0,\tau} \cdot \mathbf{E}\}_{(A)_\delta})} = \exp[-\tau[A + \varepsilon(\delta, A, \tau)]] \quad (4.32)$$

where $|\varepsilon(\delta, A, \tau)| \leq \delta$.

It is worth stressing that, although Eqs. (4.22) and (4.32) are misleadingly similar, they refer to very different situations. Transient FRs are associated to the statistics of the ensemble describing the initial (typically equilibrium) state. They describe a statistical property of many experiments of (short or long) duration τ . Differently, steady-state FRs refer to the steady-state statistics of the currents of a single object or realization of the system. They require a kind of decorrelation between initial and final macrostates, which is why t has to become large before τ does. This is not the mixing condition of ergodic theory, which corresponds to decay of correlations of microscopic events *within* a steady state [40, 41, 74]. If correlations do not decay, some kind of FRs may still hold, but they (and derived relations) would take a different form, see *e.g.* Refs. [48, 75–77].

4.2 The Generalized Nosé-Hoover Thermostat

Notwithstanding its great utility in theoretical and simulation problems, the isokinetic thermostat is known not to sample the canonical ensemble in equilibrium situations and therefore its interest is somewhat limited. Recently, a generalization of the Nosé-Hoover thermostat has been proposed for systems in external magnetic field [78]. As for the case $\mathbf{B} = 0$, this generalization is based on the extension of the phase space through conjugate variables s and ξ , mimicking the effect of a thermal bath. This thermostat can be easily modified to include a (static) external electric field (see also discussion in [78]), which allows us to extend the applicability of FRs.

As the numerical analysis of the previous section has shown, when the magnetic and electric fields are perpendicular to each other, the average dissipation tends to zero for growing τ , since the drift induced by the dissipative force is perpendicular to the force itself. For this reason, in this section we put ourselves in a situation in

which the fields are parallel along the z -axis, *i.e.* $\mathbf{B} = (0, 0, B^z)$ and $\mathbf{E} = (0, 0, E^z)$. In this way we expect an average dissipation different from zero also for $\tau \rightarrow \infty$.

The resulting generalized Nosé-Hoover dynamical system is:

$$\begin{aligned}
 \frac{dx_i}{dt} &= \frac{p_i^x}{m_i} + \omega_i y_i & \frac{dp_i^x}{dt} &= F_i^x + \omega_i(p_i^y - m_i \omega_i x_i) - \xi(p_i^x + m_i \omega_i y_i) \\
 \frac{dy_i}{dt} &= \frac{p_i^y}{m_i} - \omega_i x_i & \frac{dp_i^y}{dt} &= F_i^y - \omega_i(p_i^x + m_i \omega_i y_i) - \xi(p_i^y - m_i \omega_i x_i) \\
 \frac{dz_i}{dt} &= \frac{p_i^z}{m_i} & \frac{dp_i^z}{dt} &= F_i^z + q_i E^z - \xi p_i^z \\
 \frac{d \ln s}{dt} &= \xi & \frac{d\xi}{dt} &= \frac{1}{\tau_{\text{NH}}^2} \left[\frac{K(\Gamma) - K^*}{K^*} \right] = \frac{\delta K(\Gamma)}{\tau_{\text{NH}}^2}
 \end{aligned} \tag{4.33}$$

where τ_{NH} is the characteristic time of the thermostat. Note that the definition of a suitable microscopic temperature estimator for a system in external electric field is delicate, and it has been observed that different choices can lead to substantially different results in simulations at very high intensities of the applied field [79]. This is, however, not a major concern here since our focus is on the formal properties of the chosen dynamical system. It is important to note that the kinetic energy of this system now fluctuates around the target value K^* , related to the temperature of the system *via* $\beta = G/(2K^*)$ where G are the degrees of freedom of the system, *i.e.* $G = 3N$. As proved in [78], the dynamical system (4.33) with $\mathbf{E} = 0$ conserves the quantity $H_{\text{NH}}(\Gamma, \xi, s) = H_0(\Gamma) + K^*[\tau_{\text{NH}}^2 \xi^2 + 2 \ln s]$ and samples the equilibrium distribution

$$\rho_0(X) = \mathcal{Z}^{-1} \exp[-\beta H_0(\Gamma)] \exp\left[-\frac{G \tau_{\text{NH}}^2 \xi^2}{2}\right] \tag{4.34}$$

where $\mathcal{Z}$ is the partition function and X denotes the extended phase-space $X = (\Gamma, \xi)$. (The variable s does not affect the motion of the physical degrees of freedom and is introduced to define the conserved quantity $H_{\text{NH}}(\Gamma, \xi, s)$.) As in standard Nosé-Hoover dynamics, the marginal probability obtained integrating Eq. (4.34) with respect to ξ is the canonical density for the physical variables.

Proposition 4.3. *The system (4.33) is invariant under the transformations*

$$\mathcal{M}_{\text{ext}}^{(3)}(\Gamma, s, \xi) = (-x, y, z, p^x, -p^y, -p^z, s, -\xi) \tag{4.35a}$$

$$\mathcal{M}_{\text{ext}}^{(4)}(\Gamma, s, \xi) = (x, -y, z, -p^x, p^y, -p^z, s, -\xi) \tag{4.35b}$$

together with time inversion. The equilibrium density Eq. (4.34) is even under these transformations.

Proof. The proposition is proven by direct inspection of Eqs. (4.33) and Eq. (4.34). $\square$

The conditions for the transient FR are then verified and we can calculate the dissipation function, Eq. (2.19).

Proposition 4.4. *The instantaneous dissipation function for the dynamical system (4.33) is given by*

$$\Omega^{(0)}(X) = \beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E} \quad (4.36)$$

Proof. The dissipation function $\Omega^{(0)}(X)$ for the dynamical system (4.33) is obtained from the definition (2.19)

$$\Omega^{(0)}(X) = -\dot{X} \cdot \nabla_X \ln \rho_0 - \nabla_X \cdot \dot{X}$$

substituting $\dot{X}$ from Eq. (4.33) and the expression for ρ_0 from Eq. (4.34). Let us consider first the term $\nabla_X \cdot \dot{X}$. We have $\nabla_X \cdot \dot{X} = \nabla_\Gamma \cdot \dot{\Gamma} + \nabla_\xi \dot{\xi} = \nabla_\Gamma \cdot \dot{\Gamma}$ where the last equality holds because the variable ξ is not involved in the evolution equation for $\dot{\xi}$. The evolution equations of the physical variables in the dynamical system (4.33) can be written, in vector notation, as

$$\begin{aligned} \dot{\mathbf{r}}_i &= \nabla_{\mathbf{p}_i} H \\ \dot{\mathbf{p}}_i &= -\nabla_{\mathbf{r}_i} H - \xi (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \end{aligned} \quad (4.37)$$

where the explicit form of H is given in Eq. (3.18). Using this writing it is easy to show that

$$\begin{aligned} \nabla_X \cdot \dot{X} &= \nabla_\Gamma \cdot \dot{\Gamma} = \sum_i^N \left[\nabla_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \nabla_{\mathbf{p}_i} \cdot \dot{\mathbf{p}}_i \right] \\ &= \sum_i^N \left[\nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{p}_i} H - \nabla_{\mathbf{p}_i} \cdot \nabla_{\mathbf{r}_i} H - \xi \nabla_{\mathbf{p}_i} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \right] = -G\xi \end{aligned} \quad (4.38)$$

We now move to the calculation of the first term in the definition of the dissipation function:

$$\dot{X} \cdot \nabla_X \ln \rho_0(X) = \dot{X} \cdot \frac{1}{\rho_0} \nabla_X \rho_0(X) \quad (4.39)$$

We have

$$\frac{1}{\rho_0} \nabla_X \rho_0(X) = \frac{1}{\rho_0} \begin{pmatrix} \nabla_\Gamma \\ \nabla_\xi \end{pmatrix} \mathcal{Z}^{-1} \exp[-\beta H_0(\Gamma)] \exp\left[-\frac{G\tau_{\text{NH}}^2 \xi^2}{2}\right] = \begin{pmatrix} -\beta \nabla_\Gamma H_0(\Gamma) \\ -G\tau_{\text{NH}}^2 \xi \end{pmatrix} \quad (4.40)$$

so that

$$\dot{X} \cdot \frac{1}{\rho_0} \nabla_X \rho_0(X) = -\beta \dot{\Gamma} \cdot \nabla_\Gamma H_0(\Gamma) - G\tau_{\text{NH}}^2 \dot{\xi} \xi \quad (4.41)$$

The last term in the equation above is directly computed using the expression of $\dot{\xi}$ given in Eq. (4.33) to obtain

$$-G\tau_{\text{NH}}^2 \xi \dot{\xi} = -G\xi \delta K(\Gamma) \quad (4.42)$$

where $\delta K(\Gamma)$ has been defined in Eq. (4.33). To compute the first term of the RHS of Eq. (4.41) it is convenient to write the evolution equations for the physical variables, see Eq. (4.33), in the form

$$\begin{aligned} \dot{\mathbf{r}}_i &= \nabla_{\mathbf{p}_i} H_0 \\ \dot{\mathbf{p}}_i &= -\nabla_{\mathbf{r}_i} H_0 + q_i \mathbf{E} - \xi (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \end{aligned} \quad (4.43)$$

with H_0 defined in Eq. (3.18). Using the equations above, we have

$$\begin{aligned} -\beta \dot{\Gamma} \cdot \nabla_\Gamma H_0(\Gamma) &= -\beta \sum_i^N \left[\dot{\mathbf{r}}_i \cdot \nabla_{\mathbf{r}_i} H_0 + \dot{\mathbf{p}}_i \cdot \nabla_{\mathbf{p}_i} H_0 \right] \\ &= -\beta \sum_i^N \left[q_i \mathbf{E} \cdot \nabla_{\mathbf{p}_i} H_0 - \xi (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \cdot \nabla_{\mathbf{p}_i} H_0 \right] \end{aligned} \quad (4.44)$$

From the first of Eqs. (4.43) we have $\nabla_{\mathbf{p}_i} H_0 = \dot{\mathbf{r}}_i$, so that substituting in the first term of the RHS of Eq. (4.44) we get

$$-\beta \sum_i^N q_i \mathbf{E} \cdot \nabla_{\mathbf{p}_i} H_0 = -\beta \sum_i^N q_i \mathbf{E} \cdot \dot{\mathbf{r}}_i = -\beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E} \quad (4.45)$$

where the microscopic estimator of the electric current $\mathbf{J}(\Gamma) = \mathcal{V}^{-1} \sum_i^N q_i \dot{\mathbf{r}}_i$ has been introduced in Section 4.1.1, together with the box volume $\mathcal{V}$. The second term in the RHS of Eq. (4.44) is easily computed substituting $\nabla_{\mathbf{p}_i} H_0 = m_i^{-1} (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i))$

in its expression

$$\xi\beta \sum_i^N (\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i)) \cdot \nabla_{\mathbf{p}_i} H_0 = \xi\beta \sum_i^N \frac{(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i))^2}{m_i} = \xi\beta 2K(\Gamma) \quad (4.46)$$

where, in the last equality, we used the definition of the kinetic energy of the system, $K(\Gamma)$. Combining Eqs. (4.45) and (4.46), we then get $-\beta \dot{\Gamma} \cdot \nabla_{\Gamma} H_0(\Gamma) = -\beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E} + \xi\beta 2K(\Gamma)$. Using this result, together with Eq. (4.42), Eq. (4.41) can be rewritten as

$$\dot{X} \cdot \frac{1}{f_0} \nabla_X f_0(X) = -\beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E} + \xi\beta 2K(\Gamma) - G\xi \delta K(\Gamma) \quad (4.47)$$

Substituting Eqs. (4.47) and (4.38) in the definition of the dissipation function we get

$$\Omega^{(0)}(X) = -\dot{X} \cdot \nabla_X \ln f_0 - \nabla_X \cdot \dot{X} = \beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E} - \xi\beta 2K(\Gamma) + G\xi \delta K(\Gamma) + G\xi \quad (4.48)$$

Using the definitions of $\delta K(\Gamma)$ and of K^* and after trivial simplifications, we finally obtain

$$\Omega^{(0)}(X) = \beta \mathcal{V} \mathbf{J}(\Gamma) \cdot \mathbf{E} \quad (4.49)$$

which is the result. $\square$

The instantaneous dissipation is odd under Eqs. (4.35), as expected. In the upper panel of Figure 4.2 we show the behaviour of this quantity under $\mathcal{M}_{\text{ext}}^{(3)}$ (the behaviour under $\mathcal{M}_{\text{ext}}^{(4)}$ is the same). In the upper panel of Figure 4.2, $\Omega^{(0)}(t)$ is computed along a “forward” trajectory (in red), and along the “backward” trajectory (in blue) identified by $\mathcal{M}_{\text{ext}}^{(3)}$ for a molecular dynamics run of liquid NaCl with realistic interactions (the details of the simulation are provided in Section 4.3). More in detail, the two curves are obtained as follows: the dynamical system (4.33) is evolved for 500 fs (“forward” trajectory) and $\Omega^{(0)}(t)$ is computed along the trajectory. The operator $\mathcal{M}_{\text{ext}}^{(3)}$ is then applied to the final phase-space point obtained at the end of the evolution and the system is evolved again *via* Eqs. (4.33) for 500 fs starting from the transformed point (“backward” trajectory). Along this trajectory we compute again $\Omega^{(0)}(t)$. The odd parity of the dissipation is apparent from the upper panel of the figure. In the lower panel of Figure 4.2, we show the results for calculations in which the “backward” trajectory corresponds to standard time-reversal in the

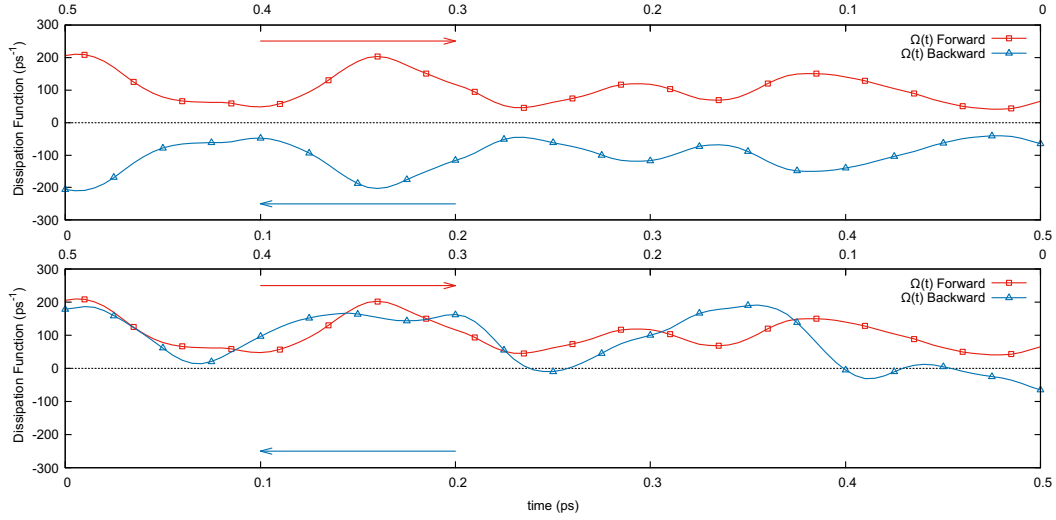


Fig. 4.2 Instantaneous dissipation function from Eq. (4.36) for 500fs of the “forward” evolution (red curve, open squares) and for 500fs of the “backward” trajectory (blue curve, open triangles) obtained *via* $\mathcal{M}_{\text{ext}}^{(3)}$ (upper panel). The opposite values of the dissipation demonstrate the odd signature under the generalized time-reversal transformation used. The same behavior is not observed when the backward trajectory is obtained applying $\mathcal{M}_{\text{ext}}^{(1)}$ (bottom panel) as the presence of the magnetic field breaks the symmetry of the system under this transformation. Results are for the nonequilibrium simulation set-up described in Section 4.3 for liquid NaCl.

Nosé-Hoover extended phase space. The figure clearly shows the lack of a specific signature for the dissipation under this transformation.

Having computed and characterised the dissipation function, we now move to discussing the associated transient FR, Eq. (2.25). Previous discussions of this relation in the presence of aligned static external electric and magnetic fields [6, 68, 69, 80], relied on standard time-reversal and employed averages with respect to equilibrium distributions associated to opposite magnetic fields. The existence of $\mathcal{M}_{\text{ext}}^{(3)}$ and $\mathcal{M}_{\text{ext}}^{(4)}$, however, enables to repeat the proof of the relation in a single-system picture. The proof follows the same steps as in the standard derivation, but invokes the new transformations instead of $\mathcal{M}^{(1)}$ where appropriate. In the next section, the validity of this single-system relation is illustrated *via* molecular dynamics simulations.

4.3 Simulation Results

In the following, the theoretical results presented in the previous section are illustrated and further validated *via* molecular dynamics simulations of a realistic model of liquid NaCl. The simulated system consists of 125 Na^+ and 125 Cl^- ions in a cubic box of side 20.9 Å. This corresponds to a physical density $\rho = 1.3793 \text{ g cm}^{-3}$ (or number density of 0.0275 Å^{-3}). The temperature is set at $T = 1550 \text{ K}$. Pair interactions are modeled using a generalised Huggins-Mayer, with the parameter proposed by Tosi and Fumi in Ref. [81] and ionic charges $q_{\text{Na}} = +1e$ and $q_{\text{Cl}} = -1e$ (with e elementary charge) for Sodium and Chloride, respectively. The magnetic field, directed along the z -axis, is set to the value of $\mathbf{B} = (0, 0, 50) \text{ cu}$ (cu stands for code units, a detailed description of these units and of the conversion factors used in the code can be found in Ref. [78]), corresponding to approximately $B_z = 5 \cdot 10^6 \text{ T}$. The intensity of the field — huge on experimental scales — is not unusual in the context of molecular dynamics simulations of interacting systems in external fields [66, 78, 82–84] and is dictated by the relative strength of the external to the interparticle forces. In particular, to observe appreciable effects of the external field in a reasonable simulation time, the ratio between the average interparticle forces and the average Lorentz forces has to be around one. The chosen intensity of the magnetic field results in a value of this ratio approximately equal to 0.2. Note that the magnetic field is part of the equilibrium Hamiltonian for our system. In the driven simulations, the electric field — also directed along the z -axis — is chosen to be $\mathbf{E} = (0, 0, 10) \text{ cu}$, corresponding approximately to $E_z = 1 \cdot 10^9 \text{ V m}^{-1}$. With this choice of the field, the ratio between the average Lorentz forces and the average electrical drift forces is *circa* 1.

In the simulations, periodic boundary conditions are enforced in all directions. The evolution equations (4.33) are integrated *via* a straightforward adaptation to the case of parallel (static and constant) magnetic and electric fields of the symplectic algorithm proposed in Ref. [78] for the evolution of a thermalized classical charged system in perpendicular fields. The long-range Coulombic interactions are treated through the Ewald summation method with an Ewald smearing parameters of $\alpha = 0.1$ in code units. A timestep of $\delta t = 0.25 \text{ fs}$ is chosen for all the simulations, ensuring that the Nosé conserved quantity remains essentially constant. The characteristic time of the generalized Nosé-Hoover thermostat is consequently set to 5 fs, in accordance with the prescriptions for the value of τ_{NH} given by Tuckerman in Ref. [51].

The results discussed in this work are obtained *via* the following simulation scheme. Initial conditions are fixed by placing the ions in a BCC lattice, and sampling initial velocities from the Maxwell-Boltzmann distribution corresponding to the target temperature. A preliminary equilibration run of 25 ps is then executed at null electric field to enforce the target temperature *via* the generalised Nosé-Hoover thermostat. Following this, a long equilibrium simulation ($\mathbf{E} = 0$) is performed to sample the equilibrium probability distribution ρ_0 . In this run, phase space configurations are sampled every 500 fs (a sufficient interval to ensure decorrelation) along a trajectory of total length equal to 25 ns, yielding a sample of $5 \cdot 10^4$ decorrelated configurations. From each of these, a nonequilibrium run is started where the electric field is switched on to the reference value of $\mathbf{E} = (0, 0, 10)$ cu. The average dissipation function is computed along each driven trajectory for a set of values of τ , ranging from 5 to 500 fs. Probability distribution functions (PDFs) for the possible values of the average dissipation at different times are then extracted through a histogramming process. Results for the PDFs are shown in Figure 4.3. From the probabilities of opposite values of the average dissipation functions, it is

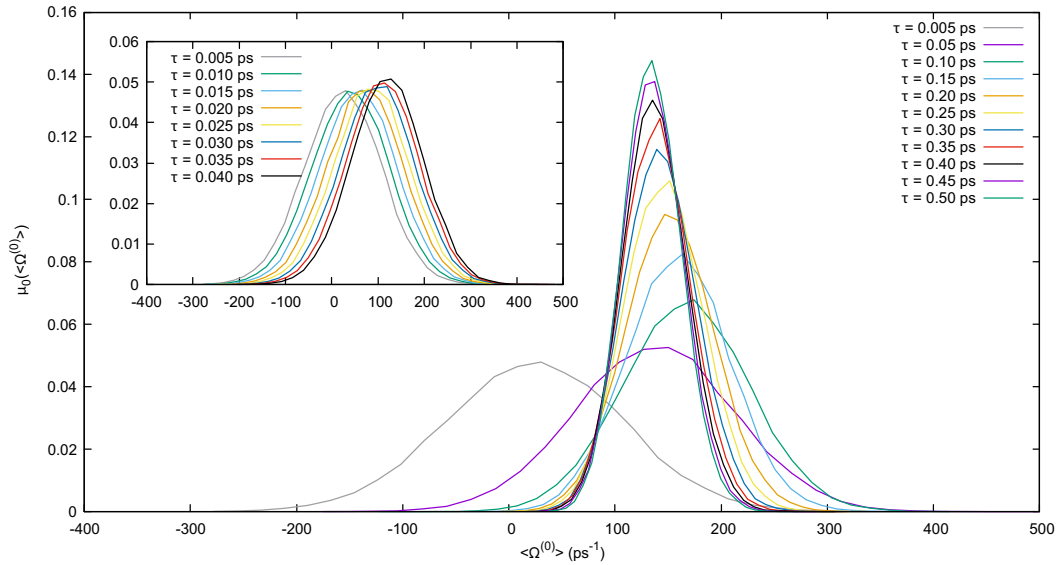


Fig. 4.3 Probability distribution functions (PDFs) estimated from the normalized histogram of the average dissipation function computed in nonequilibrium runs starting from $5 \cdot 10^4$ decorrelated equilibrium configurations for different values of τ . The main plot shows τ ranging from 0.005 to 0.5 ps, while the inset shows the trend for the low values of τ ranging from 0.005 to 0.04 ps, *i.e.* just after the switching on of the electric field that acts as the dissipative, nonequilibrium force.

possible to check Eq. (2.25) for the system under investigation. Results are reported in Figure 4.4 for τ ranging from 0.015 ps to 0.115 ps together with the corresponding theoretical expectations. In Table 4.1 the values for τ obtained by the exponential fits

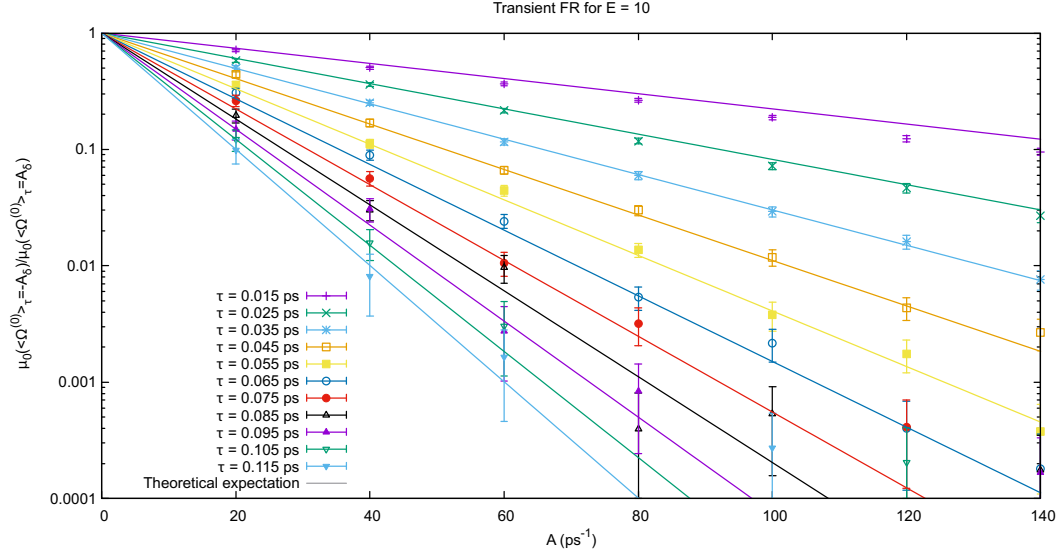


Fig. 4.4 Simulation results for the transient fluctuation relation from the simulations described in Section 4.3. The points represent the ratio between probabilities (on the y-axis) of obtaining opposite values of the average dissipation (A , on the x-axis) at different values of τ from Figure 4.3. The statistical error is obtained dividing the $5 \cdot 10^4$ nonequilibrium runs in 50 blocks of 10^3 runs each and computing the normalized histogram for each of them. The error reported on the plot is obtained from the standard deviation on the single bin of the histograms relative to different blocks. Points are the simulation results, while the solid lines represent theoretical expectations. Parameters obtained from exponential fits performed on this set of numerical results are reported in Table 4.1. Note the logarithmic scale on the y-axis.

performed on the numerical results are also reported together with their statistical errors.

4.4 Summary

We have shown that transient and steady-state FRs can be derived in the presence of a static and uniform magnetic field, without inversion of $\mathbf{B}$. This is possible because the dynamical system admits time-reversal symmetries that, at variance with the standard momentum reversal, are not violated by the field. Steady-state FRs require,

Table 4.1 Comparison between the expected value of τ and the one obtained from the exponential fits performed on the numerical results in Figure 4.4.

τ_{exp} (ps)	τ_{simul} (ps)
0.015	0.016 ± 0.001
0.025	0.026 ± 0.001
0.035	0.035 ± 0.001
0.045	0.044 ± 0.001
0.055	0.054 ± 0.001
0.065	0.063 ± 0.002
0.075	0.073 ± 0.002
0.085	0.086 ± 0.003
0.095	0.092 ± 0.003
0.105	0.103 ± 0.003
0.115	0.116 ± 0.005

as always, the decay of appropriate correlations. For $\mathbf{B} = 0$, this condition may be violated under strong drivings inducing ordered phases, in which back currents are suppressed [76, 77, 85]. The effect of magnetic fields on these correlations needs further investigation, but in the case discussed above they do not alter the validity of the FRs.

Use of a single magnetic field immediately improves the predictive power of the theory. For instance, consider a vector of n affinities $\mathcal{F}$, the corresponding n amounts of energy and matter exchanged between the reservoirs and a reference reservoir in a time interval $[0, t]$, Δx , and an n -dimensional vector of parameters λ . Let the cumulant generating function of $\mathcal{F}$ be defined by:

$$G_t(\lambda, \mathcal{F}; \mathbf{B}) = \int p_t(\Delta x, \mathcal{F}; \mathbf{B}) \exp(-\lambda \Delta x) d^n \Delta x$$

where p_t is the probability density of Δx derived from the grand-canonical ensemble, at fixed affinities and constant $\mathbf{B}$. Then, following the procedure for asymptotic (not necessarily steady-state) FRs [34], Ref. [69] defines the asymptotic generating function as $Q(\lambda, \mathcal{F}; \mathbf{B}) = -\lim_{t \rightarrow \infty} (1/t) \ln G_t(\lambda, \mathcal{F}; \mathbf{B})$. The corresponding cumulants, *i.e.* the derivatives of Q with respect to the components of λ evaluated at $\lambda = 0$, are then expanded as power series of $\mathcal{F}$, around $\mathcal{F} = 0$:

$$Q(\lambda, \mathcal{F}; \mathbf{B}) = \sum_{m,n=0}^{\infty} \frac{Q_{\alpha_1 \dots \beta_n}(\mathbf{B})}{m!n!} \lambda_{\alpha_1} \dots \lambda_{\alpha_m} \mathcal{F}_{\beta_1} \dots \mathcal{F}_{\beta_n}$$

with λ_i the i -th element of λ , $\mathcal{F}_j$ the j -th affinity and:

$$Q_{\alpha_1 \dots \beta_n}(\mathbf{B}) = \left. \frac{\partial^{m+n} Q}{\partial \lambda_{\alpha_1} \dots \partial \lambda_{\alpha_m} \partial \mathcal{F}_{\beta_1} \dots \partial \mathcal{F}_{\beta_n}} \right|_{\lambda=0; \mathcal{F}=0}$$

In terms of Q and of the reversibility based on the inversion of $\mathbf{B}$, the asymptotic FR is then written as $Q(\lambda, \mathcal{F}; \mathbf{B}) = Q(\mathcal{F} - \lambda, \mathcal{F}; -\mathbf{B})$ which imposes certain constraints on $Q_{\alpha_1 \dots \beta_n}$. For instance, Eq. (43) of Ref. [69] states that $Q_{\alpha_1 \dots \alpha_m}(0; \mathbf{B}) = (-1)^m Q_{\alpha_1 \dots \alpha_m}(0; -\mathbf{B})$. Using instead one of the valid symmetries of Eqs. (3.3) for the system under investigation, one also obtains $Q_{\alpha_1 \dots \alpha_m}(0; \mathbf{B}) = (-1)^m Q_{\alpha_1 \dots \alpha_m}(0; \mathbf{B})$ which entails the stronger result $Q_{\alpha_1 \dots \alpha_m}(0; \mathbf{B}) = 0$ for odd m and any $\mathbf{B}$.

The work presented in this chapter thus enables a reformulation of general results, based in particular on FRs *e.g.* Refs. [34, 69], lifting the prescription of opposite magnetic fields and restores the full predictive power of a number of statistical results for systems long considered as exceptions.

We have also demonstrated that the transient FR can be actually verified in nonequilibrium molecular dynamics simulations of particles subject to magnetic and electric fields, and which are Nosé-Hoover thermostatted. Although the applicability of generalized time-reversal symmetries implicitly implies the validity of the (transient) FR, based on the Nosé-Hoover canonical initial equilibrium distribution, the actual possibility of verifying it in a concrete, realistic simulation is not obvious. In the first place, to the best of our knowledge, this test has never been performed in presence of a magnetic field, which substantially modifies the dynamics of particles. In the second place, a verification of the FR may be hindered by the combination of scarce statistics, and noise in the signal. Indeed, while the thermal noise becomes irrelevant at long observation (averaging) times, such long times drastically reduce the statistics of negative dissipations. These simulations prove that the delicate balance allowing the verification of the FR, can be achieved for systems of moderately large size. Future developments will address the steady-state FR, which require further conditions to be verified, besides the time symmetry of the dynamics and of the initial phase-space probability distribution [34, 40, 44, 70].

Part II

Simulating Real Systems

Chapter 5

Motivation

The simulations carried out in Section 4.3 of Chapter 4 were performed using the so-called Rigid Ion Model (RIM) for the interaction potential of NaCl. In this model, the ions are considered to be spheres to which a charge — usually equal to the ionic charge — is associated.¹ This is a commonly adopted model and was well suited for initial investigations of charge transport in external magnetic field and, in particular, for exploring the generalized time-reversal symmetries introduced in this work. However, its accuracy is known to be unsatisfactory for many physical applications, in particular because it completely neglects effects of the polarization of the electronic cloud. These effects have been recognized to play an important role in the definition of structural properties of liquids and solids and they have been identified as the cause of deviations from experiments of transport and nonequilibrium properties of molten salts and ionic liquids [87, 88]. These limitations of RIM, apparent already in standard simulations, become critical when trying to assess the effects on transport of a magnetic field. For example, a RIM model of CaF_2 leads to the nonphysical result of an infinite values of the ionic Hall mobility [67]. This motivated our interest in investigating simulations of polarizable models of matter. Moreover, some of the force fields used for polarizable models violate one of the key hypotheses imposed to derive the generalized time-reversal transformations introduced in this work, *i.e.* the isotropy of the interaction potential. Indeed, functional forms are used that no longer depend on the module of the distance between pairs of particles but on the distance vector itself. This breaks all the time-reversal symmetries identified in the previous part, with the exception of the standard time-reversal symmetry when no magnetic field is acting on the system. On the other hand, there are hints that the transformations identified in this work could not saturate the possible time-reversal transformations that are satisfied by the system [59] and thus it would be of interest to investigate time-reversal-symmetry-based property, like Onsager, Kubo or fluctuation relations, for polarizable force fields in the presence of an external magnetic field.

Even in the case of zero magnetic field, the inclusion of polarization effects in force-field-based simulations is a challenging problem in computational chemistry. The standard approach is to introduce in the interaction potential appropriate sets of “classical” auxiliary dynamical variables that mimic changes in the electronic charge density. These variables might appear in the terms of the potential representing short-range repulsion, Coulomb and dispersion interactions, and their coupling to the

¹Some models try to include screening effect tuning the charge value to an effective charge, see for example Ref. [86]

ionic degrees of freedom is controlled by parameters obtained from comparisons with experiments or with accurate *ab initio* calculations. Consistent with their modelling of electrons, the auxiliary variables obey the condition that, in the adiabatically separated dynamics of the system, the total energy computed at the current ionic configuration is at a minimum with respect to these degrees of freedom. In the early stages of MD simulations, the computational cost of the available minimization procedures was not affordable by the available computational facilities and methods based on first-order approximations had been proposed and implemented [89, 90]. The method of Car and Parrinello [91], originally developed for *ab initio* simulations, was later readapted [92, 93] to enforce the adiabatic separation between the physical degrees of freedom and the additional variables used to represent the reorganization of the charge responsible for the dipole moment of the particles, providing an excellent, computationally cheap alternative to minimization schemes relying on self-consistent iterative loops. The increase of computational power made the direct tackling of the problem through self consistent cycles affordable and the use of these kinds of algorithms is the state of the art nowadays, in particular *via* efficient implementations of the conjugate-gradient algorithm.

In the following we propose an original approach developed in the framework of molecular dynamics of systems subject to holonomic constraints in the special case of mass-zero variables. The idea at the roots of the procedure is to interpret the minimum condition of the potential with respect to the additional variables as a set of holonomic constraints for the system in the space of the auxiliary degrees of freedom. As the derivation directly follows from the Lagrangian formulation of classical mechanics in the presence of constraints, all the formal properties of the dynamical system are automatically satisfied when appropriate numerical integration algorithms, such as Verlet and SHAKE, are used to numerically solve the equations of motion. The algorithm introduced in this approach is symplectic and time reversible in both sets of variables (physical and additional) and can be applied to every system where some kind of adiabatic separation has to be enforced. Moreover, it can be proven that the dynamics generated by the algorithm rigorously samples the Born-Oppenheimer probability distribution for the physical degrees of freedom. In the next chapters, the algorithm is derived in general and its formal properties are discussed and mathematically proven. Then its application is shown for polarizable models, for the fluctuating charge model used to simulate metal electrodes subject

to constant potential and for *ab initio* simulations in the framework of orbital-free density functional theory.

The inclusion of a magnetic field in this framework is a nontrivial problem and it remains a work in progress for what concerns this thesis. Indeed, the new algorithm is based on constrained dynamics in the presence of holonomic constraints, being the interaction potential independent from the time-derivative of the additional variables. The addition of an external magnetic field to the system, on the other hand, couples additional variables and their time-derivatives in the potential energy terms, leading to a nonholonomic condition to be satisfied. While it is possible to handle these constraints in some specific cases, a general algorithm for the solution of these kinds of constraints is still under investigation.

Chapter 6

Adiabatic Dynamics *via* Mass-Zero Constrained Evolution

In adiabatically separated systems, the evolution of a set of physical Degrees of Freedom (DoFs) is coupled to that of a separate, auxiliary set which is usually introduced to account for some specific physics or chemistry. The mass of the auxiliary DoFs is assumed much smaller than the mass(es) associated to the physical variables, and the adiabatic regime is fully achieved in the limit of null auxiliary mass. Due to the time-scale separation of the motion of the two sets of degrees of freedom, in this regime the physical variables evolve in a potential computed at the minimum with respect to the auxiliary variables. A pictorial representation of this situation in the case of nuclei (physical DoFs) and electrons (auxiliary DoFs) is shown in Figure 6.1. Depending on the specific system, additional (kinematic) conditions,

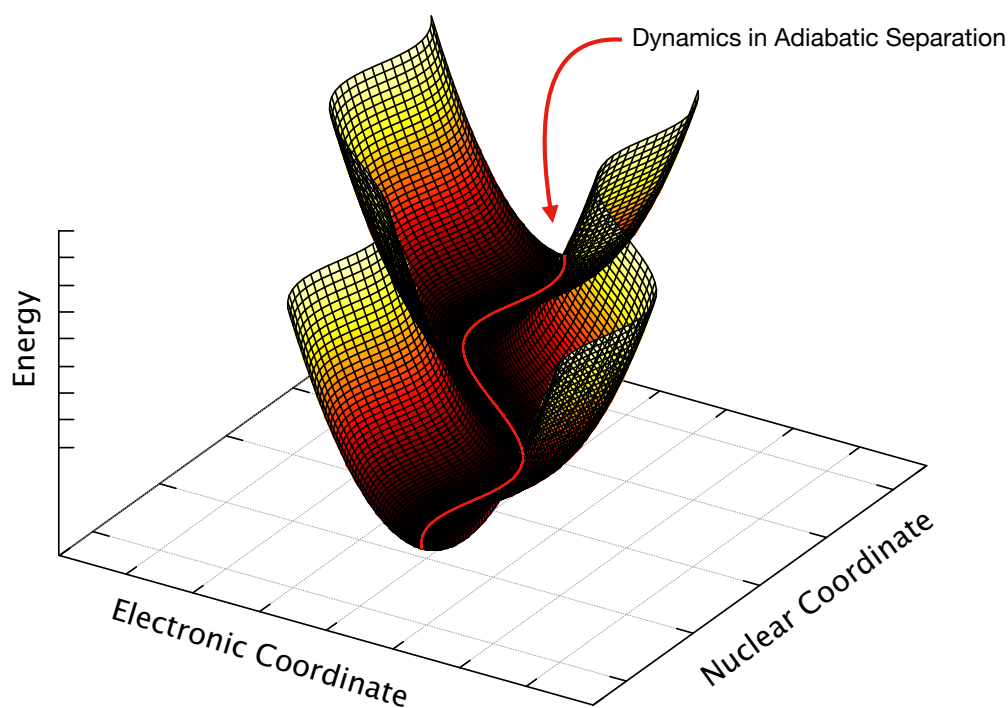


Fig. 6.1 Pictorial representation of adiabatic dynamics. The physical degrees of freedom are here represented by the nuclei, while the additional degrees of freedom are represented by the electrons. The motion is performed on the minimum of the energy with respect to the electronic coordinate at fixed nuclear positions.

such as orthonormality or sum rules, may have to be imposed on the auxiliary DoFs, affecting the minimum search. In molecular dynamics simulations, the choice of the algorithm to find the (free or conditioned) minimum is delicate. Typical schemes

adopted so far include iterative methods, such as conjugate-gradient [94, 95], extended Lagrangian schemes *à la* Car-Parrinello in which a small but finite mass is assigned to the auxiliary variables [92, 93] or, more recently, alternative *ad hoc* dynamics for the auxiliary variables like the so-called always stable predictor corrector approach [96, 97]. These methods, however, suffer from practical or conceptual limitations. Conjugate-gradient minimization is guaranteed to converge only in the case of a quadratic function to be minimized, and, for the general minimization problems typically associated with realistic condensed-phase models, can be unstable [98] or expensive [99] to fully converge. In Car-Parrinello propagation, it can be difficult or impossible to maintain adiabatic separation between the physical and auxiliary variables for sufficiently long simulation times [94] and the algorithm requires a very small timestep to integrate accurately the dynamics of the auxiliary variables. The always stable predictor corrector scheme is only approximately time reversible [96, 97] leading to energy drifts that are usually quenched *via* a Berendsen thermostat (thus raising questions on the ensemble sampled by the dynamics), and it contains system-dependent parameters that can only be determined by trial and error. In spite of several interesting and successful applications of the approaches mentioned above, these limitations justify efforts to develop new algorithms for adiabatic dynamics.

In recent work [23, 24], it has been proposed to enforce the minimum energy condition using constrained molecular dynamics [9]. In this approach, evolution equations for the physical and auxiliary DoFs are derived under the constraint that the derivatives of the Hamiltonian with respect to the auxiliary variables are zero along the trajectory of the physical DoFs. Consistent with the adiabatic prescription, this is achieved by writing the method of constraints in the special case of mass-zero constrained degrees of freedom [100]. This results in the possibility of writing down dynamical equations of motion for all the degrees of freedom of the system, keeping the adiabaticity rigorously enforced. This allows the use of standard techniques for the numerical integration of the evolution that maintain the formal property of the dynamical system, such as time reversibility and symplecticness. These formal properties guarantee exact energy conservation and stability of the evolution on the time scales and with the timestep of standard molecular dynamics for the physical DoFs without the use of thermostats.

The approach has then been extended to models where the auxiliary DoFs must satisfy additional conditions, such as specific normalization or orthogonality

requirements. This development enables, in particular, to adapt the method to the case of *first principles* molecular dynamics, but is relevant also for classical polarizable models, for example in connection with the global electroneutrality constraint in simulation of capacitors.

Having generalized the mechanics of the system, the question of the statistical mechanics associated with mass-zero constrained dynamics is discussed. As mentioned above, this approach entails an extended phase space in which both the physical and the auxiliary variables are treated as dynamical degrees of freedom. In the following, the probability density sampled in this extended phase space is derived, focusing in particular, on the marginal in the phase space of the physical variables, thus identifying unambiguously the full adiabatic limit for the probability associated to these degrees of freedom.

The chapter is organized as follows: In Section 6.1 the free variation problem is discussed and the equations of motion for the Mass-Zero constrained dynamics (MaZe) are given. The presence of additional kinematic conditions is discussed in Section 6.2. In Section 6.3 the statistical mechanics of MaZe is discussed through the probability distribution sampled by the dynamical system. It is shown that the distribution sampled is the Born-Oppenheimer one only when the adiabatic separation is rigorously enforced. Then, in Section 6.4 the algorithms used for the solution of the dynamics are discussed, laying down a general strategy for the numerical integration of the dynamical system in the framework of constrained molecular dynamics. In Section 6.5 it is shown how the numerical algorithm selected preserves the formal properties of classical mechanics, in particular time-reversibility and symplecticness even in the zero-mass limit. Finally, in Section 6.6 different methods for the solution of the equation of the constraints are described and discussed.

6.1 Free Variation Problem

Let us indicate with $\mathbf{R} \in \mathbb{R}^{3N}$ the coordinates associated with the N physical variables in the system, and with $s \in \mathbb{R}^M$ the M adiabatically separated auxiliary degrees of freedom introduced to represent specific properties of the system. The s variables may represent different types of degrees of freedom for different systems and models used to represent the same systems and their physical dimensions and number vary accordingly. We assume a form for the interaction potential described by the scalar

function $V(\mathbf{R}, s)$ where $V : \mathbb{R}^{3N} \times \mathbb{R}^M \rightarrow \mathbb{R}$. The dynamics of the system satisfies the following:

Definition 6.1 (Adiabatic condition). *The auxiliary variables, assumed of zero mass, adapt instantaneously to the position of the physical degrees of freedom so as to satisfy*

$$\sigma_\alpha(\mathbf{R}, s) \equiv \frac{\partial V(\mathbf{R}, s)}{\partial s_\alpha} = 0 \quad \alpha = 1, \dots, M \quad (6.1)$$

In the following, we indicate with $\hat{s}$ the values of the auxiliary variables satisfying the conditions above. Note that, due to the dependence of the potential on the physical degrees of freedom, $\hat{s} = \hat{s}(\mathbf{R})$. The evolution of the physical variables, of mass m_i , is then given by

$$m_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} V(\mathbf{R}, s) \Big|_{s=\hat{s}} \quad (6.2)$$

The key idea of the mass-zero constrained dynamics is to interpret Eq. (6.1) as a set of M holonomic constraints and derive the evolution equations for the overall constrained system. This is done most conveniently by assigning at first a finite fictitious¹ inertial “mass” μ_α to the auxiliary variables and considering the extended Lagrangian

$$L(\mathbf{R}, \dot{\mathbf{R}}, s, \dot{s}) = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{R}}_i^2 + \frac{1}{2} \sum_{\alpha=1}^M \mu_\alpha \dot{s}_\alpha^2 - V(\mathbf{R}, s) \quad (6.3)$$

together with Eq. (6.1) to define the generators of the dynamical system. The evolution equations are obtained through the method of the undetermined Lagrange multipliers solving the Euler-Lagrange equation given by

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_k} \right) - \frac{\partial L}{\partial q_k} = G_k \quad (6.4)$$

where we have indicated all the dynamical variables with the notation $\mathbb{R}^{3N+M} \ni q = (\mathbf{R}, s)$ and where the term G represents the constraint forces

$$G_k = - \sum_{\alpha=1}^M \lambda_\alpha \frac{\partial \sigma_\alpha}{\partial q_k} \quad (6.5)$$

The quantity $\lambda \in \mathbb{R}^M$ represents a set of time-dependent Lagrange multipliers that enforce the constraints σ .

¹Note that, depending on the physical dimensions of the auxiliary variables, the fictitious mass μ could have different units than those of a mass.

For the particular system defined by Eqs. (6.1) and (6.3) this yields

$$\begin{aligned} m_i \ddot{\mathbf{R}}_i &= -\nabla_{\mathbf{R}_i} V(\mathbf{R}, s) - \sum_{\beta=1}^M \lambda_{\beta} \nabla_{\mathbf{R}_i} \sigma_{\beta}(\mathbf{R}, s) \\ \mu_{\alpha} \ddot{s}_{\alpha} &= -\frac{\partial V(\mathbf{R}, s)}{\partial s_{\alpha}} - \sum_{\beta=1}^M \lambda_{\beta} \frac{\partial \sigma_{\beta}(\mathbf{R}, s)}{\partial s_{\alpha}} \end{aligned} \quad (6.6)$$

When full adiabatic separation is enforced, *i.e.* when the mass-zero limit is enforced for the additional degrees of freedom, the following theorem holds:

Theorem 6.1 (Mass-zero constrained dynamics). *In the limit of null fictitious masses, the equations of motion for the physical degrees of freedom become independent of the constraint forces. On the other hand, the equations of motion for the additional degrees of freedom only depends on constraint forces. In other words, the auxiliary variables, in the limit of zero auxiliary mass, are driven by the physical degrees of freedom.*

Proof. Eqs. (6.6) can be simplified by observing that the derivative of the potential in the second equation is the constraint itself, which is null due to the minimum condition. For simplicity, let us also assume that $\mu_{\alpha} = \mu \ \forall \alpha = 1, \dots, M$. The equation for the auxiliary degrees of freedom can then be rearranged as

$$\ddot{s}_{\alpha} = - \sum_{\beta=1}^M \frac{\lambda_{\beta}}{\mu} \frac{\partial \sigma_{\beta}(\mathbf{R}, s)}{\partial s_{\alpha}} \quad (6.7)$$

We now consider the limit $\mu \rightarrow 0$. The equation above shows that, in order for the auxiliary variables to have finite acceleration, the ratio $\gamma_{\alpha} = \lim_{\mu \rightarrow 0} \frac{\lambda_{\alpha}}{\mu}$ must remain finite. This implies that the Lagrange multipliers λ_{α} are proportional to μ . In the limit then, the constraint forces on the physical degrees of freedom vanish and we have

$$\begin{aligned} m_i \ddot{\mathbf{R}}_i &= -\nabla_{\mathbf{R}_i} V(\mathbf{R}, s) \\ \ddot{s}_{\alpha} &= - \sum_{\beta=1}^M \gamma_{\beta} \frac{\partial \sigma_{\beta}(\mathbf{R}, s)}{\partial s_{\alpha}} \end{aligned} \quad (6.8)$$

which proves the theorem. $\square$

Eq. (6.8) is the main result of Ref. [23] and defines the mass-zero constrained dynamics. It shows that, consistent with Eq. (6.2), the evolution of the physical

variables does not depend directly on the constraints. On the other hand, since the dynamics of the free s variables is totally controlled by the constraint forces, they directly satisfy the minimum condition. This implies that Eq. (6.1) is automatically fulfilled also in the first of Eqs. (6.8) which is then equivalent to Eq. (6.2). The system above is an exact, classical evolution for all degrees of freedom that rigorously enforces the zero-mass limit, and therefore leads to full adiabatic separation for the auxiliary variables. The numerical integration of these equations can be performed with any standard algorithm for molecular dynamics in the presence of constraints. Specific examples are provided in Section 6.4.

6.2 The Presence of Additional Conditions

So far, we have assumed that the only conditions to be satisfied by the auxiliary DoFs were those expressed by Eq. (6.1). While this is the case in many applications, there are important problems in which additional requirements are placed on these degrees of freedom. To demonstrate how mass-zero constrained method can be extended in the presence of additional kinematic conditions on the adiabatic variables, let us assume that the additional variables have to satisfy the C additional equality relations

$$f_t(s) = 0 \quad (t = 1, \dots, C) \quad (6.9)$$

with no further specification on the functional form of $f_t(s)$ with the exception of the commonly assumed continuity and differentiability of the function at least twice. Eq. (6.9) implies that not all variations of the s are independent, and this must be accounted for in the statement of the minimum condition. This can be done most conveniently using, once again, the Lagrange multiplier method by introducing the auxiliary function

$$W(\mathbf{R}, s, \mathbf{v}) \equiv V(\mathbf{R}, s) + \sum_{t=1}^C v_t f_t(s) \quad (6.10)$$

where $\mathbf{v}$ are the Lagrange multipliers associated with the additional conditions. The solution $\hat{s}$ for s satisfying Eq. (6.9) is then given by the stationary point $(\hat{s}, \hat{\mathbf{v}})$ of

$W(\mathbf{R}, s, \mathbf{v})$ [101, 102]. This leads to the $M + C$ conditions

$$\begin{aligned}\sigma_\alpha(\mathbf{R}, s, \mathbf{v}) &= \frac{\partial W(\mathbf{R}, s, \mathbf{v})}{\partial s_\alpha} = 0 \quad (\alpha = 1, \dots, M) \\ \sigma_{M+\iota}(\mathbf{R}, s, \mathbf{v}) &= \frac{\partial W(\mathbf{R}, s, \mathbf{v})}{\partial v_\iota} = 0 \quad (\iota = 1, \dots, C).\end{aligned}\tag{6.11}$$

Note that, as usual in the Lagrange multiplier scheme, the last set of equations above represents in fact the additional conditions Eq. (6.9), now obtained as a result of an optimization problem in the space that includes the Lagrange multipliers $\mathbf{v}$ as additional variables. Within this framework, we can proceed in analogy with the previous section by defining the following extended Lagrangian, which includes also $\mathbf{v}$ as auxiliary variables,

$$L(\mathbf{R}, \dot{\mathbf{R}}, s, \dot{s}, \mathbf{v}, \dot{\mathbf{v}}) = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{R}}_i^2 + \frac{1}{2} \mu_s \sum_{\alpha=1}^M \dot{s}_\alpha^2 + \frac{1}{2} \sum_{\iota=1}^C \mu_v \dot{v}_\iota^2 - W(\mathbf{R}, s, \mathbf{v}), \tag{6.12}$$

and interpreting Eq. (6.11) as $M + C$ holonomic constraints on the system. Note that, at variance with the previous section, we have now introduced two finite fictitious masses μ_s and μ_v related to the auxiliary variables associated with the additional variables s and with the Lagrange multipliers $\mathbf{v}$, respectively. This is necessary, at least, to guarantee the correct physical dimensions of the different terms in the new Lagrangian. More on the relationship between these two masses is discussed below. As in the previous section we are assuming, for simplicity, that the masses for each set of additional variables are equal.

Corollary 6.1. *In the presence of additional kinematic constraints, the set of Lagrange multipliers $\mathbf{v}$ associated to the additional conditions, behave, in the equations of motion of the dynamical system, like auxiliary degrees of freedom. A homogeneity parameter (in general one per additional condition) κ needs to be introduced when taking the adiabatic limit.*

Proof. To enforce adiabatic separation rigorously, the two auxiliary masses, μ_s and μ_v , must be sent to zero and, for this limit to be well defined, it has to be taken in a homogeneous way. To this end we set $\mu_v \equiv \mu_s / \kappa$ with κ a constant of dimensions given by the ratio of the masses. We then proceed as in the previous section to obtain,

in the limit $\mu_s \rightarrow 0$

$$\begin{aligned} m_i \ddot{\mathbf{R}}_i &= -\nabla_{\mathbf{R}_i} V(\mathbf{R}, s), \\ \ddot{s}_\alpha &= -\sum_{\beta=1}^{M+C} \gamma_\beta \frac{\partial \sigma_\beta(\mathbf{R}, s, \mathbf{v})}{\partial s_\alpha}, \\ \ddot{v}_l &= -\sum_{\beta=1}^{M+C} \gamma_\beta \kappa \frac{\partial \sigma_\beta(\mathbf{R}, s, \mathbf{v})}{\partial v_l} \end{aligned} \quad (6.13)$$

where, in the first equation, we have used the fact that $\nabla_{\mathbf{R}_i} W(\mathbf{R}, s, \mathbf{v}) = \nabla_{\mathbf{R}_i} V(\mathbf{R}, s)$, while the first derivatives of W in the second and third line vanish due to the stationary point conditions. $\square$

We are again in the situation in which we have dynamical equations of motion for the extended space of dynamical variables $(\mathbf{R}, s, \mathbf{v})$ where the adiabatic separation between the massive and massless particles is enforced rigorously. As in the previous section, the numerical integration of this system can be performed using standard algorithms for constrained molecular dynamics.

Remark 6.1. *The potential energy term $W(\mathbf{R}, s, \mathbf{v})$ is linear in $\mathbf{v}$ with the consequence that the second derivative of W is zero in this direction. Thus the matrix of second derivatives at the stationary point $(\hat{s}, \hat{\mathbf{v}})$ is nonpositive definite and $(\hat{s}, \hat{\mathbf{v}})$ is a saddle point.*

However, this does not hinder the use of constrained molecular dynamics since the latter only requires the existence of a solution for the constraint equations $\sigma_\alpha = 0 \forall \alpha$, not the positive definiteness of the matrix of second derivatives. Note that the particular form assumed by the additional conditions $f_l(s)$ does not play any role in the discussion.

6.3 Statistical Mechanics of the Mass-Zero Constrained Evolution

We now investigate the probability density sampled by the dynamical system discussed in the previous sections. This is an interesting question as the use of constraints may induce a nontrivial metrics in the phase space of the system [103] and

appropriate reweighting of averaging might then be necessary when computing statistical properties [104] in the physical phase space. To set the stage for the discussion, and proceeding in analogy with [10], it is useful to introduce the change of variables²

$$\begin{aligned} \mathbf{R}_i &\mapsto \boldsymbol{\rho}_i = \mathbf{R}_i \\ s_\alpha &\mapsto \sigma_\alpha = \sigma_\alpha(\mathbf{R}, s) \end{aligned} \quad (6.14)$$

Observables computed in the new variables will be denoted in calligraphic font. In the following, we shall also use the notation $\mathbf{v} = (\boldsymbol{\rho}, \sigma)$ where $\boldsymbol{\rho} = \{\boldsymbol{\rho}_1, \dots, \boldsymbol{\rho}_N\}$ and $\sigma = \{\sigma_1, \dots, \sigma_M\}$. The Lagrangian in the new set of coordinates is obtained from Eq. (6.3) as $\mathcal{L}(\mathbf{v}, \dot{\mathbf{v}}) = L(\mathbf{R}(\mathbf{v}), s(\mathbf{v}), \dot{\mathbf{R}}(\mathbf{v}, \dot{\mathbf{v}}), \dot{s}(\mathbf{v}, \dot{\mathbf{v}}))$. The Hamiltonian of the system in the new coordinates is then derived *via* a standard Legendre transform and can be written as

$$\mathcal{H}(\mathbf{v}, \boldsymbol{\pi}^{\mathbf{v}}) = \mathcal{K}(\mathbf{v}, \boldsymbol{\pi}^{\mathbf{v}}) + \mathcal{V}(\mathbf{v}) \equiv \frac{1}{2} \boldsymbol{\pi}^{\mathbf{v}^T} \mathbb{M}^{-1}(\mathbf{v}) \boldsymbol{\pi}^{\mathbf{v}} + \mathcal{V}(\mathbf{v}) \quad (6.15)$$

where $\mathcal{K}(\mathbf{v}, \boldsymbol{\pi}^{\mathbf{v}})$ is the kinetic energy in the new variables, and the momentum $\boldsymbol{\pi}^{\mathbf{v}}$ is given by

$$\boldsymbol{\pi}_k^{\mathbf{v}} = \frac{\partial \mathcal{L}(\mathbf{v}, \dot{\mathbf{v}})}{\partial \dot{\mathbf{v}}_k} = \begin{cases} \boldsymbol{\pi}_i^{\boldsymbol{\rho}} = \nabla_{\dot{\boldsymbol{\rho}}_i} \mathcal{L}(\boldsymbol{\rho}, \dot{\boldsymbol{\rho}}, \sigma, \dot{\sigma}) & \text{if } k = 1, \dots, 3N \\ \pi_\alpha^\sigma = \frac{\partial \mathcal{L}(\boldsymbol{\rho}, \dot{\boldsymbol{\rho}}, \sigma, \dot{\sigma})}{\partial \dot{\sigma}_\alpha} & \text{if } k = 3N + 1, \dots, 3N + M \end{cases} \quad (6.16)$$

(as always, $i = 1, \dots, N$ and $\alpha = 1, \dots, M$) and $\mathbb{M}^{-1}(\mathbf{v})$ is the inverse of the metric matrix associated with the new variables

$$\mathbb{M}_{kk'} = \sum_{i=1}^N m_i \frac{\partial \mathbf{R}_i}{\partial \mathbf{v}_k} \cdot \frac{\partial \mathbf{R}_i}{\partial \mathbf{v}_{k'}} + \sum_{\alpha=1}^M \mu \frac{\partial s_\alpha}{\partial \mathbf{v}_k} \frac{\partial s_\alpha}{\partial \mathbf{v}_{k'}} \quad (6.17)$$

The metric matrix and its inverse can be conveniently expressed in block form as

$$\mathbb{M} = \begin{bmatrix} \mathbb{A} & \mathbb{B} \\ \mathbb{B}^T & \mathbb{I} \end{bmatrix} \quad \text{with inverse} \quad \mathbb{M}^{-1} = \begin{bmatrix} \Delta & \mathbb{E} \\ \mathbb{E}^T & \mathbb{Z} \end{bmatrix} \quad (6.18)$$

²We avoid considering also the $\mathbf{v}$ variables for simplicity of notation but — as discussed at length in Section 6.2 — the extension to the case where additional conditions are present is straightforward, as the $\mathbf{v}$ variables behave exactly as the s variables with the trivial inclusion of the homogeneity parameter κ .

where $\mathbb{A}$ and $\mathbb{\Delta}$ are $3N \times 3N$ matrices, $\mathbb{B}$ and $\mathbb{E}$ are $3N \times M$ matrices, and $\mathbb{F}$ and $\mathbb{Z}$ are $M \times M$ matrices, whose expressions are given by

$$\begin{aligned}
 \mathbb{A}_{jj'} &= \sum_{i=1}^N m_i \frac{\partial \mathbf{R}_i}{\partial \boldsymbol{\rho}_j} \cdot \frac{\partial \mathbf{R}_i}{\partial \boldsymbol{\rho}_{j'}} + \sum_{\alpha=1}^M \mu \frac{\partial s_\alpha}{\partial \boldsymbol{\rho}_j} \frac{\partial s_\alpha}{\partial \boldsymbol{\rho}_{j'}} \\
 &= m_j \delta_{jj'} + \sum_{\alpha=1}^M \mu \frac{\partial s_\alpha}{\partial \boldsymbol{\rho}_j} \frac{\partial s_\alpha}{\partial \boldsymbol{\rho}_{j'}} \quad \text{for } j, j' = 1, \dots, N \\
 \mathbb{B}_{j\beta} &= \sum_{i=1}^N m_i \frac{\partial \mathbf{R}_i}{\partial \boldsymbol{\rho}_j} \cdot \frac{\partial \mathbf{R}_i}{\partial \boldsymbol{\sigma}_\beta} + \sum_{\alpha=1}^M \mu \frac{\partial s_\alpha}{\partial \boldsymbol{\rho}_j} \frac{\partial s_\alpha}{\partial \boldsymbol{\sigma}_\beta} \\
 &= \sum_{\alpha=1}^M \mu \frac{\partial s_\alpha}{\partial \boldsymbol{\rho}_j} \frac{\partial s_\alpha}{\partial \boldsymbol{\sigma}_\beta} \quad \text{for } j = 1, \dots, N, \beta = 1, \dots, M \\
 \mathbb{F}_{\beta\beta'} &= \sum_{i=1}^N m_i \frac{\partial \mathbf{R}_i}{\partial \boldsymbol{\sigma}_\beta} \cdot \frac{\partial \mathbf{R}_i}{\partial \boldsymbol{\sigma}_{\beta'}} + \sum_{\alpha=1}^M \mu \frac{\partial s_\alpha}{\partial \boldsymbol{\sigma}_\beta} \frac{\partial s_\alpha}{\partial \boldsymbol{\sigma}_{\beta'}} \\
 &= \sum_{\alpha=1}^M \mu \frac{\partial s_\alpha}{\partial \boldsymbol{\sigma}_\beta} \frac{\partial s_\alpha}{\partial \boldsymbol{\sigma}_{\beta'}} \quad \text{for } \beta, \beta' = 1, \dots, M
 \end{aligned} \tag{6.19}$$

and

$$\begin{aligned}
 \mathbb{\Delta}_{jj'} &= \sum_{i=1}^N \frac{1}{m_i} \nabla_{\mathbf{R}_i} \boldsymbol{\rho}_j \cdot \nabla_{\mathbf{R}_i} \boldsymbol{\rho}_{j'} \quad \text{for } j, j' = 1, \dots, N \\
 \mathbb{E}_{j\beta} &= - \sum_{i=1}^N \frac{1}{m_i} \nabla_{\mathbf{R}_i} \boldsymbol{\rho}_j \cdot \nabla_{\mathbf{R}_i} \boldsymbol{\sigma}_\beta \quad \text{for } j = 1, \dots, N, \beta = 1, \dots, M \\
 \mathbb{Z}_{\beta\beta'} &= \sum_{i=1}^N \frac{1}{m_i} \nabla_{\mathbf{R}_i} \boldsymbol{\sigma}_\beta \cdot \nabla_{\mathbf{R}_i} \boldsymbol{\sigma}_{\beta'} + \sum_{\alpha=1}^M \frac{1}{\mu} \frac{\partial \boldsymbol{\sigma}_\beta}{\partial s_\alpha} \frac{\partial \boldsymbol{\sigma}_{\beta'}}{\partial s_\alpha} \quad \text{for } \beta, \beta' = 1, \dots, M
 \end{aligned} \tag{6.20}$$

In Eqs. (6.19) and (6.20) note the difference between the two notations

$$\nabla_{\mathbf{u}} \mathbf{v} \cdot \nabla_{\mathbf{u}} \mathbf{v} = \sum_{\gamma \in \{x, y, z\}} \frac{\partial v_\alpha}{\partial u_\gamma} \frac{\partial v_\beta}{\partial u_\gamma} \quad \text{and} \quad \frac{\partial \mathbf{v}}{\partial \mathbf{u}} \cdot \frac{\partial \mathbf{v}}{\partial \mathbf{u}} = \sum_{\gamma \in \{x, y, z\}} \frac{\partial v_\gamma}{\partial u_\alpha} \frac{\partial v_\gamma}{\partial u_\beta} \tag{6.21}$$

which both represent 3×3 matrixes. The Hamiltonian in Eq. (6.15) can be evaluated explicitly on the constrained hypersurface in the full phase space. To that end, it is important to recognize that, since the set of constraints in Eq. (6.1) have to be fulfilled at all times, the additional conditions $\dot{\boldsymbol{\sigma}} = 0$ hold. This condition is sometimes referred to as the *hidden* constraint associated to the problem. The definition $\dot{\mathbf{v}} = \mathbb{M}^{-1} \boldsymbol{\pi}^v$ then implies that, when the constraints are imposed, the

momenta π^σ must satisfy

$$\hat{\pi}^\sigma = -\tilde{\mathbb{Z}}^{-1}\tilde{\mathbb{E}}^T \cdot \boldsymbol{\pi}^\rho \quad (6.22)$$

where the tildes indicate that all matrices are evaluated at $\sigma = 0$. The constrained motion then occurs on the hypersurface $\sigma = 0$, $\pi^\sigma = \hat{\pi}^\sigma$ and we have

$$\mathcal{H}(\boldsymbol{\rho}, \sigma = 0, \boldsymbol{\pi}^\rho, \pi^\sigma = \hat{\pi}^\sigma) = \frac{1}{2}(\boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) \begin{bmatrix} \tilde{\mathbb{A}} & \tilde{\mathbb{E}} \\ \tilde{\mathbb{E}}^T & \tilde{\mathbb{Z}} \end{bmatrix} \begin{pmatrix} \boldsymbol{\pi}^\rho \\ \hat{\pi}^\sigma \end{pmatrix} + \mathcal{V}(\boldsymbol{\rho}, \sigma = 0) \quad (6.23)$$

The Hamiltonian can be written in a more suitable form by observing that the block expression of the product $\mathbb{M}\mathbb{M}^{-1} = \mathbb{1}$ imposes $\tilde{\mathbb{A}}\tilde{\mathbb{A}} + \tilde{\mathbb{B}}\tilde{\mathbb{E}}^T = \mathbb{1}$ and $\tilde{\mathbb{A}}\tilde{\mathbb{E}} + \tilde{\mathbb{B}}\tilde{\mathbb{Z}} = 0$. These two relationships, in turn, imply $\tilde{\mathbb{A}} - \tilde{\mathbb{E}}\tilde{\mathbb{Z}}^{-1}\tilde{\mathbb{E}}^T = \tilde{\mathbb{A}}^{-1}$ so that

$$\begin{aligned} \mathcal{H}(\boldsymbol{\rho}, \sigma = 0, \boldsymbol{\pi}^\rho, \pi^\sigma = \hat{\pi}^\sigma) &= \frac{1}{2}[\boldsymbol{\pi}^{\rho T}(\tilde{\mathbb{A}} - \tilde{\mathbb{E}}\tilde{\mathbb{Z}}^{-1}\tilde{\mathbb{E}}^T)\boldsymbol{\pi}^\rho] + \mathcal{V}(\boldsymbol{\rho}, \sigma = 0) \\ &= \frac{1}{2}\boldsymbol{\pi}^{\rho T}\tilde{\mathbb{A}}^{-1}\boldsymbol{\pi}^\rho + \mathcal{V}(\boldsymbol{\rho}, \sigma = 0) \end{aligned} \quad (6.24)$$

We are now all set to prove the following

Theorem 6.2 (Marginal probability in physical space sampled by MaZe). *The marginal probability in the space of the physical degrees of freedom of the microcanonical distribution sampled by the mass-zero constrained dynamics is the Born-Oppenheimer probability distribution, implicitly defined by the expression of the average value of an observable $\mathcal{O}$*

$$\langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}_1} \int d^{3N}R d^{3N}\pi^R O(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^R, \hat{\pi}^\sigma = 0) \delta(H(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^R, \hat{\pi}^\sigma = 0) - E) \quad (6.25)$$

if the adiabatic separation between physical and auxiliary variables is enforced rigorously.

Proof. The microcanonical partition function in the full phase space $(\boldsymbol{\rho}, \sigma, \boldsymbol{\pi}^\rho, \pi^\sigma)$ can be written as

$$\mathcal{Z} = \int d^{3N}\rho d^{3N}\pi^\rho d^M\sigma d^M\pi^\sigma \delta^M(\sigma) \delta^M(\pi^\sigma - \hat{\pi}^\sigma) \delta(\mathcal{H}(\boldsymbol{\rho}, \sigma, \boldsymbol{\pi}^\rho, \pi^\sigma) - E) \quad (6.26)$$

E being the constant value of the energy at which the motion occurs, while the expression of the microcanonical average of an observable $\mathcal{O}$ is given by

$$\begin{aligned} \langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}} \int d^{3N} \rho d^{3N} \pi^\rho d^M \sigma d^M \pi^\sigma \delta^M(\sigma) \delta^M(\pi^\sigma - \hat{\pi}^\sigma) \\ \times \mathcal{O}(\boldsymbol{\rho}, \boldsymbol{\sigma}, \boldsymbol{\pi}^\rho, \pi^\sigma) \delta(\mathcal{H}(\boldsymbol{\rho}, \boldsymbol{\sigma}, \boldsymbol{\pi}^\rho, \pi^\sigma) - E) \end{aligned} \quad (6.27)$$

The expression above can be simplified by first integrating over the π^σ variables

$$\langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}'} \int d^{3N} \rho d^{3N} \pi^\rho d^M \sigma d^M \pi^\sigma \delta^M(\sigma) \mathcal{O}(\boldsymbol{\rho}, \boldsymbol{\sigma}, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) \delta(\mathcal{H}(\boldsymbol{\rho}, \boldsymbol{\sigma}, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) - E) \quad (6.28)$$

and then performing the change of variables $\sigma_\alpha \mapsto s_\alpha$, $\boldsymbol{\rho}_i \mapsto \mathbf{R}_i$ to obtain at first

$$\begin{aligned} \langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}'} \int d^{3N} R d^{3N} \pi^\rho d^M s |J(\mathbf{R})| \delta^M(\sigma(\mathbf{R}, s)) \\ \times \mathcal{O}(\mathbf{R}, \sigma(\mathbf{R}, s), \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) \delta(\mathcal{H}(\mathbf{R}, \sigma(\mathbf{R}, s), \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) - E) \end{aligned} \quad (6.29)$$

where $|J(\mathbf{R})|$ is the Jacobian of the coordinate transformation, which reduces to $\det \left[\frac{\partial \sigma}{\partial s} \right]$. Then, making the dependence on s of the delta explicit, we get

$$\begin{aligned} \langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}'} \int d^{3N} R d^{3N} \pi^\rho d^M s |J(\mathbf{R})| |J(\mathbf{R})|^{-1} \delta^M(s - \hat{s}(\mathbf{R})) \\ \times O(\mathbf{R}, s, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) \delta(H(\mathbf{R}, s, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) - E) \end{aligned} \quad (6.30)$$

where we have $O(\mathbf{R}, s, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) = \mathcal{O}(\mathbf{R}, \sigma(\mathbf{R}, s), \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma)$. In this last equality we have used the properties of the delta of a vector function of the integration variable to express the constraint condition directly as a function of the s , with $\hat{s}(\mathbf{R})$ such that $\sigma(\mathbf{R}, \hat{s}) = 0$ (we assume, as commonly done in the Born-Oppenheimer framework that this expression has, for any $\mathbf{R}$, a single root). Finally, performing the integral over the s variables, and noting that the product of Jacobians in the integrand simplifies, we obtain

$$\langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}'} \int d^{3N} R d^{3N} \pi^\rho O(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) \delta(H(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) - E) \quad (6.31)$$

where (see Eq. (6.24))

$$H(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^\rho, \hat{\pi}^\sigma) = \frac{1}{2} \boldsymbol{\pi}^{\rho T} \tilde{\mathbb{A}}^{-1} \boldsymbol{\pi}^\rho + V(\mathbf{R}, \hat{s}) \quad (6.32)$$

Let us now consider the limit $\mu \rightarrow 0$ of the expressions above. To set the stage, observe that, based on the definition in Eqs. (6.19) and (6.20), we can conveniently rewrite

$$\tilde{\mathbb{A}} = \mathbb{D} + \mu \tilde{\mathbb{R}} = \mathbb{D} \left[\mathbb{1} + \mu \mathbb{D}^{-1} \tilde{\mathbb{R}} \right] \quad (6.33)$$

where $\mathbb{D}_{jj'} = m_j \delta_{jj'}$ and $\tilde{\mathbb{R}}_{jj'} = \sum_{\alpha=1}^M \frac{\partial s_{\alpha}}{\partial \mathbf{p}_j} \cdot \frac{\partial s_{\alpha}}{\partial \mathbf{p}_{j'}}$ so that

$$\tilde{\mathbb{A}}^{-1} = \left[\mathbb{1} + \mu \mathbb{D}^{-1} \tilde{\mathbb{R}} \right]^{-1} \mathbb{D}^{-1} \quad (6.34)$$

Furthermore, the relation $\boldsymbol{\pi}^v = \mathbb{M} \dot{\mathbf{v}}$ implies, $\boldsymbol{\pi}^p = \mathbb{A} \cdot \dot{\mathbf{p}} + \mathbb{B} \dot{\boldsymbol{\sigma}}$ giving, on the constrained hypersurface

$$\boldsymbol{\pi}^p = \tilde{\mathbb{A}} \cdot \dot{\mathbf{p}} = \tilde{\mathbb{A}} \cdot \dot{\mathbf{R}} \quad (6.35)$$

where in the last equality we used $\dot{\mathbf{p}} = \dot{\mathbf{R}}$, as implied by Eq. (6.14). Finally, from $\mathbb{M} \mathbb{M}^{-1} = \mathbb{1}$, the identities $\tilde{\mathbb{A}} \tilde{\mathbb{E}} + \tilde{\mathbb{B}} \tilde{\mathbb{Z}} = 0$ and $\tilde{\mathbb{B}}^T \tilde{\mathbb{E}} + \tilde{\mathbb{F}} \tilde{\mathbb{Z}} = \mathbb{1}$ follow for the involved submatrixes. Using these identities, we obtain

$$\tilde{\mathbb{Z}}^{-1} = \tilde{\mathbb{F}} - \tilde{\mathbb{B}}^T \tilde{\mathbb{A}}^{-1} \tilde{\mathbb{B}} \quad (6.36)$$

so that

$$\begin{aligned} \hat{\boldsymbol{\pi}}^{\sigma} &= -\tilde{\mathbb{Z}}^{-1} \tilde{\mathbb{E}}^T \cdot \boldsymbol{\pi}^p \\ &= \left[\tilde{\mathbb{F}} - \tilde{\mathbb{B}}^T \tilde{\mathbb{A}}^{-1} \tilde{\mathbb{B}} \right] \tilde{\mathbb{E}}^T \cdot \boldsymbol{\pi}^p \end{aligned} \quad (6.37)$$

We can now take the limit $\mu \rightarrow 0$ by observing first that $\tilde{\mathbb{F}}$ and $\tilde{\mathbb{B}}$ are proportional to μ and therefore vanish in the limit, while $\lim_{\mu \rightarrow 0} \tilde{\mathbb{A}} = \mathbb{D}$. In the zero auxiliary mass limit then, $\hat{\boldsymbol{\pi}}^{\sigma} = 0$ and the Hamiltonian of the system becomes

$$H(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^R, \hat{\boldsymbol{\pi}}^{\sigma} = 0) = \frac{1}{2} \boldsymbol{\pi}^{R^T} \mathbb{D}^{-1} \boldsymbol{\pi}^R + V(\mathbf{R}, \hat{s}) \quad (6.38)$$

with $\mathbb{D}^{-1} = \frac{1}{m_j} \delta_{jj'}$ and where we have used the fact that, from Eq. (6.35), in the null auxiliary mass limit, $\boldsymbol{\pi}^p = \mathbb{D} \dot{\mathbf{R}} = \boldsymbol{\pi}^R$. Substituting in the expression for the average, we obtain

$$\langle \mathcal{O} \rangle = \frac{1}{\mathcal{Z}} \int d^{3N} R d^{3N} \boldsymbol{\pi}^R O(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^R, \hat{\boldsymbol{\pi}}^{\sigma} = 0) \delta(H(\mathbf{R}, \hat{s}, \boldsymbol{\pi}^R, \hat{\boldsymbol{\pi}}^{\sigma} = 0) - E) \quad (6.39)$$

which is the sought result. $\square$

The result above implicitly defines the microcanonical marginal probability in the physical phase space in the full adiabatic limit. This definition is in agreement with the form usually assumed for the Born-Oppenheimer probability. The derivation presented here indicates that the dynamical systems rigorously samples this density only in the full $\mu \rightarrow 0$ limit and that, for finite auxiliary masses, corrections to the mass matrix associated to the momenta would be needed, as indicated by Eqs. (6.34) and (6.35).

6.4 Numerical Algorithm

The numerical integration of the equations of motion in the form of Eqs. (6.8) or (6.13) can be performed using any algorithm for the integration of systems of second order ODEs. As the set of equations represents a mechanical system, it would be ideal to use integrators that preserve the properties of mechanical motion. This point will be addressed in details in the following section. The additional numerical difficulty lies in the computation of the time-dependent Lagrange multipliers which have to be calculated for a complete determination of the dynamical system. Nonetheless, many algorithms are available in the literature for solving the equations of motion of systems in the presence of holonomic constraints. In the following we will mainly consider the case in which the integration of the physical degrees of freedom is performed using the velocity-Verlet algorithm [105] and a combination of the Verlet algorithm [106] and of the SHAKE method is used for the solution of holonomic constraints [8]. At the end of the section the alternative use of velocity-Verlet with RATTLE [107] for the additional degrees of freedom is also addressed.

Let us assume to have a set of N particles and a generic set of M additional variables s subject to a set of M holonomic constraints σ

$$\sigma_\alpha(\mathbf{R}, s) = 0 \quad \alpha = 1, \dots, M \quad (6.40)$$

The incorporation of the case discussed in Section 6.2, where C additional conditions are considered, even if formally equivalent, necessitates of some additional attention and it will be discussed for the specific case of orbital-free density functional theory in Chapter 8. The equations of motion for the system considered are written in

Eq. (6.8) and the system of ODE to be solved numerically is given, in normal form, by

$$\begin{aligned}\ddot{\mathbf{R}}_i &= -\frac{1}{m_i} \nabla_{\mathbf{R}_i} V(\mathbf{R}, s) \\ \ddot{s}_\alpha &= -\sum_{\beta=1}^M \gamma_\beta \frac{\partial \sigma_\beta(\mathbf{R}, s)}{\partial s_\alpha}\end{aligned}\tag{6.41}$$

for $i = 1, \dots, N$ and $\alpha = 1, \dots, M$.

The basic structure of the algorithm is the following: At each step along the dynamics:

1. Move the particles following the dynamics given by the interaction energy.
2. Adjust the additional variables in order to satisfy the constraints.

The three-step form of the velocity-Verlet algorithm is used for the first part of the numerical integration, which involves the first half step of particles velocities and the whole step of particle positions

$$\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) = \mathbf{v}_i(t) + \frac{\delta t}{2m_i} \mathbf{F}_i(t)\tag{6.42a}$$

$$\mathbf{R}_i(t + \delta t) = \mathbf{R}_i(t) + \delta t \mathbf{v}_i\left(t + \frac{\delta t}{2}\right)\tag{6.42b}$$

where $\mathbf{v}_i = \dot{\mathbf{R}}_i$ are the velocities of the particles and $\mathbf{F}_i(t) = -\nabla_{\mathbf{R}_i} V(\mathbf{R}(t), s(t))$ are the interaction forces. This first part of the algorithm assumes the knowledge of particles positions and velocities at a given time t , in addition to the knowledge of the values of the additional variables that satisfy the constraint at time t , *i.e.* $s(t)$. The latter requirement is necessary to compute the correct forces needed to propagate particles positions. Once the new particle positions $\mathbf{R}(t + \delta t)$ are obtained, the value of the additional dynamical variables s at time $t + \delta t$ is computed. To this end it is necessary the knowledge of the Lagrange multipliers γ . This is done *a posteriori*, imposing that the constraints are exactly satisfied at the time $t + \delta t$. Since the interaction potential V does not depend on $\dot{s}$ an accurate knowledge of the evolution of the time derivative of the additional degrees of freedom is not necessary

and the Verlet algorithm can be employed to evolve the variables s .³ The Verlet algorithm yields a value for the additional variables at $t + \delta t$ as a function of the multipliers γ given by

$$s_\alpha(\gamma; t + \delta t) = 2s_\alpha(t) - s_\alpha(t - \delta t) + \delta t^2 J_\alpha(\gamma; t) \quad (6.44)$$

where the constraint accelerations J at time t are defined by

$$J_\alpha(\gamma; t) = - \sum_{\beta=1}^M \gamma_\beta \frac{\partial \sigma_\beta(\mathbf{R}(t), s(t))}{\partial s_\alpha} \quad (6.45)$$

for $\alpha = 1, \dots, M$. The multipliers γ are computed solving the set of equations

$$\sigma_\alpha(\mathbf{R}(t + \delta t), s(\gamma; t + \delta t)) = 0 \quad \alpha = 1, \dots, M \quad (6.46)$$

in γ , which ensures the satisfaction of the constraints at each step along the dynamics and prevents the propagation of the error due to the accumulation of numerical noise. The particular method chosen to solve Eq. (6.46), as long as it is exact,⁴ does not interfere with the properties of the algorithm. Some common methods for the solution of Eq. (6.46) are discussed in Section 6.6. Once the correct Lagrange multipliers γ are obtained, they can be used to compute the constraint accelerations in Eq. (6.45) and the additional variables are updated using Eq. (6.44). To this end it is necessary the knowledge and storage of two steps of the evolution of the additional variables, in addition to the already mentioned informations on the positions of the particles. While this is a negligible cost in terms of memory, it makes algorithm non-self starting. Different choices for the initialization will be discussed case by case in the following chapters.

From the knowledge of $s(t + \delta t)$ it is possible to get the interaction forces on the particles at time $t + \delta t$ and to complete the step of the velocity-Verlet algorithm

³If needed, approximate information on the time derivative of the additional variables $v^s \equiv \dot{s}$ could be obtained through the discretized form

$$v^s(t) = \frac{s(t + \delta t) - s(t - \delta t)}{2\delta t} \quad (6.43)$$

at the cost of one order of accuracy in δt . Note, however, that these velocities are not assured to satisfy the hidden constraint $\dot{\sigma} = 0$ and their use is not recommended for accurate computation of observables.

⁴numerically exact

computing the propagated velocities as

$$\mathbf{v}_i(t + \delta t) = \mathbf{v}_i\left(t + \frac{\delta t}{2}\right) + \frac{\delta t}{2m_i} \mathbf{F}_i(t + \delta t) \quad (6.47)$$

where $\mathbf{F}_i(t + \delta t) = -\nabla_{\mathbf{R}_i} V(\mathbf{R}(t + \delta t), s(t + \delta t))$. The algorithm described above yields the evolution of all the degrees of freedom of the system under the constraint $\sigma = 0$. Note that, because of the way we compute the time derivative of the additional variables, *i.e.* through Eq. (6.43), this form of the algorithm does not guarantee the hidden constraint $\dot{\sigma}(\mathbf{R}, s) = \nabla_{\mathbf{R}} \sigma \cdot \dot{\mathbf{R}} + \nabla_s \sigma v^s = 0$ to be satisfied at all times, even if the initial conditions are chosen in such a way to have $\dot{\sigma} = 0$. As mentioned above, this does not compromise the overall propagation of the physical degrees of freedom, because the velocities of the auxiliary variables do not appear in the estimate of the $s(t + \delta t)$ or in the interaction potential $V(\mathbf{R}, s)$.

However, a way out of this issue is to use the combination of velocity-Verlet and RATTLE for the evolution of the additional variables s, v^s . Assuming knowledge of $\mathbf{R}(t), \mathbf{v}(t)$ and $s(t), v^s(t)$ such that $\sigma(\mathbf{R}(t), s(t)) = \dot{\sigma}(\mathbf{R}(t), s(t)) = 0$, Eqs. (6.42) can be used for the computation of $\mathbf{v}(t + \frac{\delta t}{2})$ and $\mathbf{r}(t + \delta t)$. Then, a first guess of the evolution of the additional variables can be computed as

$$v_\alpha^s\left(\gamma; t + \frac{\delta t}{2}\right) = v_\alpha^s(t) - \frac{\delta t}{2} J_\alpha(\gamma; t) \quad (6.48a)$$

$$s_\alpha(\gamma; t + \delta t) = s(t) + \delta t v_\alpha^s\left(\gamma; t + \frac{\delta t}{2}\right) \quad (6.48b)$$

where $J_\alpha(\gamma; t)$ is defined by Eq. (6.45) and it is a function of the Lagrange multipliers γ . Once again, the additional variables at time t can be made to satisfy the constraints at time $t + \delta t$ by computing the γ *a posteriori* solving Eq. (6.46). Once the values of $s(t + \delta t)$ have been computed, it is possible to use Eq. (6.47) to obtain the velocities of the particles at $t + \delta t$, *i.e.* $\mathbf{v}(t + \delta t)$, as the forces do not depend on the time derivatives of the additional variables. The values of $v^s(t + \delta t)$ can finally be computed introducing another set of Lagrange multipliers γ' as

$$v_\alpha^s(\gamma'; t + \delta t) = v_\alpha^s\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{2} J_\alpha(\gamma'; t + \delta t) \quad (6.49)$$

where the accelerations $J(\gamma', t + \delta t)$ are again given by Eq. (6.45) with γ' in place of γ and $\mathbf{R}(t + \delta t), s(t + \delta t)$ in place of $\mathbf{R}(t), s(t)$. The values of γ' can be obtained

solving the equation of the hidden constraint, which can be written as

$$0 = \dot{\sigma}_\alpha(\mathbf{R}(t + \delta t), s(\gamma'; t + \delta t)) = \sum_{i=1}^N \nabla_{\mathbf{R}_i} \sigma_\alpha(\mathbf{R}(t + \delta t), s(t + \delta t)) \cdot \mathbf{v}_i(t + \delta t) + \sum_{\beta=1}^M \frac{\partial \sigma_\alpha(\mathbf{R}(t + \delta t), s(t + \delta t))}{\partial s_\beta} v_\beta^s(\gamma'; t + \delta t) \quad (6.50)$$

for $\alpha = 1, \dots, M$. This algorithm ensures the satisfaction of the constraint σ and of its hidden counterpart $\dot{\sigma}$ at every step of the algorithm. However, from Eq. (6.50) it is evident the source of additional computational burden which accompanies the choice of velocity-Verlet + RATTLE as opposed to Verlet + SHAKE in the evolution of the additional variables. Indeed, the former requires the expression and the additional numerical computation of the gradient of the constraints with respect to the physical degrees of freedom, in addition of the numerical cost associated to the solution of Eq. (6.50) in the variables γ' .⁵ In practice, not only has it been shown [108] that SHAKE and RATTLE yields identical solutions for the variables involved in the constraints at all timesteps — the only difference is in their time derivatives — but also that the two methods are equivalent in a certain, mathematically precise sense [109]. Therefore, it is safe to use Verlet + SHAKE for the additional variables when no information or accuracy on their time derivatives is required by the numerical experiment.

6.5 Symplecticness and Time Reversibility of Mass-Zero Constrained Algorithm

Symplecticness and time reversibility are two key features of the numerical integrators for mechanical systems which are deeply connected to stability and accuracy of the algorithm. For a symplectic algorithm, for example, it is possible to show [110] that it conserves exactly a quantity, sometimes called the *shadow* Hamiltonian, which is a perturbation of the order of some power of the integration step of the Hamiltonian of the physical system. This implies that even though the real Hamiltonian is not

⁵For this latter point note, however, that the expression of the hidden constraint is always linear in the new set of Lagrange multipliers γ' , so the solution of the Eq. (6.50) is expected to be simpler than Eq. (6.46).

exactly conserved, the energy will not drift and it will just fluctuate around the physical value. Similar properties of stability and accuracy can be inferred from the time reversibility of an algorithm. Furthermore, when time reversibility is required to study specific aspects of the dynamical and statistical properties of a system as done in the first part of the thesis, it becomes essential to employ a numerical solver that does not violate it.

To formally discuss the symplecticness of an algorithm it is necessary to go through some definitions in the area of the differential forms that we briefly summarize in what follows. For a more detailed description the interested reader is redirected to Ref. [111].

Definition 6.2 (1-form). *Let $\mathbb{R}^m$ a m -dimensional real vector space. A 1-form $\omega : \mathbb{R}^m \rightarrow \mathbb{R}$ is a scalar-valued function which is linear in the argument*

$$\omega(\lambda_1 x_1 + \lambda_2 x_2) = \lambda_1 \omega(x_1) + \lambda_2 \omega(x_2)$$

where $x_1, x_2 \in \mathbb{R}^m$ and $\lambda_1, \lambda_2 \in \mathbb{R}$.

The set of all 1-forms on $\mathbb{R}^m$ is a real vector space of dimension m and it is called the dual $(\mathbb{R}^m)^*$ of $\mathbb{R}^m$. Suppose we chose a coordinate system in $\mathbb{R}^m$ identified by the basis vectors $e_1, \dots, e_m \in \mathbb{R}^m$. Each 1-form can be written in this basis as

$$\omega = a_1 e_1 + \dots + a_m e_m \quad a_1, \dots, a_m \in \mathbb{R} \quad (6.51)$$

The value of the 1-form ω on the point x can then be written, using Eq. (6.51), as

$$\omega(x) = a_1 e_1(x) + \dots + a_m e_m(x) = a_1 x^1 + \dots + a_m x^m = a \cdot x$$

where $\{e_i(x) = x^i\}_{i=1}^m$ are the components of the vector x in the basis $e_1, \dots, e_m$.

Example 6.1 (Differential of a function in a point). *The differential of a function in a point is a 1-form. Indeed, given a function $f : \mathbb{R}^m \rightarrow \mathbb{R}$ its differential in $x \in \mathbb{R}^m$, $df_x : T\mathbb{R}_x^m \rightarrow \mathbb{R}$ is defined as*

$$df_x(\xi) = \nabla f|_x \cdot \xi$$

where $\xi \in T\mathbb{R}_x^m$ and $T\mathbb{R}_x^m$ is the tangent space of $\mathbb{R}^m$ in the point x .

Definition 6.3 (2-form). A 2-form $\psi : \mathbb{R}^m \times \mathbb{R}^m \rightarrow \mathbb{R}$ is a scalar-valued function of two vectors $(x, y \in \mathbb{R}^m)$ which is linear in each argument and which is antisymmetric, i.e.

$$\begin{aligned}\psi(\lambda_1 x_1 + \lambda_2 x_2, y) &= \lambda_1 \psi(x_1, y) + \lambda_2 \psi(x_2, y) & x_1, x_2 \in \mathbb{R}^m \\ \psi(x, \lambda_1 y_1 + \lambda_2 y_2) &= \lambda_1 \psi(x, y_1) + \lambda_2 \psi(x, y_2) & y_1, y_2 \in \mathbb{R}^m \\ \psi(x, y) &= -\psi(y, x)\end{aligned}$$

where $\lambda_1, \lambda_2 \in \mathbb{R}$.

Definition 6.4 (Wedge product). The wedge product $\omega_1 \wedge \omega_2$ of two 1-forms ω_1, ω_2 is a 2-form and it is defined by

$$\omega_1 \wedge \omega_2(x, y) = \omega_1(x)\omega_2(y) - \omega_1(y)\omega_2(x)$$

It is possible to show that every 2-form ψ in the m -dimensional space in the coordinate system identified by the basis vectors $e_1, \dots, e_m$ can be represented as

$$\psi = \sum_{i < j} A_{ij} e_i \wedge e_j \quad (6.52)$$

where the matrix $\mathbb{A}$ of components A_{ij} is the representation of the 2-form ψ in the canonical basis $\bar{e}_1, \dots, \bar{e}_m$, i.e. the basis in which the basis vector $\bar{e}_i$ has all zero components except for the one in position i which is equal to 1.

Definition 6.5 (Symplectic 2-form). Let $\mathbb{R}^m$ be an even-dimensional real vector space so that $m = 2n$. A symplectic 2-form ψ_S is a 2-form which, when written in the form of Eq. (6.52), yields

$$\mathbb{A} = \begin{bmatrix} 0 & \mathbb{1}^{(n)} \\ -\mathbb{1}^{(n)} & 0 \end{bmatrix} = \mathbb{J} \quad (6.53)$$

where $\mathbb{1}^{(n)}$ is the identity in the space of the $n \times n$ matrices and $\mathbb{J}$ is the so-called symplectic matrix.

The concept of 1- and 2-forms (in general of k -forms) can be generalized to the tangent bundle TM of some manifold M , which is defined as the union of all the tangent spaces arising from M :

$$TM = \bigcup_x TM_x$$

where $x \in M$. These generalizations are called differential 1- and 2-forms (in general k -forms). For example, a differential 1-form on a manifold M is a smooth map $\omega : TM \rightarrow \mathbb{R}$ of the tangent bundle TM to the real line, which is linear on each tangent space TM_x . In particular, the differential df of a function $f : \mathbb{R}^m \rightarrow \mathbb{R}$ is a differential 1-form which maps the tangent bundle $T\mathbb{R}^m$ to the real line. It is differentiable with respect to x and it is linear in each tangent space $T\mathbb{R}_x^m$. Generalizations of Eqs. (6.51) and (6.52) are also possible for differential 1- and 2-forms in which the coefficients a_i and A_{ij} are replaced by smooth functions $a_i(x)$ and $A_{ij}(x)$. It is now possible to define a symplectic map:

Definition 6.6 (Symplectic map). *An isomorphic map in phase space $\mathcal{F} : \mathfrak{M} \rightarrow \mathfrak{M}$ is said to be symplectic if it preserves the symplectic differential 2-form.*

For a discrete map associated to a Hamiltonian dynamical system, this definition is equivalent to the conservation of the wedge product in phase space, *i.e.* to the condition $dq(t + \delta t) \wedge dp(t + \delta t) = dq(t) \wedge dp(t)$ where q and p are (generalized) coordinates and the associated conjugate momenta, respectively [109].

The presence of holonomic constraints in the dynamics of the system restricts the motion on a hypersurface of the phase space defined by the condition $\sigma = 0$ and by the hidden constraint $\dot{\sigma} = 0$. Therefore, for a constrained system, a map is symplectic if it conserves the wedge product and if it keeps the motion on the manifold defined by the constraints. We are now going to prove that the combination of Verlet and SHAKE algorithm for the solution of mass-zero constrained dynamics defines indeed a symplectic map in the sense of the constrained systems. To this end let us first prove the following:

Lemma 6.1. *For any vector u and for any Hermitian matrix A the wedge product $u \wedge Au$ is zero.*

Proof. Using the skew-symmetry $u \wedge v = -v \wedge u$ and bilinearity $u \wedge Av = A^\dagger u \wedge v$ of the wedge product together with the Hermitianity of the matrix A we have the result, *i.e.*

$$u \wedge Au = -Au \wedge u = -A^\dagger u \wedge u = -u \wedge Au = 0 \quad (6.54)$$

□

We can now prove the following:

Theorem 6.3 (Symplecticness of MaZe). *The numerical algorithm defined by the combination of Verlet and SHAKE for the solution of the mass-zero constrained dynamics satisfies the symplectic property of constrained dynamical systems.*

Proof. For the mass-zero constrained algorithm, the symplectic property can be proved for the subsystems concerning the physical and additional variables separately noting that. Both the physical and additional set of degrees of freedom satisfy relations of the kind $d\mathbf{v} = m^{-1}d\mathbf{p}$ hold, where for the additional variables, the limit of the zero-mass has to be taken before computing the differential. Therefore, the symplectic property for the physical variables can be proven starting from the differentials of the equations for the update of $\mathbf{R}$ and $\mathbf{v}$ in Eqs. (6.42) and (6.47)

$$d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) = d\mathbf{v}_i(t) - \frac{\delta t}{2m_i} \left\{ \sum_{j=1}^N \nabla_{\mathbf{R}_j \mathbf{R}_i}^2 V(t) \cdot d\mathbf{R}_j(t) + \sum_{\gamma=1}^M \frac{\partial \nabla_{\mathbf{R}_i} V(t)}{\partial s_\gamma} ds_\gamma(t) \right\} \quad (6.55a)$$

$$d\mathbf{R}_i(t + \delta t) = d\mathbf{R}_i(t) + \delta t d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \quad (6.55b)$$

$$d\mathbf{v}_i(t + \delta t) = d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{2m_i} \left\{ \sum_{j=1}^N \nabla_{\mathbf{R}_j \mathbf{R}_i}^2 V(t + \delta t) \cdot d\mathbf{R}_j(t + \delta t) + \sum_{\gamma=1}^M \frac{\partial \nabla_{\mathbf{R}_i} V(t + \delta t)}{\partial s_\gamma} ds_\gamma(t + \delta t) \right\} \quad (6.55c)$$

where we have introduced the notation $V(t) \equiv V(\mathbf{R}(t), s(t))$ and $V(t + \delta t) \equiv V(\mathbf{R}(t + \delta t), s(t + \delta t))$. The equations above must be completed by the expression of the differential of the constraint equation

$$d\sigma_\alpha(\mathbf{R}(t), s(t)) = \sum_{i=1}^N \nabla_{\mathbf{R}_i} \sigma_\alpha(t) \cdot d\mathbf{R}_i(t) + \sum_{\beta=1}^N \frac{\partial \sigma_\alpha(t)}{\partial s_\beta} ds_\beta(t) = 0 \quad (6.56)$$

where the same notation $\sigma(t) \equiv \sigma(\mathbf{R}(t), s(t))$ has been used for the constraints σ . Computing the wedge product of Eqs. (6.55b) and (6.55c) we have

$$\begin{aligned} d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) &= d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \\ &- d\mathbf{R}_i(t + \delta t) \wedge \frac{\delta t}{2m_i} \left\{ \sum_{j=1}^N \nabla_{\mathbf{R}_j \mathbf{R}_i}^2 V(t + \delta t) \cdot d\mathbf{R}_j(t + \delta t) \right. \\ &\left. + \sum_{\gamma=1}^M \frac{\partial \nabla_{\mathbf{R}_i} V(t + \delta t)}{\partial s_\gamma} ds_\gamma(t + \delta t) \right\} \end{aligned} \quad (6.57)$$

From the hermitianity of the Hessian $\nabla_{\mathbf{R}_j \mathbf{R}_i}^2 V$ and from Lemma 6.1 it follows that

$$\begin{aligned} d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) &= d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \\ &- d\mathbf{R}_i(t + \delta t) \wedge \frac{\delta t}{2m_i} \sum_{\gamma=1}^M \frac{\partial \nabla_{\mathbf{R}_i} V(t + \delta t)}{\partial s_\gamma} ds_\gamma(t + \delta t) \end{aligned} \quad (6.58)$$

Moreover, using the definition of the constraints for the mass-zero constrained dynamics Eq. (6.1) and the relation

$$\frac{\partial \nabla_{\mathbf{R}_i} V(t + \delta t)}{\partial s_\gamma} = \nabla_{\mathbf{R}_i} \frac{\partial V(t + \delta t)}{\partial s_\gamma} = \nabla_{\mathbf{R}_i} \sigma_\gamma(t + \delta t) \quad (6.59)$$

we get

$$\frac{\delta t}{2m_i} \sum_{\gamma=1}^M \frac{\partial \nabla_{\mathbf{R}_i} V(t + \delta t)}{\partial s_\gamma} ds_\gamma(t + \delta t) = \frac{\delta t}{2m_i} \sum_{\gamma=1}^M \nabla_{\mathbf{R}_i} \sigma_\gamma(t + \delta t) ds_\gamma(t + \delta t) \quad (6.60)$$

Substituting Eq. (6.60) into Eq. (6.58) we obtain

$$\begin{aligned} d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) &= d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \\ &- d\mathbf{R}_i(t + \delta t) \wedge \frac{\delta t}{2m_i} \sum_{\gamma=1}^M \nabla_{\mathbf{R}_i} \sigma_\gamma(t + \delta t) ds_\gamma(t + \delta t) \end{aligned} \quad (6.61)$$

The bilinearity of the wedge product means that for any pair of vectors u, v and for any matrix A , the property $v \wedge Au = A^\dagger v \wedge u$ holds, so that for Eq. (6.61) this reads

$$\begin{aligned} d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) &= d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \\ &\quad - \frac{\delta t}{2m_i} \sum_{\gamma=1}^N \nabla_{\mathbf{R}_i} \sigma_\gamma(t + \delta t) d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{s}_\gamma(t + \delta t) \end{aligned} \quad (6.62)$$

Using now the definition of the differential of the constraint equation in Eq. (6.56) we obtain

$$\begin{aligned} d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) &= d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \\ &\quad + \frac{\delta t}{2m_i} \sum_{\beta=1}^M \frac{\partial \sigma_\gamma(t + \delta t)}{\partial s_\beta} ds_\beta(t + \delta t) \wedge d\mathbf{s}_\gamma(t + \delta t) \end{aligned} \quad (6.63)$$

Again, Lemma 6.1 used with the Hessian $\frac{\partial \sigma_\gamma}{\partial s_\beta}$, nullify the last term of Eq. (6.63), finally yielding

$$d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) = d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \quad (6.64)$$

Inserting the differential for particles positions at $t + \delta t$ we obtain

$$d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) = d\mathbf{R}_i(t) \wedge d\mathbf{v}_i\left(t + \frac{\delta t}{2}\right) \quad (6.65)$$

where it has been recognized that $v \wedge v = 0$. Retracing now the same steps used for the expression of $d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t)$ yields

$$d\mathbf{R}_i(t + \delta t) \wedge d\mathbf{v}_i(t + \delta t) = d\mathbf{R}_i(t) \wedge d\mathbf{v}_i(t) \quad (6.66)$$

Let us now consider the subsystem of the additional variables. The evolution algorithm written in the standard Verlet form

$$s_\alpha(t + \delta t) = 2s_\alpha(t) - s_\alpha(t - \delta t) - \delta t^2 \sum_{\beta=1}^M \gamma_\beta \frac{\partial \sigma_\beta(t)}{\partial s_\alpha} \quad (6.67)$$

for $\alpha = 1, \dots, M$, is not suited for a discussion of the symplecticness of the map, for which an expression using variables and corresponding velocities (as done for the physical variables) is the natural choice. We therefore introduce the quantity

$$v_\alpha^s\left(t + \frac{\delta t}{2}\right) = v_\alpha^s(t) - \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t) \frac{\partial \sigma_\beta(t)}{\partial s_\alpha} \quad (6.68)$$

which allows to rewrite the discretized equations of motion in the form

$$v_\alpha^s\left(t + \frac{\delta t}{2}\right) = v_\alpha^s(t) - \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t) \frac{\partial \sigma_\beta(t)}{\partial s_\alpha} \quad (6.69a)$$

$$s_\alpha(t + \delta t) = s_\alpha(t) + \delta t v_\alpha^s\left(t + \frac{\delta t}{2}\right) \quad (6.69b)$$

$$v_\alpha^s(t + \delta t) = v_\alpha^s\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t + \delta t) \frac{\partial \sigma_\beta(t + \delta t)}{\partial s_\alpha} \quad (6.69c)$$

Note that $\gamma(t)$ and $\gamma(t + \delta t)$ represent the Lagrange multipliers computed at the corresponding timestep, *i.e.* the ones satisfying the constraints $\sigma(t)$ and $\sigma(t + \delta t)$, respectively. For the definition of symplecticness for a constrained system given above, this map cannot be symplectic as, even if $\sigma = 0$ is satisfied at every discretized step, the hidden constraint will typically fail to do the same. On the other hand, restricting the problem to the manifold identified by the constraints $\sigma = 0$ (see Ref. [109]), it is possible to show that the map conserves the wedge product along the discretized evolution, *i.e.* $ds(t + \delta t) \wedge dv^s(t + \delta t) = ds(t) \wedge dv^s(t)$. Indeed, considering the differentials of Eqs. (6.69) we get

$$dv_\alpha^s\left(t + \frac{\delta t}{2}\right) = dv_\alpha^s(t) - \frac{\delta t}{2} \sum_{\beta=1}^M d\left[\gamma_\beta(t) \frac{\partial \sigma_\beta(t)}{\partial s_\alpha}\right] \quad (6.70a)$$

$$ds_\alpha(t + \delta t) = ds_\alpha(t) + \delta t dv_\alpha^s\left(t + \frac{\delta t}{2}\right) \quad (6.70b)$$

$$dv_\alpha^s(t + \delta t) = dv_\alpha^s\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{2} \sum_{\beta=1}^M d\left[\gamma_\beta(t + \delta t) \frac{\partial \sigma_\beta(t + \delta t)}{\partial s_\alpha}\right] \quad (6.70c)$$

which must be completed by the differential of the constraint equations in the Born-Oppenheimer approximation given by

$$d\sigma_\alpha(s(t+\delta t)) = \sum_{\beta=1}^M \frac{\partial \sigma_\alpha(s(t+\delta t))}{\partial s_\beta} ds_\beta = 0 \quad (6.71)$$

for $\alpha = 1, \dots, M$. Note that Eq. (6.71) differs from Eq. (6.56) since when strict adiabatic separation is enforced — the zero limit of the fictitious mass of the additional variables is enforced rigorously — the physical particles are treated as external parameters in the equations of motion of the auxiliary degrees of freedom, as prescribed by the Born-Oppenheimer approximation. For this reason, “from the point of view” of the additional variables, the differential $d\mathbf{R}(t) = 0 \forall t$ and the gradient of the constraint with respect to $\mathbf{R}$ does not appear in Eq. (6.71).

We can now prove the conservation of the wedge product. To this end we compute

$$\begin{aligned} ds_\alpha(t+\delta t) \wedge dv_\alpha^s(t+\delta t) &= ds_\alpha(t+\delta t) \wedge dv_\alpha^s\left(t + \frac{\delta t}{2}\right) \\ &\quad - ds_\alpha(t+\delta t) \wedge \frac{\delta t}{2} \sum_{\beta=1}^M d\left[\gamma_\beta(t+\delta t) \frac{\partial \sigma_\beta(t+\delta t)}{\partial s_\alpha}\right] \end{aligned} \quad (6.72)$$

The differential in the second term of the RHS of the equation above yields

$$\begin{aligned} d\left[\gamma_\beta(t+\delta t) \frac{\partial \sigma_\beta(t+\delta t)}{\partial s_\alpha}\right] &= \frac{\partial \sigma_\beta(t+\delta t)}{\partial s_\alpha} d\gamma_\beta(t+\delta t) \\ &\quad + \gamma_\beta(t+\delta t) \sum_{\lambda=1}^M \frac{\partial^2 \sigma_\beta(t+\delta t)}{\partial s_\lambda \partial s_\alpha} ds_\lambda(t+\delta t) \end{aligned} \quad (6.73)$$

In this way, the wedge product in Eq. (6.72) can be written as

$$\begin{aligned} ds_\alpha(t+\delta t) \wedge dv_\alpha^s(t+\delta t) &= ds_\alpha(t+\delta t) \wedge dv_\alpha^s\left(t + \frac{\delta t}{2}\right) \\ &\quad - ds_\alpha(t+\delta t) \wedge \frac{\delta t}{2} \sum_{\beta=1}^M \frac{\partial \sigma_\beta(t+\delta t)}{\partial s_\alpha} d\gamma_\beta(t+\delta t) \\ &\quad - ds_\alpha(t+\delta t) \wedge \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t+\delta t) \sum_{\lambda=1}^M \frac{\partial^2 \sigma_\beta(t+\delta t)}{\partial s_\lambda \partial s_\alpha} ds_\lambda(t+\delta t) \end{aligned} \quad (6.74)$$

The second term of the equation above is zero as a consequence of the bilinearity of the wedge product which implies

$$\begin{aligned} ds_\alpha(t + \delta t) \wedge \frac{\delta t}{2} \sum_{\beta=1}^M \frac{\partial \sigma_\beta(t + \delta t)}{\partial s_\alpha} d\gamma_\beta(t + \delta t) \\ = \frac{\delta t}{2} \sum_{\alpha=1}^M \frac{\partial \sigma_\beta(t + \delta t)}{\partial s_\alpha} ds_\alpha(t + \delta t) \wedge d\gamma_\beta(t + \delta t) \end{aligned} \quad (6.75)$$

The first term of the wedge product on the RHS of Eq. (6.75) can be recognized to be the differential of the constraints in the Born-Oppenheimer approximation in Eq. (6.71) and it is therefore zero. The last term of Eq. (6.74) is also zero by means of Lemma 6.1 used with the Hessian of the constraints (being the constraints smooth functions of the additional variables derivable at least twice). Eq. (6.72) then reads

$$ds_\alpha(t + \delta t) \wedge dv_\alpha^s(t + \delta t) = ds_\alpha(t + \delta t) \wedge dv_\alpha^s\left(t + \frac{\delta t}{2}\right) \quad (6.76)$$

Substituting Eqs. (6.70b) and (6.70a) we have

$$\begin{aligned} ds_\alpha(t + \delta t) \wedge dv_\alpha^s\left(t + \frac{\delta t}{2}\right) \\ = \left[ds_\alpha(t) + \delta t dv_\alpha^s\left(t + \frac{\delta t}{2}\right) \right] \wedge dv_\alpha^s\left(t + \frac{\delta t}{2}\right) = ds_\alpha(t) \wedge dv_\alpha^s\left(t + \frac{\delta t}{2}\right) \quad (6.77) \\ = ds_\alpha(t) \wedge \left[dv_\alpha^s(t) - \frac{\delta t}{2} \sum_{\beta=1}^M d\left(\gamma_\beta(t) \frac{\partial \sigma_\beta(t)}{\partial s_\alpha}\right) \right] \end{aligned}$$

Retracing the same steps that yield Eq. (6.76) from Eq. (6.72) we obtain the conservation of the wedge product for a dynamics step of the additional variables, *i.e.*

$$ds_\alpha(t + \delta t) \wedge dv_\alpha^s(t + \delta t) = ds_\alpha(t) \wedge dv_\alpha^s(t) \quad (6.78)$$

which finally completes the proof. $\square$

The time reversibility of the algorithm can be proved starting again from Eqs. (6.69). First we have the following:

Definition 6.7 (Time-reversible map). *A map $\mathcal{G} : \mathfrak{M} \rightarrow \mathfrak{M}$, whose discretized step is defined by $\Gamma(t + \delta t) = \mathcal{G}_{\delta t}(\Gamma(t))$ is said to be time reversible under the involution*

$\mathcal{M} : \mathfrak{M} \rightarrow \mathfrak{M}$, if $\mathcal{G}$ is symmetric, i.e. $\mathcal{G}_{-\delta t} = \mathcal{G}_{\delta t}^{-1}$ and if it satisfies the property $\mathcal{G}_{\delta t} = \mathcal{M} \mathcal{G}_{-\delta t} \mathcal{M}$.

The proof will be carried over in the subspace of the additional variables only, as the proof for the physical variables is obtained by the standard proof of time reversibility of the Verlet algorithm [109]. Let us start by verifying

Lemma 6.2. *Eqs. (6.69) define a symmetric map.*

Proof. The inverse map is obtained by the substitution $t + \delta t \mapsto t$, while the map for $-\delta t$ is obtained replacing every δt by $-\delta t$ in the RHS of Eqs. (6.69). The inverse map is then given by

$$v_{\alpha}^s\left(t + \frac{\delta t}{2}\right) = v_{\alpha}^s(t + \delta t) - \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_{\beta}(t + \delta t) \frac{\partial \sigma_{\beta}(t + \delta t)}{\partial s_{\alpha}} \quad (6.79a)$$

$$s_{\alpha}(t) = s_{\alpha}(t + \delta t) + \delta t v_{\alpha}^s\left(t + \frac{\delta t}{2}\right) \quad (6.79b)$$

$$v_{\alpha}^s(t) = v_{\alpha}^s\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_{\beta}(t) \frac{\partial \sigma_{\beta}(t)}{\partial s_{\alpha}} \quad (6.79c)$$

which, rearranging terms, can be written as

$$v_{\alpha}^s\left(t + \frac{\delta t}{2}\right) = v_{\alpha}^s(t) + \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_{\beta}(t) \frac{\partial \sigma_{\beta}(t)}{\partial s_{\alpha}} \quad (6.80a)$$

$$s_{\alpha}(t + \delta t) = s_{\alpha}(t) - \delta t v_{\alpha}^s\left(t + \frac{\delta t}{2}\right) \quad (6.80b)$$

$$v_{\alpha}^s(t + \delta t) = v_{\alpha}^s\left(t + \frac{\delta t}{2}\right) + \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_{\beta}(t + \delta t) \frac{\partial \sigma_{\beta}(t + \delta t)}{\partial s_{\alpha}} \quad (6.80c)$$

Eqs. (6.80) can be easily recognized to be Eqs. (6.69) with the substitution $\delta t \mapsto -\delta t$. $\square$

The map defined by Eqs. (6.69) then establishes a symmetric algorithm. To prove time reversibility it is now necessary to check that the definition of time-reversal symmetry is satisfied for some involution $\mathcal{M}$. The natural choice is to consider the standard time-reversal symmetry $\mathcal{M}^{(1)}$ defined in Section 3.1, but note that other choices are possible, provided that the hypotheses on the interaction potential are

satisfied. Note also that the involution now acts on the phase space of the additional variables, so that the action of $\mathcal{M}^{(1)}$ is defined by

$$\mathcal{M}^{(1)}(s, v^s) = (s, -v^s) \quad (6.81)$$

We can now prove the following:

Theorem 6.4. (*Time reversibility of MaZe*) *The numerical algorithm defined by the combination of Verlet and SHAKE for the solution of the mass-zero constrained dynamics defines a time-reversible map.*

Proof. Application of the inverse of the map obtained from Lemma 6.2, Eqs. (6.80) on the initial point $\mathcal{M}^{(1)}(s(t), v^s(t))$ yields

$$v_\alpha^s\left(t + \frac{\delta t}{2}\right) = -v_\alpha^s(t) + \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t) \frac{\partial \sigma_\beta(t)}{\partial s_\alpha} \quad (6.82a)$$

$$s_\alpha(t + \delta t) = s_\alpha(t) - \delta t v_\alpha^s\left(t + \frac{\delta t}{2}\right) \quad (6.82b)$$

$$v_\alpha^s(t + \delta t) = v_\alpha^s\left(t + \frac{\delta t}{2}\right) + \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t + \delta t) \frac{\partial \sigma_\beta(t + \delta t)}{\partial s_\alpha} \quad (6.82c)$$

and finally, a further application of the standard time-reversal transformation $\mathcal{M}^{(1)}$ on the propagated point $s(t + \delta t), v^s(t + \delta t)$ yields the sought result

$$v_\alpha^s\left(t + \frac{\delta t}{2}\right) = -v_\alpha^s(t) + \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t) \frac{\partial \sigma_\beta(t)}{\partial s_\alpha} \quad (6.83a)$$

$$s_\alpha(t + \delta t) = s_\alpha(t) - \delta t v_\alpha^s\left(t + \frac{\delta t}{2}\right) \quad (6.83b)$$

$$v_\alpha^s(t + \delta t) = -v_\alpha^s\left(t + \frac{\delta t}{2}\right) - \frac{\delta t}{2} \sum_{\beta=1}^M \gamma_\beta(t + \delta t) \frac{\partial \sigma_\beta(t + \delta t)}{\partial s_\alpha} \quad (6.83c)$$

where Eqs. (6.69) for the evolved points at time $t + \delta t$ are recovered by the substitution of Eq. (6.83a) into Eqs. (6.83b) and (6.83c). $\square$

6.6 The Solution of the Constraints Equation

To obtain the set of Lagrange multipliers γ that satisfies the constraint σ at time $t + \delta t$ it is necessary to solve Eqs. (6.46)

$$\sigma_\alpha(\mathbf{R}(t + \delta t), s(\gamma; t + \delta t)) = 0 \quad \alpha = 1, \dots, M$$

in the unknowns γ , implicitly contained in the definition of $s(\gamma; t + \delta t)$ given in Eq. (6.44). The additional variable s at time $t + \delta t$ — in the following, only the dependence on γ will be retained as no confusion is produced — can be considered as composed by two contributions

$$s_\alpha(\gamma) = s_\alpha^P + \delta s_\alpha(\gamma) \quad (6.84)$$

where

$$s_\alpha^P = 2s_\alpha(t) - s_\alpha(t - \delta t) \quad \text{and} \quad \delta s_\alpha(\gamma) = -\delta t^2 \sum_{\beta=1}^M \gamma_\beta \frac{\partial \sigma_\beta(\mathbf{R}(t), s(t))}{\partial s_\alpha} \quad (6.85)$$

A Newton-Raphson approach can then be used to find the zeroes of the function $\sigma(\gamma)$ iteratively. Starting from $\gamma^{(0)} = 0$ the Newton-Raphson algorithm [112] prescribes the value of the unknown at iteration (n) as given by

$$\gamma_\alpha^{(n+1)} = \gamma_\alpha^{(n)} - \sum_{\beta=1}^M \left[\frac{\partial \sigma(\mathbf{R}(t + \delta t), s(\gamma^{(n)}))}{\partial \gamma} \right]_{\alpha\beta}^{-1} \sigma_\beta(\mathbf{R}(t + \delta t), s(\gamma^{(n)})) \quad (6.86)$$

The matrix that has to be inverted in Eq. (6.86) is

$$\left[\frac{\partial \sigma(\mathbf{R}(t + \delta t), s(\gamma^{(n)}))}{\partial \gamma} \right]_{\alpha\beta} = \frac{\partial \sigma_\alpha(\mathbf{R}(t + \delta t), s(\gamma^{(n)}))}{\partial \gamma_\beta} \quad (6.87)$$

The derivative in Eq. (6.87) can be expressed using the chain rule and Eq. (6.85) as

$$\begin{aligned} \frac{\partial \sigma_\alpha(\mathbf{R}(t + \delta t), s(\gamma^{(n)}))}{\partial \gamma_\beta} &= \sum_{\lambda=1}^N \frac{\partial \sigma_\alpha(\mathbf{R}(t + \delta t), s(\gamma^{(n)}))}{\partial s_\lambda} \frac{\partial s_\lambda(\gamma^{(n)})}{\partial \gamma_\beta} \\ &= -\delta t^2 \sum_{\lambda=1}^N \frac{\partial \sigma_\alpha(\mathbf{R}(t + \delta t), s^{(n)})}{\partial s_\lambda} \frac{\partial \sigma_\beta(\mathbf{R}(t), s(t))}{\partial s_\lambda} \end{aligned} \quad (6.88)$$

where, in the final term, the notation $s(\gamma^{(n)}) \equiv s^{(n)}$ has been introduced. Eq. (6.88) defines a matrix, sometimes called the SHAKE matrix, given by

$$\mathbb{S}_{\alpha\beta}^{(n)} = \delta t^2 \sum_{\lambda=1}^M \frac{\partial \sigma_{\alpha}(\mathbf{R}(t + \delta t), s^{(n)})}{\partial s_{\lambda}} \frac{\partial \sigma_{\beta}(\mathbf{R}(t), s(t))}{\partial s_{\lambda}} \quad (6.89)$$

The final expression for the Newton-Raphson update of the variable γ can finally be written as

$$\gamma_{\alpha}^{(n+1)} = \gamma_{\alpha}^{(n)} + \sum_{\beta=1}^M \left[\mathbb{S}_{\alpha\beta}^{(n)} \right]^{-1} \sigma_{\beta}(\mathbf{R}(t + \delta t), s^{(n)}) \quad (6.90)$$

This value is then used to compute the updated $s(t + \delta t)$ through Eq. (6.85) and, from it, the force acting on the physical degrees of freedom at time $t + \delta t$. This algorithm to find the Lagrange multipliers is sometimes known as M-SHAKE [113]. The inversion of the SHAKE matrix $\mathbb{S}^{(n)}$ usually becomes the most time-consuming part of the algorithm as soon as the number of constraints becomes physically interesting for statistical mechanics systems. Indeed, the M-SHAKE algorithm necessitates of one matrix calculation and inversion for each iteration of the algorithm, so this procedure is mostly employed when the dimensionality of the matrix $\mathbb{S}^{(n)}$ is very low or when the matrix is constant during the simulation and therefore the inverse can be computed only once. An exception is represented by problems in which the constraints take a linear form: In this (very special) situation the procedure converges, in principle,⁶ to numerical precision at the first iteration. When this is not the case, approximate schemes (discussed in the next sections) need to be exploited to reduce the computational cost of the procedure.

6.6.1 The SHAKE Algorithm and the Successive Over Relaxation

When the number of additional variables of the system becomes large, it is possible to reduce the computational cost using an iterative procedure called SHAKE [8]. The basic ingredient of this procedure is to approximate the matrix $\mathbb{S}^{(n)}$ by its diagonal

⁶In this case the convergence of the procedure depends solely on the numerical algorithm used to invert the matrix and what usually controls the performances of the algorithm is the condition number of the SHAKE matrix $\mathbb{S}^{(n)}$.

elements

$$\mathbb{S}_{\alpha\beta}^{(n)} \approx \mathbb{S}_{\alpha\alpha}^{(n)} = \delta t^2 \sum_{\lambda=1}^M \frac{\partial \sigma_{\alpha}(\mathbf{R}(t + \delta t), s^{(n)})}{\partial s_{\lambda}} \frac{\partial \sigma_{\alpha}(\mathbf{R}(t), s(t))}{\partial s_{\lambda}} \quad (6.91)$$

In this way, Eq. (6.90) takes the trivial form given by

$$\gamma_{\alpha}^{(n+1)} = \gamma_{\alpha}^{(n)} + \frac{\sigma_{\alpha}(\mathbf{R}(t + \delta t), s^{(n)})}{\mathbb{S}_{\alpha\alpha}^{(n)}} \quad (6.92)$$

for all $\alpha = 1, \dots, M$.

In this set-up, it is possible to loop over constraints, which are computed one at a time and to immediately update the additional variables s , to obtain an estimate of their value at the next iteration. After looping over the whole set of constraints, the procedure is repeated until full convergence. At iteration (n) , the value of the additional variables are updated with the contribution arising from the constraint β as

$$s_{\alpha}^{(n+1)} = s_{\alpha}^{(n)} + \delta \gamma_{\beta}^{(n)} \frac{\partial \sigma_{\beta}(\mathbf{R}(t), s(t))}{\partial s_{\beta}} \quad (6.93)$$

for $\alpha = 1, \dots, M$. The value of the partial Lagrange multiplier $\delta \gamma^{(n)} = \gamma^{(n)} - \gamma^{(n-1)}$ is given by

$$\delta \gamma_{\beta}^{(n)} = \frac{\sigma_{\beta}(\mathbf{R}(t + \delta t), s^{(n)})}{\mathbb{S}_{\beta\beta}^{(n)}} \quad (6.94)$$

and the Lagrange multiplier associated to the constraint β is consequently computed as $\gamma_{\beta} = \sum_n \delta \gamma_{\beta}^{(n)}$. A schematic pseudocode of the SHAKE algorithm can be found in Figure 6.2. The backbone of the routine is composed by three nested loops: The outermost controls the number of iterations to convergence (loop over n) and checks if the tolerance is satisfied, the one in the middle runs over the constraints (loop over β), computes σ and γ and updates the gradient of the constraints using the value of the updated variables computed by the innermost loops (loops over α) in order to compute the shake denominator.

A variant of this algorithm has been proposed by Leimkuhler and coworkers in Ref. [114] and it suggests to modify Eq. (6.93) by the introduction of the parameter η so to have

$$s_{\alpha}^{(n+1)} = s_{\alpha}^{(n)} + \eta \delta \gamma_{\beta}^{(n)} \frac{\partial \sigma_{\beta}(\mathbf{R}(t), s(t))}{\partial s_{\beta}} \quad (6.95)$$

Result: Find $s(t + \delta t)$ that satisfies $\sigma(s(t + \delta t)) = 0$

Input: $s^P, \nabla_s \sigma(s(t))$

Output: s^P

Data: max_iter, tol, M

Locals: $discr, sigold, denom, gam$

$n \leftarrow 0$

while $n < max_iter$ **do**

$discr \leftarrow 0$

for $\beta \leftarrow 1$ **to** M **do**

$sigold \leftarrow \sigma_\beta(s^P)$

if $|sigold| > tol$ **then**

if $|sigold| > discr$ **then** $discr \leftarrow |sigold|$

for $\alpha \leftarrow 1$ **to** M **do**

$denom \leftarrow denom + \nabla_{s_\alpha} \sigma_\beta(s^P)$

end for

$gam \leftarrow sigold / denom$

for $\alpha \leftarrow 1$ **to** M **do**

$s_\alpha^P \leftarrow s_\alpha^P + gam \cdot \nabla_{s_\alpha} \sigma_\beta(s(t))$

end for

end if

end for

if $discr = 0$ **then return**

$n \leftarrow n + 1$

end while

Fig. 6.2 The SHAKE algorithm: The routine takes as input the value of the provisional variables s^P and the gradient of the constraints computed at previous timestep, *i.e.* $\nabla_s \sigma(s(t))$. It yields as output the variables $s(t + \delta t)$ such that $\sigma(s(t + \delta t)) = 0$ as the updated input provisional variable s^P . The backbone of the routine is made by three nested loops: The first runs over the iterations n and checks if the constraints are all satisfied; the second runs over the components β of the constraint vector σ one at a time and computes the Lagrange multiplier γ_β relative to the particular component of σ ; the two innermost loops run over the variables involved in the particular constraint σ_β : the first one computes the SHAKE denominator using the value of the gradient of the constraints computed with the variables s at the previous iteration and the second performs the update of the additional variables s . The procedure is successfully stopped when each component of the constraint vector is less than a user-defined tolerance. Otherwise an error occurs when the maximum number of iterations allowed is exceeded. Pseudocode is from Appendix B of Ref. [9].

The authors first introduced the algorithm for efficiency purposes, as a value of $\eta > 1$ is supposed to increase the speed up the convergence of the algorithm. For this reason the algorithm is known under the name of successive over relaxation (SOR). Nonetheless it has been shown recently in the framework of the mass-zero constrained dynamics [115] that a value of the parameter smaller than one, *i.e.* $0 < \eta < 1$, could improve the stability of the iterative procedure when dealing with particularly stiff potentials or additional conditions.

Due to the approximation in Eq. (6.91), the method has its best performances when the matrix is sparse and diagonally dominant, as in the case of bond constraints. Good performances with the SHAKE algorithm have been obtained also in dense matrix where the off-diagonal terms decay at some power of their distance to the diagonal [23, 115].

6.6.2 The Truncated Newton Algorithm

The SHAKE algorithm solves very well the problem of inverting the matrix at each iteration of the procedure, but it still relies on the computation of the SHAKE denominator many times per timestep. Indeed, the SHAKE denominator is still dependent on the value of the additional variables at iteration (n) and this can be a numerical bottleneck when very complex constraints are involved in the computation. A way out of this issue is to use the so-called truncated Newton method [116, 117]. This algorithm prescribes the value of the unknown γ at iteration ($n + 1$) as

$$\gamma_{\alpha}^{(n+1)} = \gamma_{\alpha}^{(n)} - \sum_{\beta=1}^M \left[\frac{\partial \sigma(\mathbf{R}(t + \delta t), s(\gamma^{(0)}))}{\partial \gamma} \right]_{\alpha\beta}^{-1} \sigma_{\beta}(\mathbf{R}(t + \delta t), s(\gamma^{(n)})) \quad (6.96)$$

which, retracing the steps of Section 6.6, can be recast in the form

$$\gamma_{\alpha}^{(n+1)} = \gamma_{\alpha}^{(n)} + \sum_{\beta=1}^M \left[\mathbb{S}_{\alpha\beta}^{(0)} \right]^{-1} \sigma_{\beta}(\mathbf{R}(t + \delta t), s^{(n)}) \quad (6.97)$$

where the truncated SHAKE matrix is defined by

$$\mathbb{S}_{\alpha\beta}^{(0)} = \delta t^2 \sum_{\lambda=1}^M \frac{\partial \sigma_{\alpha}(\mathbf{R}(t + \delta t), s^{(0)})}{\partial s_{\lambda}} \frac{\partial \sigma_{\beta}(\mathbf{R}(t), s(t))}{\partial s_{\lambda}} \quad (6.98)$$

In Eq. (6.98) the truncated Newton method prescription of computing the derivative with respect to γ for $s(\gamma^{(0)})$ yields $s^{(0)} = s^P$, but other choices are possible (see for example the next section). The only side effects expected from this approximation are an increase in the number of iterations for convergence of the iterative procedure and a smaller radius of convergence of the algorithm [117]. These are generally fully balanced by the minor computational time spent in the calculation of the SHAKE matrix and of the gradient of the constraints, which now only need to be computed at the beginning of the iterative procedure. The use of this method together with the SHAKE algorithm discussed in the previous section removes the two main bottlenecks of the standard Newton-Raphson algorithm, *i.e.* the computation and inversion of the SHAKE matrix at each iteration of the procedure. The simultaneous exploitation of the two algorithms only modifies Eq. (6.94) of the previous section, which now reads

$$\delta\gamma_\beta^{(n)} = \frac{\sigma_\beta(\mathbf{R}(t + \delta t), s^{(n)})}{\mathbb{S}_{\beta\beta}^{(0)}} \quad (6.99)$$

6.6.3 The Weinbach-Elber Algorithm

Another very powerful algorithm based on an iterative solution of the equation for the Lagrange multipliers $\sigma(\gamma) = 0$ is discussed in Ref. [118]. The method was originally intended to provide a highly scalable and parallelizable alternative to the SHAKE method, which is intrinsically serial, but its utility has been demonstrated also for nonparallelized code. The idea at the roots of the algorithm relies on the solution of the linear system (obtained from Eq. (6.90) inserting the definition of $\delta\gamma^{(n+1)}$)

$$\delta\gamma_\alpha^{(n+1)} = \sum_{\beta=1}^M \left[\mathbb{S}_{\alpha\beta}^{(n)} \right]^{-1} \sigma_\beta(\mathbf{R}(t + \delta t), s^{(n)}) \quad (6.100)$$

by means of the widespread algorithm of the linear conjugate gradient [119]. To be able to fully employ the speed and stability of the linear conjugate-gradient method, the SHAKE matrix has to be symmetrized. Indeed, the presence of positions and additional variables computed at different steps of the evolution and of the iterative procedure in the definition of the SHAKE matrix in Eq. (6.89) makes the latter asymmetric. In principle, every (asymmetric) linear system of the form $Ax = b$ could be written in a form suitable for conjugate gradient minimization, simply by solving the equivalent, symmetric problem $F(x) = (Ax - b)^T(Ax - b) = 0$. Nonetheless,

the matrix-vector multiplications involved in the definition of $F(x)$ would make the computation scale as $o(M^3)$ in worst case scenario, with the additional computational overhead that, with the usual exception of the linear constraints, the function F , as well as the matrix A , should be recomputed at each iteration of the procedure.

A good way around is to replace the definition of $\mathbb{S}$ given in Eq. (6.89), with its symmetric form given by

$$\mathbb{S}_{\alpha\beta}^{\text{symm}} = \delta t^2 \sum_{\lambda=1}^M \frac{\partial \sigma_{\alpha}(\mathbf{R}(t), s(t))}{\partial s_{\lambda}} \frac{\partial \sigma_{\beta}(\mathbf{R}(t), s(t))}{\partial s_{\lambda}} \quad (6.101)$$

With this modification, the matrix $\mathbb{S}^{\text{symm}}$ is also positive definite by definition, being now computed as the second power of a nonsingular matrix. Note that, if the gradient of the constraints does not depend on the physical variables, the expression in Eq. (6.101) corresponds to the one given for the truncated Newton method in Eq. (6.98) with the — admissible — choice $s^{(0)} = s(t)$ in place of $s^{(0)} = s^P$.

The linear system in Eq. (6.100) can now be solved using a standard linear (preconditioned) conjugate gradient algorithm like the one reported in Figure 6.3. When the constraint are nonlinear functions of the additional variables, a single conjugate-gradient minimization is, in general, not sufficient to satisfy the constraints exactly and the procedure has to be iterated.

6.7 Summary

In this chapter, we presented a new algorithm to solve the dynamics of systems where two sets of degrees of freedom are adiabatically separated. The algorithm exploits the formalism of constrained molecular dynamics, in the special case of degrees of freedom with zero mass, and can be implemented *via* a combination of standard integration methods for the ions (*e.g.* Verlet algorithm) and SHAKE to enforce the constraint. The new propagation scheme presented in this chapter is symplectic and time reversible and it is expected to guarantee stable integration for arbitrary simulation length. We have also shown how the mass-zero constrained dynamics can be adapted to models that impose additional conditions on the dynamics of the auxiliary variables and we have analyzed the statistical mechanics associated to the dynamical system, deriving the fully adiabatic marginal probability in the physical phase space.

Result: Find $\delta\gamma$ that satisfies $\mathbb{S}\delta\gamma = \sigma(s^{(n)})$

Input: $\delta\gamma, s^{(n)}, \sigma(s^{(n)}), \mathbb{S}, \mathbb{P}$

Output: $\delta\gamma$

Data: max_iter, tol

Locals: $r, y, p, \alpha, \beta, \xi_{new}, \xi_{old}$

$r \leftarrow \mathbb{S}\delta\gamma - \sigma(s^{(n)})$

if $\sqrt{r \cdot r} < tol$ **then return**

$y \leftarrow \mathbb{P}^{-1}r$

$\xi_{new} \leftarrow r \cdot y$

$p \leftarrow -r$

$k \leftarrow 0$

while $k < max_iter$ **do**

$\alpha \leftarrow \frac{r \cdot y}{p \cdot \mathbb{S}p}$

$\delta\gamma \leftarrow \delta\gamma + \alpha p$

if $k \% 50 = 0$ **then**

$r \leftarrow \mathbb{S}\delta\gamma - \sigma(s^{(n)})$

else

$r \leftarrow r + \alpha \mathbb{S}p$

end if

if $\sqrt{r \cdot r} < tol$ **then return**

$y \leftarrow \mathbb{P}^{-1}r$

$\xi_{old} \leftarrow \xi_{new}$

$\xi_{new} \leftarrow r \cdot y$

$\beta \leftarrow \frac{\xi_{new}}{\xi_{old}}$

$p \leftarrow -y + \beta p$

$k \leftarrow k + 1$

end while

Fig. 6.3 The preconditioned linear conjugate-gradient algorithm for solving the linearized constraint equation. Note that this algorithm only yields the solution of the linearized equation and, in presence of nonlinear constraints, the procedure has to be iterated up to convergence. The procedure is initialized with $s^{(0)} = s^P$. The matrix $\mathbb{S}^{\text{symm}}$ in Eq. (6.101) is indicated for simplicity by $\mathbb{S}$ in the algorithm. The matrix $\mathbb{P}$ is the preconditioner and its form is dependent from the particular problem to be solved. The tol and max_iter data variables need not to be the same of the Newton-Rapshon procedure. Among the local variables, the Latin letters indicate vectors of dimension M , while Greek letters indicate scalars. The procedure is successfully stopped when the norm of the residuals r is less then a user-defined tolerance. Otherwise an error occurs when the maximum number of iterations allowed is exceeded. Pseudocode is from Ref. [119].

This probability coincides with the one typically assumed in Born-Oppenheimer sampling. The discussion presented here focused on the microcanonical ensemble, but the generalization to other ensembles is straightforward. Finally, we have discussed numerical implementations of the method, presenting three different algorithms to solve the equations of the constraints. In the next chapters these methods will be applied to physically relevant systems to show the efficiency and accuracy of the mass-zero constrained algorithm compared to available alternatives.

Chapter 7

Classical Models for Supercapacitors

Supercapacitors are high power electricity storage devices that can be fully charged/discharged in a few seconds. They have a much larger energy density than conventional capacitors and play an important role complementing batteries in the field of energy storage. They are, for example, used in the Kinetic Energy Recovery System (KERS) in Formula One or in the Stop & Start technology recently introduced in conventional cars. There is, however, still a tremendous need for increasing the energy density of supercapacitors, a goal to be achieved mostly by enhancing their capacitance. Electrochemical Double Layer Capacitors (EDLC) constitute the main family of supercapacitors. In these devices, the charge is stored at the electrode/electrolyte interface through reversible ion adsorption at high-surface-area carbon electrodes [11]. In combination with the electrodes, the electrolyte is the main component of EDLC that can be optimized to increase the capacitance [12]. Two main families of electrolytes have been studied so far. On the one hand, the organic electrolytes, typically made of an organic salt (*e.g.* tetraethylammonium tetrafluoroborate, $\text{NEt}_4\text{-BF}_4$, or 1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonimide, EMIM-TFSI) dissolved in a solvent with high dielectric constant such as acetonitrile or propylene carbonate. On the other hand, the ionic liquids, solvent-free electrolytes liquid at room temperature (EMIM-TFSI is an ionic liquid, $\text{NEt}_4\text{-BF}_4$ is not). The charging mechanisms of EDLC is well understood thanks to a combination of electrochemical, spectroscopic and simulation studies [13], but understanding of the microscopic structure of the adsorbed fluid remains qualitative due to the lack of accurate models of the carbon-electrolyte interface. Due to the computational costs involved, most studies have relied on a simplification of the porous carbon structure (*e.g.* using nanotube or slit-pore geometries [120]) or of the ionic liquid representation (through the use of coarse-grained models [14]). The main difficulty consists in describing accurately the polarization effects both inside the electrode (which needs to be held at constant potential [121, 122]) and inside the ionic liquid. Current simulations exploit algorithms based on conjugate-gradient minimization [99] or other analogous techniques. The convergence of the optimization procedures is however slow and does not take fully into account the mutual interactions of the electrodes and electrolyte, hindering the study of technologically interesting systems. In this chapter we show how to adapt the mass-zero constrained algorithm to the simulation of polarizable electrolytes and of metallic electrodes, laying the basis for the extension of the method to calculations in which electrode and electrolyte auxiliary degrees of freedom are treated together and on equal footing.

The chapter is organized as follows: In Section 7.1 a simple model of polarizable electrolyte is discussed through the formalism of mass-zero constrained dynamics, the equations of motion for the dynamical systems are presented and a comparison of the efficiency of the method with available alternatives is discussed showing better performance in efficiency and stability. In Section 7.2 the fluctuating charges model for the simulation of metallic electrodes is discussed. Mass-zero constrained dynamics is applied to a test system of nonpolarizable water between two carbon electrodes held at constant potential and with electroneutrality constraint enforced. Also in this case, the use of mass-zero constrained dynamics is compared with other state-of-the-art alternatives and a comparison in efficiency and stability is performed, showing promising results. Finally, in Section 7.3 the simultaneous presence of polarizable electrolyte and of metallic electrodes is discussed in the framework of the mass-zero constrained dynamics and the foundations for a unified treatment of the problem are discussed together with the equations of motion of the dynamical system and with the microscopic model for the interaction potential.

7.1 The Shell Model for Polarizable Electrolytes

The proper description of polarization effects has long been recognized as a key ingredient in the simulation of ionic systems [123]. These effects are, for example, essential to obtain accurate phonon dispersion curves of ionic crystals, transport and structural properties of ionic fluids, and to explain, without the need to invoke charge transfer effects, some apparently anomalous ordered structures observed in crystals and melts. Simulations based on *ab initio* potentials could, in principle, account directly for polarization *via* the quantum treatment of the charge distribution. However, the size and time scales required for calculating significant properties of ionic systems are substantial, and semi-empirical potentials are still the preferred modeling tool for these systems. In these potentials, changes in the electronic charge distribution are mimicked *via* appropriate sets of auxiliary dynamical variables that embody different effects. These variables appear in different terms of the potential energy, *e.g.* short-range repulsion, Coulomb and dispersion interactions, and are coupled to the ionic degrees of freedom through parameters determined *via* comparisons with experiments or with accurate *ab initio* calculations. One of the first examples of this kind was the Shell Model [124] (SM), which accounts

for dipole polarization, followed by improvements including the interactions due to quadrupoles [125] and changes in the ions size and shape [126].

In molecular dynamics (MD) simulations, the values of the auxiliary variables are determined by imposing the condition that, at each time step, the total energy at the current ionic configuration is at a minimum with respect to these degrees of freedom. The choice of the algorithm to find this minimum is a delicate, and critical, aspect of these simulations. In earlier calculations for the SM, iterative steepest descent or conjugate-gradient methods were adopted. Both methods, however, suffer from instabilities and relatively high computational cost hindering long simulations. In the early 1990s, a different approach, based on a classical application of the Car-Parrinello scheme, was then adopted [92, 93]. In this case, an extended Lagrangian for the ionic and auxiliary variables is constructed and the evolution equations for the coupled system are propagated. In analogy with the electronic problem, it can be shown that the ions evolve on the correct energy surface provided that no, or very slow, energy transfer between the ions and the auxiliary degrees of freedom occurs (adiabatic condition). Some successful applications notwithstanding, this scheme too has limitations: for models involving a large number of auxiliary variables, maintaining adiabaticity for the long times required by the simulations proves difficult if not impossible [94]. Furthermore, the algorithm requires the use of a very small time step to integrate the dynamics of the auxiliary variables. Due to these problems, more recent calculations adopt again a conjugate-gradient minimization and the propagation is similar to that of Born-Oppenheimer *first principles* molecular dynamics [94, 95]. The latest algorithms are quite effective, but are known to fail to converge (*e.g.* structural studies of glasses at high temperatures [98] or simulations including quadrupoles) or become too expensive (*e.g.* electrode/electrolytes simulations with models accounting for their mutual polarization [99]) in relevant applications. These limitations motivate the development of an alternative, cost-effective and stable algorithm in this area.

In the following, we discuss how to enforce the minimum energy condition *via* mass-zero constrained molecular dynamics [23]. This will be done, following the strategy detailed in the previous chapter, by writing for this system the method of constraints in the special case of zero mass constrained degrees of freedom, consistent with the physical assumptions of polarizable models where the physical mass is localized only on the ions. The resulting dynamical system is integrated combining Verlet propagation of the ions with the SHAKE algorithm to satisfy

the constraint (thus ensuring that the algorithm is symplectic and time reversible). We then illustrate the performance of the algorithm by comparing the results of a proof-of-principle calculation on SM polarizable NaCl with those of a calculation based on conjugate-gradient minimization. For simplicity, in this work, we focus on the specific SM adopted by Jacucci *et al.* in Ref. [90], but the method can be easily extended to more recent polarizable models.

7.1.1 The Model

In the SM model, the electronic charge density of an ion in a condensed-phase environment responds to the instantaneous configuration of the other ions through electrostatic and short-range effects due to overlap of charge density. In its simplest version, the SM describes the ion's polarization by assuming that its total charge is divided between a core (representing the nucleus) and a massless shell (representing the electronic charge density). The core and its shell are bound by a harmonic potential. Let us indicate with $\mathbf{r} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ and $\boldsymbol{\rho} = \{\boldsymbol{\rho}_1, \dots, \boldsymbol{\rho}_N\}$, where N is the number of ions. The SM potential considered in [90] is then of the form¹

$$\begin{aligned}
 U(\mathbf{r}, \boldsymbol{\rho}) = & \sum_{i=1}^N \frac{1}{2} k_i (\boldsymbol{\rho}_i - \mathbf{r}_i)^2 \\
 & + \sum_{i \neq j} \left\{ \frac{\chi_i \chi_j}{|\boldsymbol{\rho}_i - \boldsymbol{\rho}_j|} + \frac{\chi_i Q_j}{|\boldsymbol{\rho}_i - \mathbf{r}_j|} + \frac{Q_i \chi_j}{|\mathbf{r}_i - \boldsymbol{\rho}_j|} + \frac{Q_i Q_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right. \\
 & \left. + A_{ij} \exp \left[-\frac{|\boldsymbol{\rho}_i - \boldsymbol{\rho}_j|}{\lambda} \right] - \frac{C_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|^6} - \frac{D_{ij}}{|\mathbf{r}_i - \mathbf{r}_j|^8} \right\}
 \end{aligned} \quad (7.1)$$

where Q_i and χ_i represent the charge assigned to the core and the shell of the ion i , respectively² and k_i , A_{ij} , λ , C_{ij} and D_{ij} are force-field parameters dependent on the particular species considered. The dynamics of the system is defined in accordance with the Born-Oppenheimer approximation: The shells, being of zero mass, are assumed to adapt instantaneously to the positions of the cores so as to satisfy

$$\sigma_h^\alpha \equiv \frac{\partial U(\mathbf{r}, \boldsymbol{\rho})}{\partial \rho_h^\alpha} = 0 \quad (7.2)$$

¹Since in this and, in particular, in the following sections, the electrostatic potential will often be central in the description of the models, we will leave the more familiar symbol V for this physical quantity, while indicating the interaction energy by U .

²The parameters Q_i and χ_i are subject to the condition $Z_i = Q_i + \chi_i$, where Z_i is the ionic charge.

with $h = 1, \dots, N$ and $\alpha = x, y, z$. We shall now interpret Eq. (7.2) as a set of $3N$ holonomic constraints and derive the evolution equations for the constrained system of cores and shells in the framework of the mass-zero constrained dynamics described in Chapter 6. We start by assigning the same finite mass μ to the shells and, proceeding in analogy with the derivation in Section 6.1, *i.e.* taking the limit $\mu \rightarrow 0$, the equations of motion for the extended system are given by

$$\begin{aligned} m_i \ddot{\mathbf{r}}_i &= -\nabla_{\mathbf{r}_i} U(\mathbf{r}, \boldsymbol{\rho}) \\ \ddot{\boldsymbol{\rho}}_i &= -\sum_{k=1}^N \sum_{\beta=x,y,z} \gamma_k^\beta \nabla_{\boldsymbol{\rho}_i} \sigma_k^\beta \end{aligned} \quad (7.3)$$

where m_i represents the mass of the ion i . In the simulations, these equations are integrated using Verlet (not velocity Verlet as indicated in the previous chapter) for the ionic degrees of freedom. SHAKE is then used to enforce the constraint on the shell variables. This choice does not affect the theory or the effectiveness of the approach.

7.1.2 Simulation Details and Results

In the following, Eq. (7.3) is applied to compute static and transport properties of a simple SM of NaCl. The simulation set up is similar to the one adopted by Jacucci *et al.* in Ref. [90], with a cubic simulation box containing 108 Na^+ and 108 Cl^- ions. Periodic boundary conditions are enforced in all directions. The interaction potential and the simulation parameters used in our calculations are those reported in Ref. [90]. At variance with that paper, which employed Ewald sums to treat the long range forces, all interactions are truncated at a cut off radius $r_c = 0.5L$, where L is the side of the simulation box. The potential is shifted at r_c to enforce smoothness of the first two derivatives. While this is the standard approach to deal with short-range forces, its use for Coulomb interactions might appear crude. Recently, however, this approach has been often adopted when large systems are studied or when no particular accuracy of the exact physical value of the energy is required [127–129]. In this work, it was enforced for the sake of simplicity since our simulations are intended as a test of the algorithm and not focused on computing the (well known) physical properties of NaCl. Note that, when the inclusion of Ewald sums is necessary, computing the second derivatives of the potential to propagate

the shell variables (see Eq. (7.3)) does not pose any additional analytical problem since these derivatives are explicit functions of the shell coordinates. The additional cost associated with the fact that the Ewald terms in the gradient of the constraints should be evaluated at each iteration in the SHAKE algorithm is expected to be compensated by a smaller number of iterations to convergence. Moreover, the computational burden can be lighten using one of the other algorithms discussed in Section 6.6. Furthermore, preliminary calculations indicate that including Ewald sums in the constrained algorithm for more recent and commonly used polarizable models (see, for example, Ref. [125]) does not modify significantly its performance relative to alternative propagation schemes. This is due to the fact that the quadratic form of the energy in the auxiliary variables enables to perform the simulation with a single evaluation of the gradient of the constraint per timestep (see Sections 7.2 and 7.3 for more detail).

Two calculations are presented here. In the first, the system is in the solid state at temperature $T_L \approx 300$ K and molecular number density $\rho_L = 2.18 \cdot 10^{-2} \text{ \AA}^{-3}$. The second simulation was performed at $T_H \approx 1550$ K (*i.e.* well in the molten phase — the melting temperature of the system is $T_M = 1073$ K) and molecular number density $\rho_H = 1.38 \cdot 10^{-2} \text{ \AA}^{-3}$. The simulations are initialized as follows: the Na^+ and Cl^- cores are placed at the appropriate simple cubic lattice sites and then shifted *via* a small uniform random displacement in all directions. The initial positions of the shells are then determined *via* a conjugate-gradient minimization of the potential energy in these variables. Initial velocities for all degrees of freedom are set equal to zero. The first step is then performed obtaining $\mathbf{r}_i(\delta t)$ and $\mathbf{p}_i(\delta t)$ *via* their second order Taylor expansion in δt . Note that the first order term in the expansion is zero for both sets of variables due to the choice of the initial velocities, and the second derivatives with respect to time are given by Eqs. (7.3). Standard (*i.e.* Verlet plus SHAKE) integration is started from step two. This procedure ensures that the constraints are satisfied, to second order in the timestep, also in the initialization of the simulations. Equilibration to the target temperatures is obtained by propagating the system for $4 \cdot 10^3$ timesteps and rescaling velocities whenever the temperature differs from the target more than a given tolerance (typically 10% of the target temperature). In the simulations discussed in the following, the temperatures estimated after equilibration are within 4% of their target. NVE production runs of length $4 \cdot 10^3$ timesteps are then performed to compute properties for both systems. The timestep employed in the Verlet evolution is set to $\delta t = 3.5$ fs for all simulations.

Table 7.1 Comparison between conjugate-gradient (CG) and SHAKE (SH) based algorithms for different values of the tolerance threshold, Tol, of the minimization method. The data refers to the simulation at $T = 306\text{K}$. In the legend τ is the average CPU time per time step and n is the average number of iterations necessary to reach convergence of the minimum condition for a given tolerance.

Tol	Alg	n	τ (s)	$\frac{\Delta E}{\Delta V}$ (10^{-3})	$\frac{100\sqrt{\langle r_{Na}^2 \rangle}}{d}$	$\frac{100\sqrt{\langle r_{Cl}^2 \rangle}}{d}$
$4.5 \cdot 10^{-12}$	CG	63.3	9.7	3.0	12.0	10.8
$4.5 \cdot 10^{-12}$	SH	14.2	3.3	3.0	12.0	10.8
$4.5 \cdot 10^{-9}$	CG	43.9	6.7	3.0	12.0	10.8
$4.5 \cdot 10^{-9}$	SH	11.0	2.6	3.0	12.0	10.8
$4.5 \cdot 10^{-6}$	CG	17.2	2.7	3.0	12.0	10.8
$4.5 \cdot 10^{-6}$	SH	8.0	2.0	3.0	12.0	10.8
$4.5 \cdot 10^{-3}$	CG	6.0	1.1	16	11.9	10.8
$4.5 \cdot 10^{-3}$	SH	4.2	1.2	7.8	13.2	12.1

For comparison, we also present calculations in which the minimum energy condition is enforced, at each step along the trajectory of the cores, *via* a conjugate-gradient algorithm [130, 131]. To focus on the effect of the minimization procedure, all the NVE runs for a given temperature were started from the same initial condition, obtained *via* the equilibration procedure described above applied to the mass-zero constrained algorithm.

Let us begin by comparing the precision and efficiency of the simulations performed *via* mass-zero constrained dynamics and conjugate-gradient minimization. In the third and fourth column of Tables 7.1 and 7.2, we report the average number of iterations, n , and the average CPU time to convergence to the minimum, τ , for the two methods. In both cases, convergence of the minimization is controlled *via* a tolerance parameter. Convergence is achieved when the maximum component of the force acting on each shell is less than this predefined tolerance. In the tables, we report, indicating it with “Tol”, the value of the tolerance parameter relative to the root mean square force on the cores to provide a reference. The results in Tables 7.1 and 7.2 show that, as the level of precision is increased, the mass-zero constrained algorithm requires considerably less iterations, about a factor of two for $\text{Tol} \approx 10^{-6}$, and a factor of about 4.5 for the highest convergence threshold. This reduction translates in shorter average CPU time to reach convergence, up to a factor of about three for the highest precision. It should be pointed out that the

Table 7.2 Results for the system in the molten phase at $T = 1550$ K and $\rho = 1.3793$ g cm $^{-3}$. The first five columns are the same as Table 7.1. The remaining columns report the diffusion coefficients of the two ionic species.

Tol	Alg	n	τ (s)	$\frac{\Delta E}{\Delta V}$ (10^{-3})	D_{Na} (10^{-4} cm ^{2} s $^{-1}$)	D_{Cl} (10^{-4} cm ^{2} s $^{-1}$)
$1.3 \cdot 10^{-12}$	CG	73.9	11.7	4.4	2.3	1.8
$1.3 \cdot 10^{-12}$	SH	15.3	3.6	4.8	2.2	1.8
$1.3 \cdot 10^{-9}$	CG	49.0	7.8	4.4	2.3	1.9
$1.3 \cdot 10^{-9}$	SH	12.0	2.9	4.4	2.2	1.8
$1.3 \cdot 10^{-6}$	CG	17.5	2.8	4.4	2.3	1.7
$1.3 \cdot 10^{-6}$	SH	8.5	2.1	4.8	2.2	1.8
$1.3 \cdot 10^{-3}$	CG	8.2	1.4	24	2.4	1.9
$1.3 \cdot 10^{-3}$	SH	5.2	1.4	4.9	2.4	1.8

cost of a single step in the iterations to reach convergence is not equal for the two methods. The conjugate-gradient procedure, in fact, requires only the calculation of the gradient of the potential. The constraint condition, on the other hand, necessitates the evaluation of second derivatives of the potential and it is therefore numerically more demanding. This numerical disadvantage is, however, largely compensated by the reduction in the number of iterations. The relative energy fluctuations for the different convergence thresholds are shown in column five of the tables showing that very good accuracy can be obtained with both methods for $\text{Tol} \leq 10^{-3}$.

In columns six and seven of Table 7.1, we also show the mean square displacement relative to the distance of the Na and Cl lattice sites, d , for the positive and negative cores, respectively. The results are reasonable in view of those reported by Jacucci *et al.* ($\frac{100\sqrt{\langle r_{J+}^2 \rangle}}{d} = 12.6$ and $\frac{100\sqrt{\langle r_{J-}^2 \rangle}}{d} = 11.0$) at the same molecular number density.

As a final check of the equivalence of constrained and conjugate-gradient based MD, let us now consider the results for the run in the molten phase. The radial distribution functions for the different pairs of ionic species at $T = 1550$ K are shown in Figure 7.1. The results from constrained MD, represented as solid curves, and those from conjugate-gradient based calculations, open symbols, are essentially superimposed. Here and in the following figure, runs with $\text{Tol} \approx 10^{-12}$ are considered. The shape and position of the peaks in the plot are also in agreement with previous calculations [78]. The very good performance of the constrained algorithm is confirmed

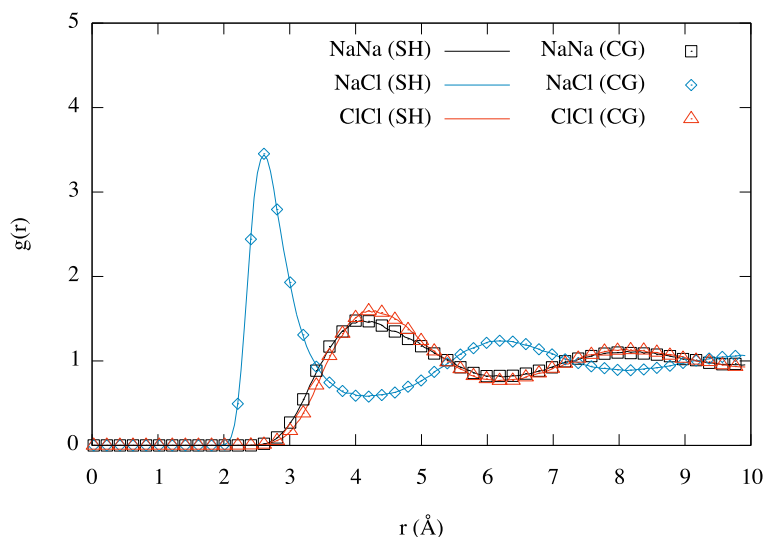


Fig. 7.1 Radial distribution functions for the ionic species in the system at $T = 1550$ K. As detailed in the legend, results for the constrained algorithm are reported as solid curves, while open symbols show results of the calculation based on conjugate-gradient minimization.

when computing dynamical properties. In the main panel of Figure 7.2, we report the velocity autocorrelation functions of the positive (top panel) and negative (bottom panel) ions. In this case too, the constrained and conjugate-gradient algorithms produce essentially indistinguishable curves, whose characteristics are also in good agreement with previous simulations [87]. The insets in Figure 7.2 show the integrals of the velocity autocorrelation function for the two species plotted as a function of the upper limit of the time integral. The diffusion coefficients, estimated from the plateau value of these integrals, are reported in the last two columns of Table 7.2, showing good agreement between the two algorithms. The estimated diffusions are also in agreement with previous simulations and experimental results [87].

7.2 The Fluctuating Charge Model for Metallic Electrodes

Electrochemical systems involve many complex interfaces which are difficult to characterize experimentally and to simulate accurately. Different phenomena may occur at the molecular scale, such as electron transfers, ions adsorption, chemical reactions, *etc.* [132, 133]. In the case of electrochemical energy storage devices,

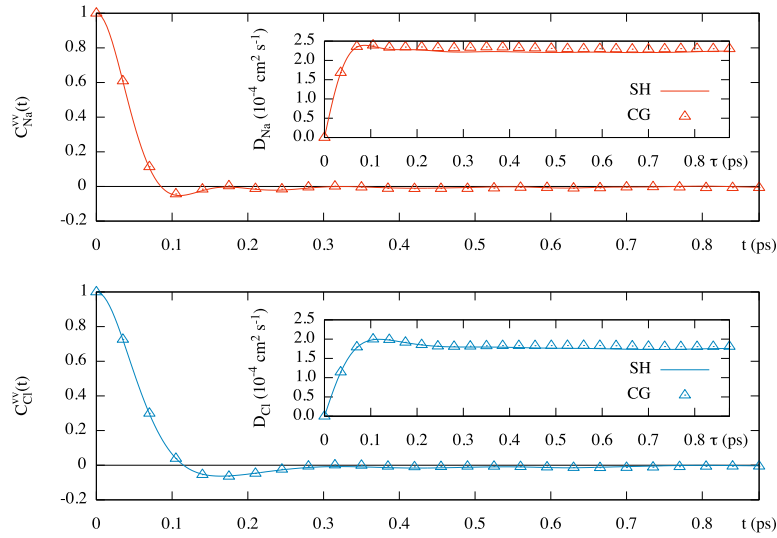


Fig. 7.2 Velocity autocorrelation function, $C_{\alpha}^{vv}(t) = \frac{1}{3N_{\alpha}} \sum_{i=1}^{N_{\alpha}} \langle \mathbf{v}_{\alpha}^i(0) \cdot \mathbf{v}_{\alpha}^i(t) \rangle$ - where α indicates the ionic species, (main panel) and their integral, $D_{\alpha} = \int_0^{\tau} dt C_{\alpha}^{vv}(t)$ as a function of the maximum integration time, τ , (inset) for Na^+ (top panel) and Cl^- (bottom panel) for the simulation at $T = 1550\text{ K}$. As detailed in the legend, results for the constrained algorithm are reported as solid curves, while open symbols show results of the calculation based on conjugate-gradient minimization.

which are often operated at rather large voltages and for the largest number of cycles possible [11, 134], understanding all these processes is unavoidable to design new electrode materials and/or electrolytes. From the simulation point of view, several methods can be used depending on the target properties and the scale at which the system needs to be represented. In particular, Density Functional Theory (DFT) calculations allow to determine the thermodynamics of reactions in close proximity of the electrode [135–137]. However, there are many problems for which it is necessary to treat the interface at length scales going beyond the nanometer, for example in order to understand the structure of the adsorbed layer that forms and how it screens the electrode charge [13, 133]. In such cases, thermal fluctuations play an important role, but DFT-based molecular dynamics cannot be used because of the large system sizes that are involved (typically thousands of atoms). It is thus necessary to use a more approximate method such as Classical Molecular Dynamics (CMD).

Indeed, CMD is commonly used to study extended systems over long time-scales. As an example, hundreds of thousands of atoms can be simulated for microsec-

onds to study biochemical mechanisms. Yet, in most classical calculations, the molecules/materials at play are electronically insulating, so that they are conveniently represented as collections of fixed charges over the whole simulation. This is of course not adequate to represent electrodes. More complex electrostatic schemes have been derived, among which a constant potential method was proposed by Siepmann and Sprik to account for the delocalized nature of the electronic cloud inside a metallic material and its perturbation by an external charge arising from the electrolyte [138]. Their method allowed to fix the potential of each electrode, therefore providing the correct framework for studying electrochemical energy storage devices. The method was later extended by Reed *et al.* to the case of two-dimensional periodic systems, [139] opening the way towards systematic studies of complete electrochemical cells [14].

The main ingredient of the Siepmann-Sprik method is the use of fluctuating electrode charges, in the same spirit as the charge equilibration [140, 141] scheme for molecular systems. These charges are thus treated as additional degrees of freedom in a similar way as the positions of the shells for the shell model described in the previous section, the induced dipoles involved in polarizable force fields [142] or the wavefunction coefficients in DFT-based molecular dynamics [143]. The evolution equations of this model can therefore be solved using algorithms originally developed for these more common cases. In their seminal work, Siepmann and Sprik have used the Car-Parrinello algorithm [91], which consists in introducing a fictitious mass to each additional variable and treating it as a full dynamical degree of freedom. Along the years this algorithm was progressively replaced by Born-Oppenheimer-based approaches, in which the degrees of freedom other than the atomic positions are determined either in a self-consistent way or through energy minimization techniques. In this section we analyze the application of the mass-zero constrained algorithm to the simulation of metallic electrodes [25], showing that this approach is also very efficient for computing the fluctuating charges of the electrodes under constant applied potential conditions, allowing further to enforce the overall electroneutrality of the system. We test the algorithm on a simple capacitor made of graphite electrodes and a pure water electrolyte. It yields instantaneous charges in perfect agreement with other techniques, and accurate properties of the system when long simulations are performed.

7.2.1 The Model

The system of interest is an electrochemical cell composed of two metallic electrodes kept at constant potential and separated by an electrolyte. To set the stage, let us recall that the electric potential $V(\mathbf{r})$ generated by a spatial charge distribution $\rho(\mathbf{r})$ is given by the Poisson equation

$$\nabla^2 V(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \quad (7.4)$$

complemented with appropriate boundary conditions. (Atomic units are used throughout this section.) In our case, these conditions must reflect the fact that the electrodes are conductors and therefore the potential is constant in the space they occupy. Thus

$$V(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \Psi_{\Omega_{\pm}} \quad (7.5)$$

where $\mathbf{r}$ is a point in the region $\Omega_{\pm}$, occupied by electrode $\pm$ and $\Psi_{\Omega_{\pm}}$ is the known value of the potential on each electrode. An equivalent representation of the system, better suited for the introduction of the extended Lagrangian required by mass-zero constrained dynamics, is obtained by recalling that the Coulomb energy associated to the spatial charge density $\rho(\mathbf{r})$ can be written as

$$U_c[\rho] = \frac{1}{2} \int d^3r d^3r' \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{2} \int d^3r V(\mathbf{r})\rho(\mathbf{r}) \quad (7.6)$$

The above equation implies that the electric potential can be obtained as the functional derivative of the Coulomb energy and that, in particular, the boundary condition in Eq. (7.5) can also be expressed as

$$\frac{\delta U_c[\rho]}{\delta \rho(\mathbf{r})} = \Psi_{\Omega_{\pm}} \quad (7.7)$$

for $\mathbf{r} \in \Omega_{\pm}$. A more explicit expression for the Coulomb energy of the system is obtained by specifying the charge distribution of the electrolyte and of the electrodes. In analogy with standard models of charged solutions, the electrolyte charge density is represented as a set of point charges located at the positions of its N atoms. This part of the charge density will be indicated as $\rho_i^q(\mathbf{r}) = q_i \delta^3(\mathbf{r} - \mathbf{r}_i)$ where q_i is the fixed charge of particle i , $\delta(x)$ is the Dirac delta function and $\mathbf{r}_i$ are the positions of the particles of the electrolyte. The specific feature of the fluctuating charge model,

on the other hand, is to replace the continuous physical charge density of the metallic electrodes with a discrete set of M Gaussian charges centered at fixed locations, $\mathbf{R}_\alpha$, in the $\Omega_\pm$ regions. The charge distribution assigned to the site $\mathbf{R}_\alpha$ is given by

$$\rho_\alpha^Q(\mathbf{r}) = Q_\alpha \left(\frac{\eta^2}{\pi} \right)^{\frac{3}{2}} \exp \left[-\eta^2 (\mathbf{r} - \mathbf{R}_\alpha)^2 \right] \quad (7.8)$$

where η is a system-dependent parameter, fixed *a priori* in the model. The Q_α , that represent the integrated charge on each electrode site, have to be determined for each configuration of the system to enforce the conditions in Eq. (7.7). In particular, in a molecular dynamics simulation of the capacitor, these variables must be determined at each time step, as they respond to the evolution of the coordinates of the particles in the electrolyte along the trajectory. Substituting the total charge density $\rho(\mathbf{r}) = \sum_{\alpha=1}^M \rho_\alpha^Q(\mathbf{r}) + \sum_{i=1}^N \rho_i^q(\mathbf{r})$ in Eq. (7.6) and performing the integrals in the second equality, leads to the following explicit expression for the Coulomb energy

$$\begin{aligned} U_c(\mathbf{r}, Q) = & \sum_{\alpha=1}^M \sum_{\beta < \alpha} \frac{Q_\alpha Q_\beta}{R_{\alpha\beta}} \operatorname{erf}[\sqrt{2}\eta R_{\alpha\beta}] + \sum_{\alpha=1}^M \frac{\eta}{\sqrt{2\pi}} Q_\alpha^2 \\ & + \sum_{\alpha=1}^M \sum_{i=1}^N \frac{Q_\alpha q_i}{|\mathbf{R}_\alpha - \mathbf{r}_i|} \operatorname{erf}[\eta |\mathbf{R}_\alpha - \mathbf{r}_i|] + \sum_{i=1}^N \sum_{j < i} \frac{q_i q_j}{r_{ij}} \end{aligned} \quad (7.9)$$

where we have used the notation $\mathbf{r} \equiv \{\mathbf{r}_i\}$, $Q \equiv \{Q_\alpha\}$, and where $R_{\alpha\beta} = |\mathbf{R}_\alpha - \mathbf{R}_\beta|$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Note that in this potential the $\mathbf{R}_\alpha$ are time-independent parameters, specified by the geometry of the model. Given the assumed form of the charge density on the electrodes, the condition in Eq. (7.7) can be reformulated in terms of the discrete “variational” parameters Q_α as

$$\frac{\partial U_c(\mathbf{r}, Q)}{\partial Q_\alpha} = \Psi_\pm \quad (7.10)$$

($\alpha = 1, \dots, M$). In this discrete model for the electrode charge distribution, the condition of constant potential is enforced only at sites $\mathbf{R}_\alpha$, *i.e.* at the center of the Gaussian charge distributions, in contrast with Eq. (7.7) which holds at all positions in the metal. Previous work [139] has shown that, in spite of the approximate treatment of the charge distribution, this still enables accurate simulations of electrochemical system.

Recently, it was suggested to modify the original fluctuating charge model by forcing the Q variables to respect also the so-called electroneutrality condition

$$f(Q) = \sum_{\alpha=1}^M Q_{\alpha} = 0 \quad (7.11)$$

for all accessed configurations of the electrolyte. Note that the sum in Eq. (7.11) runs over the atoms of both the electrodes, implying global electroneutrality of the capacitor. The condition above mimics the presence of an ideal generator connected to the electrodes and enables a closed description of the system, *i.e.* one that does not require to take explicitly into account interactions with a charge reservoir. As discussed in previous work [122], Eq. (7.11) also ensures that relevant physical properties such as the capacitance depend only on the potential difference between the electrodes and not on their absolute potential. In simulations, this condition has the added benefit to simplify the Ewald treatment of electrostatic interactions, avoiding the necessity of a background charge to compensate for the otherwise possible nonneutrality of the system [144]. While electroneutrality is only enforced on average by real generators, the more stringent condition (7.11) has been used in simulations [122, 145] providing accurate results.

The dynamics of the system within the fluctuating charge model is again defined in the framework of the Born-Oppenheimer hypothesis: The charges Q_{α} , mimicking the reorganization of the electronic charge density within the electrodes, adapt instantaneously to the configuration of the particles in the electrolyte. The constraints (7.10) can be trivially interpreted as the requirement that the function $U(\mathbf{r}, Q) \equiv U_c(\mathbf{r}, Q) - \sum_{\alpha=1}^M \Psi_{\alpha} Q_{\alpha}$ (where we indicated with Ψ_{α} the potential at site $\mathbf{R}_{\alpha}$) is at a minimum with respect to Q . Eq. (7.11), however, implies that not all variations of the Q_{α} are independent, and, as previously discussed, this must be accounted for when stating the minimum condition. Following the discussion in Section 6.2 we introduce the auxiliary function

$$W(\mathbf{r}, Q, \nu) = U(\mathbf{r}, Q) + \nu f(Q) \quad (7.12)$$

where ν is the Lagrange multiplier associated to the electroneutrality condition. It is easy to see, looking at the definition of $U(\mathbf{r}, Q)$ and of $f(Q)$, that ν actually corresponds to a potential shift as already noted in previous work [122]. The minimum solution $\hat{Q}$ with Q satisfying also Eq. (7.11) is then given by the stationary

point $\{\hat{Q}, \hat{v}\}$ of $W(\mathbf{r}, Q, v)$ in the extended space that includes also v , the Lagrange multiplier enforcing the electroneutrality condition, as an auxiliary variable. This leads to the $M + 1$ conditions

$$\begin{aligned}\sigma_\beta(\mathbf{r}, Q, v) &= \frac{\partial W(\mathbf{r}, Q, v)}{\partial Q_\beta} = 0 \quad \beta = 1, \dots, M \\ \sigma_{M+1}(Q) &= \frac{\partial W(\mathbf{r}, Q, v)}{\partial v} = 0\end{aligned}\tag{7.13}$$

As usual in the Lagrange multiplier scheme, the last equation above is in fact the electroneutrality condition but now obtained as a result of an optimization problem. Proceeding in analogy with the derivations in Section 6.2, we then extend the space of the dynamical degrees of freedom to include the variables Q and v and define the Lagrangian of the extended system as

$$L = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 + \frac{1}{2} \sum_{\alpha=1}^M \mu_Q \dot{Q}_\alpha^2 + \frac{1}{2} \mu_v \dot{v}^2 - W(\mathbf{r}, Q, v)\tag{7.14}$$

In the equations above, we have introduced two (arbitrary and fictitious) masses, μ_Q and μ_v , associated with the variables Q and v , respectively. To set the stage for the homogeneous limit that we will take on these quantities, we set $\frac{\mu_Q}{\mu_v} \equiv \kappa$, with κ a constant of appropriate physical dimensions. Conditions (7.13) are then interpreted as a set of $M + 1$ holonomic constraints and, in the limit $\mu_Q \rightarrow 0$, the dynamical system takes the form

$$\begin{aligned}m_i \ddot{\mathbf{r}}_i &= -\nabla_{\mathbf{r}_i} U_c(\mathbf{r}, Q) \\ \ddot{Q}_\alpha &= -\sum_{\beta=1}^{M+1} \gamma_\beta \frac{\partial \sigma_\beta}{\partial Q_\alpha} \\ \ddot{v} &= -\sum_{\beta=1}^{M+1} \gamma_\beta \kappa \frac{\partial \sigma_\beta}{\partial v},\end{aligned}\tag{7.15}$$

In the first of Eqs. (7.15), we used the fact that, given Eq. (7.12) and the definition $U(\mathbf{r}, Q) \equiv U_c(\mathbf{r}, Q) - \sum_{\alpha=1}^M \Psi_\alpha Q_\alpha$, we have $\nabla_{\mathbf{r}_i} W(\mathbf{r}, Q, v) = \nabla_{\mathbf{r}_i} U_c(\mathbf{r}, Q)$.

Eq. (7.15) defines the mass-zero constrained dynamics for the fluctuating charge model with electroneutrality constraint. The homogeneity parameter κ introduced to take the limit of zero masses is a free parameter in the derivation of these equations of motions. To fix this parameter, one can note that it has the dimension $[\kappa] = \frac{[v]^2}{[Q]^2}$, that is the inverse of the square of a capacitance and that it is independent of the presence

of the electrolyte. The numerical value of the parameter can then be estimated from a “typical” capacitance for the system, *e.g.* the capacitance of the empty cell, C_{empty} . Exploratory calculations also showed that the numerical stability of the algorithm is insensitive to κ in a very wide range around this value (see the discussion in Section 7.2.2).

Numerical integration of Eqs. (7.15) can be now performed as described in Section 6.4. Note that this model is particularly favorable for the use of the M-SHAKE algorithm for two reasons: First the extended interaction potential W is at most quadratic in the additional variables Q , which means that the constraints are linear and that the linearization of the constraint equation is exact. In particular, this implies that the M-SHAKE procedure does not need iterations and the accuracy of the numerical method is only determined by the condition number of the SHAKE matrix $\mathbb{S}$. Moreover, since the SHAKE matrix is fixed by the geometry of the electrodes, $\mathbb{S}$ is constant during the simulation, as it is its inverse. In particular, this means that the inversion of the matrix — a procedure which is usually very demanding when the dimensionality of the system is large — can be performed only once at the beginning of the simulation.

We conclude this section noting that extending the set of auxiliary variables to include v is not the only way to enforce the electroneutrality condition. For this particular case, it is in fact trivial to identify a set of generalized coordinates constraining the system to the correct hypersurface by reducing the dimensionality of the Q to $M - 1$ variables and setting, for example, $Q_1 = -\sum_{\alpha=2}^M Q_\alpha$. The method proposed in this section, however, is completely general and can be applied also in cases where the definition of appropriate generalized coordinates is problematic. The only potential limitation of the method is numerical, stemming from the computational cost of enlarging the space of auxiliary variables.

7.2.2 Simulation Details and Results

To test the accuracy and the efficiency of the algorithm in real electrochemical simulations, the method described above has been implemented in the software package *MetalWalls*, a dedicated code for the simulation of electrochemical cells [146]. The basic step of the algorithm adopted combines the three-step form of the velocity Verlet propagation for the physical degrees of freedom with Verlet integration, incor-

porating the M-SHAKE solution of the constraints for the evolution of the auxiliary variables. Initial conditions are chosen *via* standard procedures for the physical variables, while the initialization of the auxiliary variables at t and $t - \delta t$, necessary for the Verlet algorithm, is performed using constrained conjugate-gradient minimization [147]. The convergence threshold for conjugate-gradient minimization is set to $10^{-12} E_h e^{-1}$, where E_h is the unit of energy in Hartree atomic units and e is the electron charge, in order to satisfy the constraints up to numerical precision from the beginning of the simulation.³

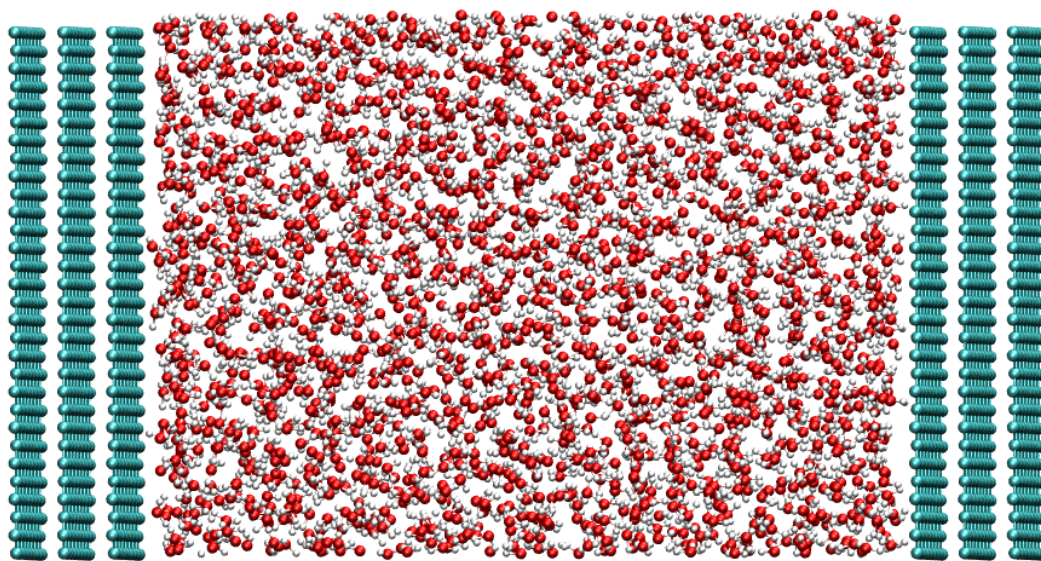


Fig. 7.3 Representative snapshot of the simulated system (turquoise: C, red: O and white: H atoms). The z -direction is perpendicular to the carbon electrodes.

A nontrivial test calculation is presented below to illustrate the properties of the algorithm. We simulate a system consisting of a slab of liquid water between two graphite electrodes, with the two interfaces perpendicular to the z -direction of the box, as shown in Figure 7.3. Despite its apparent simplicity, this system is very representative of current simulation works, which aim at characterizing the hydration of metal surfaces, both from the structural [148, 149] and the dynamical [150] points of view. The extension to more complex systems, such as dilute aqueous solutions [151, 152], ionic liquids [14, 153, 154] or superconcentrated electrolytes [155], is trivial and does not require further technical development.

³The different initialization scheme proposed in Section 7.1 for the Shell Model, even if more rigorous, turned out to be impractical to implement in *MetalWalls*. Use of the conjugate-gradient minimization, on the other hand, is available in the code. This choice of initialization did not cause visible problems and has negligible additional cost.

The simulated system contains 2160 water molecules and 2880 carbon atoms in total. Each electrode is made of three graphene planes of 480 atoms each, with an interplane distance of 3.354 Å. Two-dimensional boundary conditions were used with no periodicity in the z -direction. The box lengths along x and y were respectively fixed to $L_x = 34.101$ Å and $L_y = 36.915$ Å. The Lennard-Jones parameters were taken from Refs. [156, 157], with the various cross-terms chosen accordingly to the Lorentz-Berthelot mixing rules [158, 159]. A cut-off radius of 17.05 Å was used for the van der Waals interactions. Electrostatic interactions were computed using the two-dimensional Ewald summation technique [139, 160]. Electrode atoms have a Gaussian charge distribution of width $\eta^{-1} = 0.56$ Å.

A timestep of 1 fs was used to integrate the equations of motion. The system was first equilibrated for 500 ps with the electrode charges set to zero at constant temperature of 298 K and atmospheric pressure. The latter condition was enforced by allowing the positions of the electrode atoms to vary along the z direction only, treating them as rigid bodies, in the presence of an external force corresponding to the target pressure. The separation between the two electrodes fluctuated around an equilibrium value of 55.11 Å. This value was chosen to fix the positions of the graphene planes in the following simulations. The system was then equilibrated for another 100 ps run in the NVT ensemble, with the two electrodes potential fixed to $\Psi_- = -0.5$ and $\Psi_+ = 0.5$ V using the conjugate-gradient method. A NVE ensemble production run of 500 ps was then performed using the mass-zero constrained dynamics algorithm. The standard deviation of the total energy along the simulation is $\approx 6 \times 10^{-4} E_h$, *i.e.* less than 1% of the standard deviation of the potential energy of the system.

To fix the homogeneity parameter κ , tests of the efficiency of the algorithm and of the accuracy of the simulation results have been performed varying κ around and above the value obtained from the capacitance of the empty cell $\kappa_{\text{empty}} = C_{\text{empty}}^{-2} = 0.08 E_h^2 e^{-4}$. The Condition Number (CN) of the SHAKE matrix $\mathbb{S}$ is reported as a function of the value of κ in the lower panel of Figure 7.4. The CN affects the accuracy of the numerical inversion of the matrix and is therefore important for the numerical stability of the algorithm. We find that this indicator is stable for values of the homogeneity parameter around κ_{empty} and remains stable when increasing the homogeneity parameter over two orders of magnitude. On the other hand, for $\kappa < \kappa_{\text{empty}}$, after a first range where the trend is basically constant, the value of the condition number (and consequently the numerical noise resulting from the

numerical inversion of the matrix) increases rapidly. This behaviour is reflected in the accuracy of the computed electrode charges as seen considering the relative error on the computed charges with different values of κ with respect to the value of $\kappa = 1 E_h^2 e^{-4}$ (in the middle of the tested interval). The average $\overline{\Delta Q}$ over the number of electrode atoms for 100 steps of MD of

$$\Delta Q_\alpha^\kappa = \left| \frac{Q_\alpha^\kappa - Q_\alpha^{\kappa=1}}{Q_\alpha^{\kappa=1}} \right| \quad (7.16)$$

is reported in the upper panel of Figure 7.4 as a function of κ .

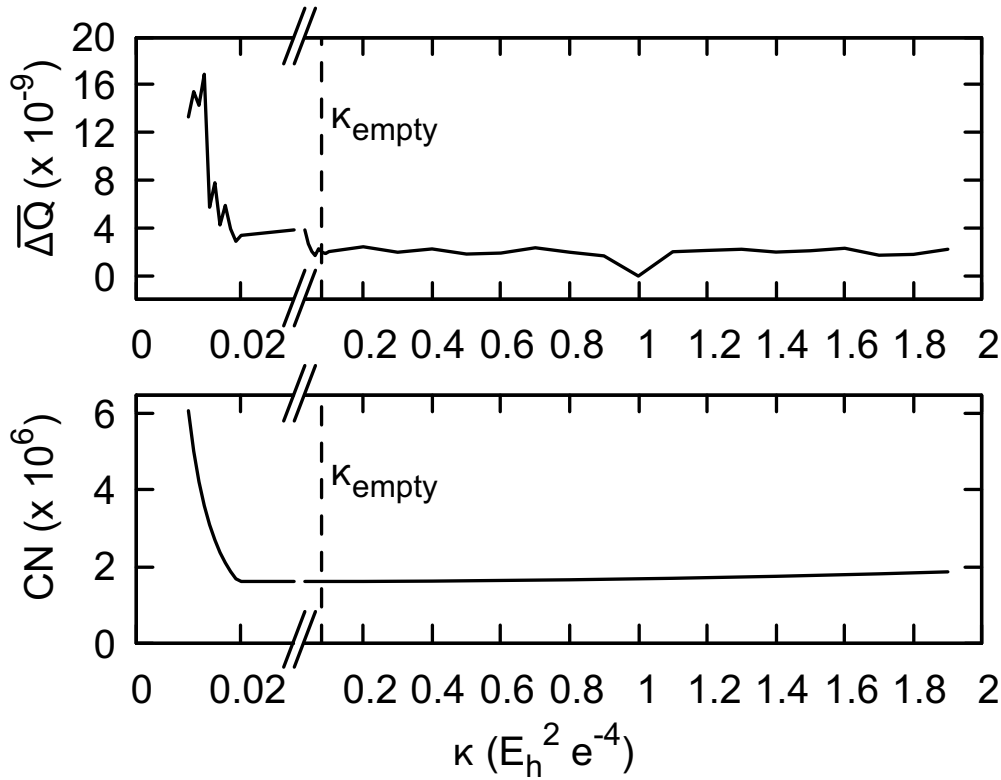


Fig. 7.4 Condition Number (CN) of the SHAKE matrix (lower panel) and mean relative error on charges (upper panel) as a function of the homogeneity parameter κ . Both indicators are stable for values of κ above κ_{empty} (indicated with dashed lines in both panels) of at least two orders of magnitude. For $\kappa < \kappa_{\text{empty}}$, after a small range of constant value, they increase rapidly. Note the two different scales on the x -axes of both panels.

This analysis shows that simulation results and performance of the algorithm are not really sensitive to the value of the homogeneity parameter for $\kappa > \kappa_{\text{empty}}$. In fact, even choosing $\kappa < \kappa_{\text{empty}}$ still leads to very good agreement of the fluctuating

charges with their reference value. In the calculations reported in the following, the homogeneity parameter was set to $\kappa = 1 E_h^2 e^{-4}$.

In a first step, we compare the new method, which is noted as MaZe in the following, to the generic Born-Oppenheimer approaches, which either employ a conjugate gradient (CG) minimization [139] or a matrix inversion [161] (MI) while enforcing electroneutrality at each timestep. A comparison of the performance of the three methods is made in Table 7.3. In terms of performance, a typical step using

Table 7.3 Performance comparison of MaZe with respect to other Born-Oppenheimer approaches (first column). The tolerance of the minimization procedure is reported in the second column (for MI and MaZe this is not a tunable parameter, but it results from the numerical inversion of the matrix). In the last column, wall timings for a single MD step on a single core (Intel Xeon E5-2670v3) are reported.

Method	Tolerance ($E_h e^{-1}$)	Time (s)
MI	10^{-12}	1.29
MaZe	10^{-12}	1.30
CG	10^{-6}	3.12
	10^{-8}	4.93
	10^{-10}	6.41
	10^{-12}	8.13

MaZe only requires 1% more CPU time than the MI method. Note that for systems with fixed positions, $\mathbf{R}_\alpha$, of the electrode's sites, these two methods are considerably faster than the CG. The conditions of the model are satisfied to a tolerance of the order of $10^{-12} E_h e^{-1}$ with both MaZe and MI. CG calculations targeting the lower, typical, tolerance of $10^{-6} E_h e^{-1}$ are, notably, up to a factor 2.4 slower. When numerical precision is sought, the slow down goes up to a factor of 6. For models with fixed positions of the electrode's charges, the only numerical bottleneck for MaZe and MI is the calculation of the matrix at the first time step, but this overhead is negligible for typical simulations. MaZe also yields electrode charges that are in agreement with MI: we computed the charges with the two methods for 100 configurations along a trajectory and estimated the relative error $\Delta Q_\alpha^{\text{alg}}$ on the electrode atom charges by computing

$$\Delta Q_\alpha^{\text{alg}} = \left| \frac{Q_\alpha^{\text{MaZe}} - Q_\alpha^{\text{MI}}}{Q_\alpha^{\text{MI}}} \right| \quad (7.17)$$

We obtain, on average, a relative error on the charges of 6.29×10^{-9} . The maximal error is 3.85×10^{-6} (a single atomic charge of $-1.65120899 \times 10^{-9} e$ instead of

$-1.65121536 \times 10^{-9} e$), which can be attributed to numerical errors. Another important test concerns the fulfillment of the electroneutrality constraint. Along the trajectory, we obtain a maximal value for the total charge of $2.68 \times 10^{-12} e$, which is again very low and arises from the various numerical errors.

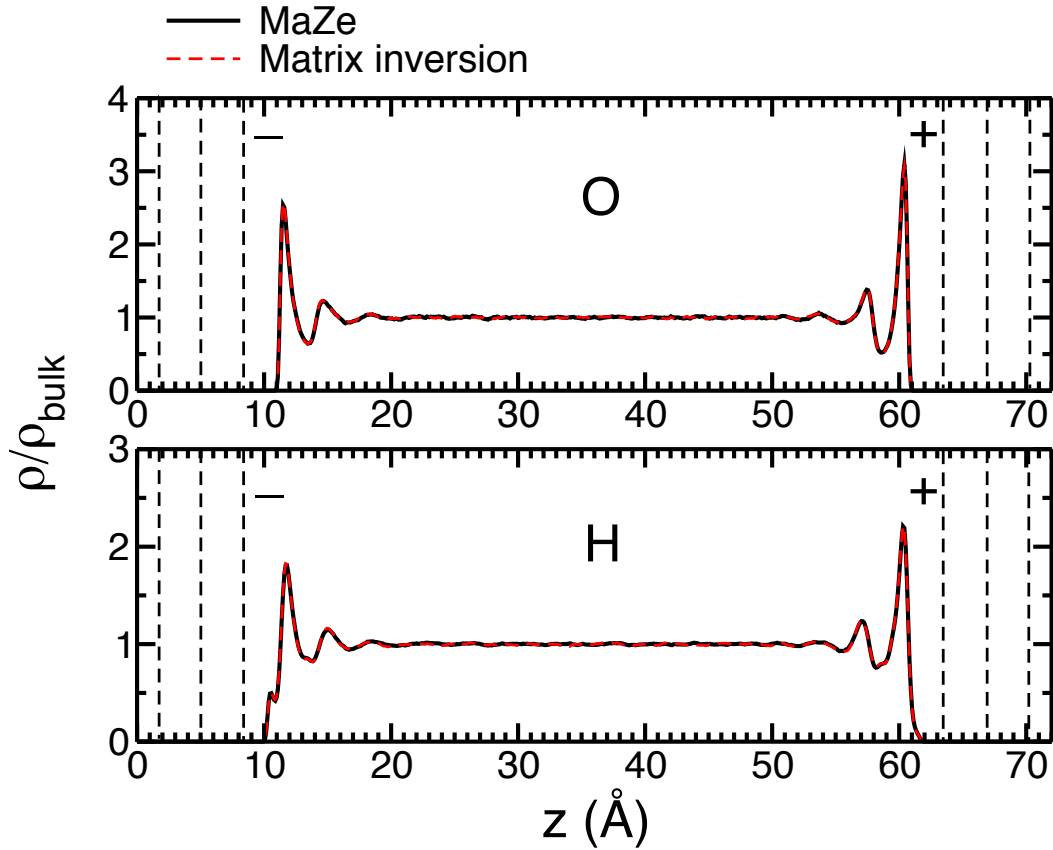


Fig. 7.5 Normalized atomic density profiles along the z -direction (normal to the surface of the electrodes) computed with MI and MaZe. The profiles are normalized by their bulk value. Top: Oxygen atoms, bottom: Hydrogen atoms. The positions of the electrode planes are shown with black dashed lines.

Based on the excellent agreement for the calculation of the individual charges with respect to the MI method, we can expect MaZe to provide the correct properties of the system. To illustrate this, we first calculate the total charge on the positive electrode, which is one of the most important target properties when simulating such systems since it gives access to the interfacial capacitance. For the latter quantity, we obtain a value of $2.89 \mu\text{F cm}^{-2}$, in agreement with a previous simulation work on the same system, conducted with the CG method [162].

In electrochemical devices, the structure of the liquid adsorbed at the electrode surface is difficult to characterize. Very complex experimental setups are needed, and they generally do not provide details at the molecular resolution. This structure is therefore a quantity often determined *via* molecular simulations. The atomic density profiles computed with MI and MaZe for our system are shown and compared in Figure 7.5 showing excellent agreement. These curves are also in agreement with previous studies [162] and can be qualitatively understood as follows. The presence of electrified walls leads to the formation of two layers of liquid with densities differing from the one of the bulk liquid, over a distance of approximately 10 Å. The density profile for the oxygen atoms shows a more intense peak close to the positive electrode (on the right hand side), while the hydrogen atoms profile is characterized by the presence of a prepeak on the negative electrode side. These features are readily attributed to the polarity of water molecule. Contrarily to the case of transition metals [149, 163], we do not observe the formation of particular hydrogen bonding patterns at the surface of the graphite electrode.

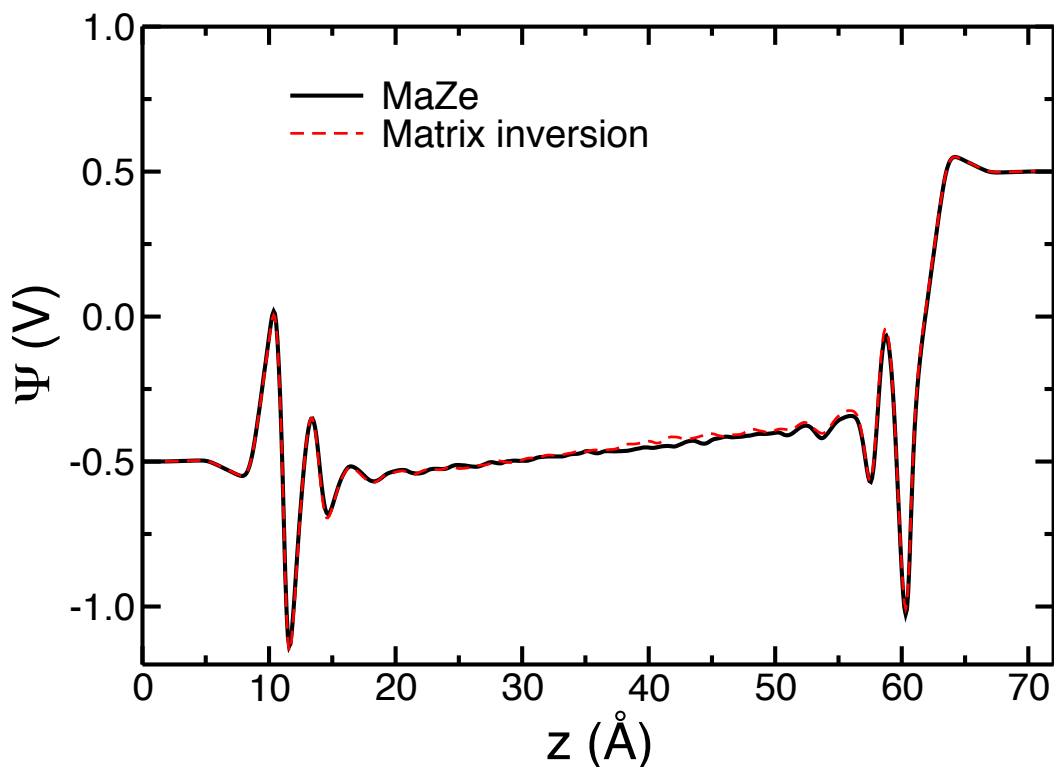


Fig. 7.6 Poisson potential across the simulation cell computed with MI and MaZe.

The knowledge of the surface charge and of the atomic densities is not sufficient to determine the screening properties of the liquid. To better characterize the interface, it is necessary to determine the average charge density along the z -direction, $\langle \rho(z) \rangle$, in order to compute the Poisson potential across the cell, integrating twice Eq. (7.4) on the z -axis

$$\Psi(z) = \Psi(z_0) - 4\pi \int_{z_0}^z dz' \int_{z_0}^{z'} dz'' \langle \rho(z'') \rangle \quad (7.18)$$

where z_0 is a reference point. Here we choose a z_0 value within the left electrode, for which $\Psi(z_0) = \Psi_- = -0.5$ V. As can be seen in Figure 7.6, the imposed applied potential difference is recovered since the potential equals $+0.5$ V inside the right electrode. In between these two values, the Poisson potential shows several interesting features. Firstly, in the vicinity of the two electrodes, strong oscillations occur, which are due to the formation of polarized layers of water molecules. Secondly, the bulk liquid experiences a finite electric field, which differs from the applied voltage due to the screening of the adsorbed water layers [148]. By changing the applied potential, it is possible to determine further quantities such as the electric field dependence of the dielectric constant of the fluid [162]. The figure also shows that results obtained with MI and MaZe are in perfect agreement in this case too.

7.3 Induced Dipoles with Metallic Electrodes

A further development that follows logically the two problems discussed in the previous two sections is a simulation in which both the metallicity of the electrodes and the polarizability of the electrolyte particles are taken into account. This point is crucial for simulation of realistic systems that could lead to progress in the field of material science and in advances in the engineering of supercapacitors by means of numerical simulation studies.

In typical models of supercapacitors, the polarizability of the electrolyte is represented *via* induced dipoles [7]. In this model, the whole dipole $\mu = q\mathbf{d}$ is treated as an additional variable at variance with the shell model where the distance $\mathbf{d}$ between the (fixed) charges forming the dipole is the focus of the dynamics.⁴ The great advantage of the induce dipole model compared to the shell model is that, in the

⁴Other models exist in which the geometry of the charges forming the dipole is fixed and the dynamics is focused on the value of the q [92].

former, electrostatic interactions are quadratic with respect to the additional variables, but physically the two models are equivalent. In this framework, the dipoles become the additional dynamical variables subject to the “Born-Oppenheimer” condition, *i.e.* their dynamics is obtained by minimizing interactions with respect to these additional degrees of freedom at each time-step. Note that this condition is equivalent to imposing that the total electric field generated by the dipoles is zero [164, 165]. The constant potential at the electrodes is imposed as discussed in the previous section, as is the electroneutrality condition. Although no simulations will be presented for this model (work is in progress), we indicate here how to extend the mass-zero constrained approach also to this physically significant case. Indeed, also here the mass-zero constrained method allows to deal with this situation in a straightforward and elegant way.

Considering the geometry of the electrodes fixed, the Lagrangian of the system will be a function of the dynamical variables $\{\mathbf{r}_i\}_{i=1}^N$, $\{\boldsymbol{\mu}_i\}_{i=1}^{N_p}$ and $\{Q_i\}_{i=1}^{N_e}$ representing the positions of the electrolyte particles, the dipoles associated to the polarizable species and the integrated charges on the electrode sites, respectively. The Lagrangian of the extended system is then given by

$$L = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 + \frac{1}{2} \mu_{\boldsymbol{\mu}} \sum_{i=1}^{N_p} \dot{\boldsymbol{\mu}}_i^2 + \frac{1}{2} \mu_Q \sum_{i=1}^{N_e} \dot{Q}_i^2 - U(\mathbf{r}, \boldsymbol{\mu}, Q) \quad (7.19)$$

where the particular form of the interaction potential $U(\mathbf{r}, \boldsymbol{\mu}, Q)$ will be discussed in the next section. Note the difference between the induced dipoles $\boldsymbol{\mu}$ and the two fictitious masses $\mu_{\boldsymbol{\mu}}$ and μ_Q introduced to define the Lagrangian of the system. For simplicity, we have assumed in Eq. (7.19) that no electroneutrality condition has to be enforced, but the extension to this case can be done in complete analogy to Section 7.2, *i.e.* by extending further the space of dynamical variables *via* the Lagrange multiplier v . The dynamics of the system is obtained from Eq. (7.19) and by requiring the dipoles and the electrode charges to adapt instantaneously to the motion of the electrolyte particles in such a way to cancel the electric field generated by dipoles and in order to keep a constant potential between the plates of

the capacitor. These two conditions are expressed by the set of $3N_p + N_e$ constraints

$$\sigma_k^\alpha(\mathbf{r}, \boldsymbol{\mu}, Q) \equiv \frac{\partial U(\mathbf{r}, \boldsymbol{\mu}, Q)}{\partial \mu_k^\alpha} = 0 \quad \alpha \in \{x, y, z\}, k = 1, \dots, N_p \quad (7.20a)$$

$$\sigma_{3N_p+h}(\mathbf{r}, \boldsymbol{\mu}, Q) \equiv \frac{\partial U(\mathbf{r}, \boldsymbol{\mu}, Q)}{\partial Q_h} - \Psi_h = 0 \quad h = 1, \dots, N_e \quad (7.20b)$$

where Ψ_h is again the applied potential to the atom site h . Following the discussion of Sections 7.1 and 7.2, the equations of motion for the system are obtained *via* the mass-zero constrained method and are given by

$$m_i \ddot{\mathbf{r}}_i = -\nabla_{\mathbf{r}_i} U(\mathbf{r}, \boldsymbol{\mu}, Q) \quad (7.21a)$$

$$\ddot{\boldsymbol{\mu}}_j = -\sum_{k=1}^{N_p} \sum_{\alpha=x,y,z} \gamma_k^\alpha \nabla_{\boldsymbol{\mu}_j} \sigma_k^\alpha - \sum_{h=1}^{N_e} \gamma_{3N_p+h} \nabla_{\boldsymbol{\mu}_j} \sigma_{3N_p+h} \quad (7.21b)$$

$$\ddot{Q}_g = -\sum_{k=1}^{N_p} \sum_{\alpha=x,y,z} \zeta \gamma_k^\alpha \frac{\partial \sigma_k^\alpha}{\partial Q_g} - \sum_{h=1}^{N_e} \zeta \gamma_{3N_p+h} \frac{\partial \sigma_{3N_p+h}}{\partial Q_g} \quad (7.21c)$$

with $i = 1, \dots, N$, $j = 1, \dots, N_p$ and $g = 1, \dots, N_e$. Note the factor ζ arising from the homogeneous limit $\mu_\mu \rightarrow 0$ after having defined $\mu_Q = \mu_\mu / \zeta$. Including the electroneutrality condition would require, in complete analogy with the discussion in the previous section, extending the set of variables to include the Lagrange multiplier v . The extended dynamical system would then contain also the homogeneity parameter κ , different, in general, from ζ .

7.3.1 The Induced Dipole Model

While the fluctuating charge model has been described at length in Section 7.2 the discussion on dipoles has been focused on the shell model, leaving the induced dipoles model out of the scene up to now. As mentioned earlier, the two models are physically equivalent and analogies in the functional form can also be found at a closer look. For a system of N particles to which a point charge q_i and a point dipole

μ_i are attached, the induced dipole model [7, 164, 165] is defined by

$$U^{\mu\mu}(\mathbf{r}, \boldsymbol{\mu}) = \frac{1}{2} \sum_{i \neq j}^N \left\{ \frac{q_i q_j}{r_{ij}} + A_{ij} \exp \left[-\frac{r_{ij}}{\lambda} \right] - \frac{C_{ij}}{r_{ij}^6} f_{ij}^6(r_{ij}) - \frac{D_{ij}}{r_{ij}^8} f_{ij}^8(r_{ij}) \right\} + \sum_i^{N_p} \frac{|\boldsymbol{\mu}_i|^2}{2\alpha_i} \\ + \sum_{j < i}^{N_p} \left\{ \left[\frac{\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij} q_j}{r_{ij}^3} f_{ji}^4(r_{ij}) - \frac{q_i \mathbf{r}_{ij} \cdot \boldsymbol{\mu}_j}{r_{ij}^3} f_{ij}^4(r_{ij}) \right] + \left[\frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_i)(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_j)}{r_{ij}^5} \right] \right\} \quad (7.22)$$

where α_i represents the polarizability of the ion i and the functions $f_{ij}^n(r)$ are the so-called Tang-Tonnes damping functions, whose scope is to avoid the well-known problem of the polarization catastrophe [166]. Their form⁵ is given by

$$f_{ij}^n(r) = 1 - c_{ij}^n e^{-b_{ij}^n r} \sum_{k=0}^n \frac{(b_{ij}^n r)^k}{k!} \quad (7.23)$$

The model for the interaction of a system of polarizable particles in a electrochemical cell with metal electrodes it is then given by the combination of Eq. (7.22) for the dipoles with Eq. (7.9) for the metallic electrodes. However, an additional term is necessary to account for the interactions between dipoles and electrode charges and this term, never treated in the literature up to the authors' knowledge, is the object of the next section.

7.3.2 Interaction Between Electrode Charges and Electrolyte Dipoles

The interaction between the electrode charges and the dipoles can be constructed again from Eq. (7.6), *i.e.*

$$U = \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} d^3 r d^3 r' \frac{\rho(\mathbf{r}') \rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{2} \int_{\mathbb{R}^3} d^3 r V(\mathbf{r}) \rho(\mathbf{r}) \quad (7.24)$$

where the electrostatic potential $V(\mathbf{r})$ is defined by

$$V(\mathbf{r}) = \int_{\mathbb{R}^3} d^3 r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (7.25)$$

⁵As these are functions only of the electrolyte particles positions, they do not pose any issue in the computation of the gradient or the Hessian with respect to the additional variables required by the mass-zero constrained algorithm.

A dipole is a neutral system composed by two equal and opposite point charges with module q separated by a distance $\mathbf{d}$. The characteristic quantity of a dipole is its dipole moment $\boldsymbol{\mu} = q\mathbf{d}$. It is easy to associate to the electric dipole the charge density

$$\rho_{\mathbf{d}}^{\boldsymbol{\mu}}(\mathbf{r}) = -q\delta^3(\mathbf{r}) + q\delta^3(\mathbf{r} - \mathbf{d}) \quad (7.26)$$

where $\delta^3(\mathbf{r})$ is the three-dimensional Dirac's delta function and where it has been assumed the negative charge placed in the origin. Substituting Eq. (7.26) in Eq. (7.25) we obtain

$$v_{\mathbf{d}}^{\boldsymbol{\mu}}(\mathbf{r}) = \int_{\mathbb{R}^3} d^3r' \frac{\rho_{\mathbf{d}}^{\boldsymbol{\mu}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = q \left(\frac{|\mathbf{r}| - |\mathbf{r} - \mathbf{d}|}{|\mathbf{r}||\mathbf{r} - \mathbf{d}|} \right) \quad (7.27)$$

The point-dipole approximation is computed taking the limit for $\mathbf{d} \rightarrow 0$. The denominator of Eq. (7.27) trivially yields $|\mathbf{r}|^2$, while the second term of the numerator can be Taylor-expanded to the first order in $\mathbf{d}$, in order to obtain $\hat{\mathbf{r}} \cdot \mathbf{d} - |\mathbf{r}|$, where $\hat{\mathbf{r}} = \mathbf{r}/|\mathbf{r}|$ represents the unitary vector directed along $\mathbf{r}$. The electrostatic potential of a point dipole is then given by

$$v^{\boldsymbol{\mu}}(\mathbf{r}) = \lim_{\mathbf{d} \rightarrow 0} v_{\mathbf{d}}^{\boldsymbol{\mu}}(\mathbf{r}) = \frac{\boldsymbol{\mu} \cdot \mathbf{r}}{r^3} \quad (7.28)$$

where the definition of the dipole moment has been recognized and the notation $r = |\mathbf{r}|$ has been introduced. The generalization of this result to a set of N_p dipoles placed at positions $\{\mathbf{r}_i\}_{i=1}^{N_p}$ is trivially obtained by superposition principle as

$$V^{\boldsymbol{\mu}}(\mathbf{r}) = \sum_{i=1}^{N_p} v^{\boldsymbol{\mu}}(\mathbf{r} - \mathbf{r}_i) = \sum_{i=1}^{N_p} \frac{\boldsymbol{\mu}_i \cdot (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3} \quad (7.29)$$

The electrostatic energy for a system of N_p point dipoles and N_e Gaussian-distributed charges centered at $\{\mathbf{R}_{\alpha}\}_{\alpha=1}^{N_e}$ can then be computed as

$$U^{\mathcal{Q}\boldsymbol{\mu}} = \frac{1}{2} \int_{\mathbb{R}^3} d^3r \sum_{\alpha=1}^{N_e} \rho^{\mathcal{Q}}(\mathbf{r} - \mathbf{R}_{\alpha}) V^{\boldsymbol{\mu}}(\mathbf{r}) \quad (7.30)$$

where the Gaussian-density distribution has been defined in Eq. (7.8) and is given by:

$$\rho^{\mathcal{Q}}(\mathbf{r} - \mathbf{R}_{\alpha}) = Q_{\alpha} \left(\frac{\eta^2}{\pi} \right)^{\frac{3}{2}} \exp[-\eta^2(\mathbf{r} - \mathbf{R}_{\alpha})^2] \quad (7.31)$$

Substituting Eqs. (7.31) and (7.29) in Eq. (7.30), and after some trivial change of variables in the integral, we obtain

$$U^{Q\mu} = \frac{1}{2} \left(\frac{\eta^2}{\pi} \right)^{\frac{3}{2}} \int_{\mathbb{R}^3} d^3r \exp[-\eta^2 r^2] \sum_{\alpha=1}^{N_e} \sum_{i=1}^{N_p} Q_{\alpha} \frac{\boldsymbol{\mu}_i \cdot (\mathbf{R}_{\alpha} - \mathbf{r}_i - \mathbf{r})}{|\mathbf{R}_{\alpha} - \mathbf{r}_i - \mathbf{r}|^3} \quad (7.32)$$

Integrating over the whole space we get the final expression for the interaction between electrode charges and induced dipole as

$$U^{Q\mu} = \frac{1}{2} \sum_{\alpha=1}^{N_e} \sum_{i=1}^{N_p} \left[Q_{\alpha} \frac{\boldsymbol{\mu}_i \cdot (\mathbf{R}_{\alpha} - \mathbf{r}_i)}{|\mathbf{R}_{\alpha} - \mathbf{r}_i|^3} \left(\operatorname{erf}[\eta |\mathbf{R}_{\alpha} - \mathbf{r}_i|] + \right. \right. \\ \left. \left. - \frac{2\eta}{\sqrt{\pi}} |\mathbf{R}_{\alpha} - \mathbf{r}_i| \exp[-\eta^2 |\mathbf{R}_{\alpha} - \mathbf{r}_i|^2] \right) \right] \quad (7.33)$$

The final expression for the interaction potential of a system of Gaussian-distributed charges interacting with polarizable electrolyte particles is then computed as $U = U^{\mu\mu} + 2U^{Q\mu} + U^{QQ}$, where $U^{\mu\mu}$ is given in Eq. (7.22), $U^{Q\mu}$ in Eq. (7.33) and U^{QQ} is given by the first three terms of Eq. (7.9). All together, these terms account for the interaction between point charges, point dipoles, Gaussian-distributed charges and all the cross-interaction terms.

7.4 Summary

In this chapter we have shown how to apply the mass-zero constrained algorithm to the simulation of realistic electrochemical systems like supercapacitors with polarizable electrolytes. We have presented calculations for a polarizable model of ionic system demonstrating the accuracy and efficiency of the method in the test case of the shell model for NaCl first proposed by Jacucci *et al.* [90]. Simulations for a graphene double layer capacitor at constant potential were also presented to show how the algorithm can be adapted to the simulations of systems described by the fluctuating charge model and how to enforce additional conditions such as electroneutrality.

For both cases, the convergence of MaZe is faster when compared to the conjugate gradient method and other alternative methods, while the same accuracy in computing observables is retained. In addition, the method has the advantage to allow additional

conditions of arbitrary number and form to be introduced in a natural way. The simplecticness and time reversibility of the algorithm guarantee the accuracy of the numerical results regardless the length of the simulation.

The formal generalization of the method to a more realistic model of supercapacitors has also been presented. The equations of motion of a system composed by metallic electrodes and a polarizable electrolyte have been discussed together with a physical model for the interaction potential. This paves the way for future work in which mass-zero constrained dynamics will be used to study systems consisting of constant potential electrodes combined with a polarizable fluid. We also expect this method to allow fixing the charges on the two electrodes independently, thus opening the way towards comparison with more complex electrochemical experiments.

Chapter 8

***Ab Initio* Molecular Dynamics: An Orbital-Free DFT Study**

The empirical models for polarization described in the previous chapter provide a good description of several systems and are the only option when a very large number of degrees of freedom must be considered. This is often the case when simulating supercapacitors or batteries. However, there are also situations where these empirical models are insufficient to capture with sufficient details the reorganization of the electronic density due to electromagnetic interactions in the system. In these cases, it is then necessary to go beyond a fully classical treatment of the system and *ab initio* molecular dynamics becomes the tool of choice. In this chapter, we show how the MaZe formalism can play a role also in this type of simulations.

At variance with classical, force-field-based simulations, *ab initio* molecular dynamics combines classical propagation of the nuclei with a quantum calculation of the forces, obtained on-the-fly from accurate electronic structure calculations. The use of nonempirical force fields enables to describe a system over its whole phase diagram and, perhaps more importantly, to simulate chemical bonding processes. In practice, however, this comes at a significant computational cost since each step of the nuclear trajectory requires an (expensive) electronic structure calculation, which limits accessible sizes and time-scales. Currently, the best compromise between cost and accuracy is offered by density functional theory (DFT) and, in the following, we shall then focus on DFT-based *ab initio* MD even though the ideas discussed in this chapter are applicable beyond this approach. The cornerstone of *ab initio* simulations is the Born-Oppenheimer approximation: the Hamiltonian of the system is separated into a nuclear (nuclear kinetic energy, nuclear Coulomb interactions) and an electronic part (electronic kinetic and Coulomb energies, and Coulomb interactions between electrons and nuclei). Adiabatic separation of the nuclear and electronic degrees of freedom is then invoked to claim that, at each nuclear configuration, the electronic subsystem has relaxed in its ground state. The ground state energy, parametrically dependent on the nuclear coordinates, is found by minimizing the quantum expectation value of the electronic Hamiltonian (a functional of the electronic density) with respect to the electronic state. In Born-Oppenheimer *ab initio* MD, this part of the algorithm, usually based on a self-consistent cycle or some analogous minimization technique, is the most demanding numerically. The force on the nuclei is obtained as the gradient of the minimized electronic Hamiltonian, including, when appropriate, the so-called Pulay and non-self-consistent forces, plus the nuclear Coulomb interaction and, if present, external fields depending on the nuclear coordinates. Since the mid-1980s, in particular thanks to the breakthrough

of the extended Lagrangian Car-Parrinello approach [91], the field has seen an impressive growth and *ab initio* MD is currently used in areas ranging from materials modeling to drug design [167–169]. The success of current methods, however, still leaves room for methodological and algorithmic improvements to secure stable and unbiased efficient long-time evolution as witnessed by several recent efforts [170–180]. In particular, long-time stability is likely to become an increasingly important issue, as the growing computational power available provides the bare resources to further extend the length of calculated trajectories.

In what follows, we show how to apply the mass-zero constrained molecular dynamics for the interesting case of the orbital-free density functional theory. Madden and coworkers [181] were among the first to present the orbital-free DFT approach to MD as a computationally convenient alternative to the more expensive Kohn-Sham DFT Car-Parrinello molecular dynamics. Kohn-Sham DFT, in fact, requires the introduction of M orthonormal orbitals $\psi_1(\mathbf{r}), \dots, \psi_M(\mathbf{r})$ to represent the kinetic energy of the N_{el} electrons of the system as

$$E_K = \sum_i^M f_i \int d^3r \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) \quad (8.1)$$

which is a functional of the electronic orbitals themselves and where f_i represents the occupation number of the i -th orbital (constrained to $\sum_i^M f_i = N_{\text{el}}$). All the other terms of the energy are instead defined as functionals of the electronic density, $n(\mathbf{r})$, which is connected to the orbitals by

$$n(\mathbf{r}) = \sum_i^M f_i |\psi_i(\mathbf{r})|^2 \quad (8.2)$$

The use of the Kohn-Sham representation of the kinetic energy in Eq. (8.1) for Car-Parrinello molecular dynamics leads to a set of M functional differential equations to describe the time evolution of the electronic state along the trajectory of the nuclei. Orthonormality constraints for the orbitals have to be explicitly included in these equations in order to keep the occupied orbitals orthonormal. The orthonormalization process becomes rapidly the most time-consuming part of the algorithm with increasing system size. Orbital-free DFT seeks a way out of this bottleneck by searching for a sufficiently good approximation of the kinetic energy directly as a functional of the density. This leads to evolution equations for the electronic

density (no longer for its representation in terms of Kohn-Sham orbitals), subject to a single constraint enforcing conservation of the number of electrons in the system, simplifying enormously the computational effort for their solution. For this reason, developing reliable and transferable kinetic energy functionals for general systems and different phases of matter is an important challenge, which is however still open [182]. Universal use and easily transferable models for this functional are still out of reach, but applications for metals have proven to be very promising and efforts to extend the applicability of the approach for nonmetallic systems have yielded encouraging results. In general orbital-free DFT remains a very useful tool, often enabling to simulate system sizes out of reach for alternative methods [182, 183]. In what follows we will consider the application of the method to metallic systems.

8.1 Real and Reciprocal Space Grid with Plane Waves

Let us start by introducing the key concepts for orbital-free DFT, beginning with a convenient representation of the electronic density. The periodicity of a crystalline metal, together with periodic boundary conditions, usually exploited in molecular dynamics to reduce finite-size effects and to eliminate the problem of the boundaries, provide a natural basis for the expression of the electronic density: the plane-waves basis. The unit cell of a 3-dimensional periodically repeated system is defined by the Bravais lattice vector $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$. Combining these vectors in a matrix $H = (\mathbf{a}^1, \mathbf{a}^2, \mathbf{a}^3)$ yields the volume of the cell as $\Omega = \det[H]$. The reciprocal lattice vectors $\mathbf{b}^1, \mathbf{b}^2, \mathbf{b}^3$ are defined by the relation

$$\mathbf{a}^i \cdot \mathbf{b}^j = 2\pi \delta^{ij} \quad (8.3)$$

where δ^{ij} is the Kronecker delta. Plane waves form a complete and orthonormal basis given by the set of functions

$$\phi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (8.4)$$

with reciprocal space vectors $\mathbf{G} = 2\pi[H^T]^{-1}\mathbf{g}$ where $\mathbf{g} = (g^x, g^y, g^z)$ is a triple of integer numbers. Any periodic field $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{L})$, where the direct vectors $\mathbf{L}$

represent the periodicity of the function, can be expanded in the plane-wave basis as

$$f(\mathbf{r}) = \sum_{\mathbf{G}} f_{\mathbf{G}} \phi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} f_{\mathbf{G}} \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (8.5)$$

with $f_{\mathbf{G}}$ representing the coefficient (or coordinates) of the field f in the plane-waves basis. In principle the sum over the $\mathbf{G}$ vectors runs to infinity.

To be able to handle numerically this sum it is necessary to truncate it at some point. Quantities computed in plane-waves basis converge rapidly with the increasing of the modulus of the wavevector $\mathbf{G}$ and therefore it is possible to consider only the ones with a kinetic energy lower than a certain cutoff E_{cut} . The maximum value of the reciprocal space vector, $\mathbf{G}_{\text{max}}$, is derived from the square root of the cutoff energy, and it corresponds to a maximum index g of

$$g_{\text{max}} = \frac{L}{2\pi} \sqrt{E_{\text{cut}}} \quad (8.6)$$

which, in turn, yields a grid size in direct space given by the sampling theorem [184]

$$N = 2g_{\text{max}} + 1 \quad (8.7)$$

Points and grid indexes in real space are connected by the relation

$$\mathbf{r} = \frac{L}{N} \mathbf{q} \quad (8.8)$$

where $\mathbf{q} = (q^x, q^y, q^z)$ is another triple of integers. Fast Fourier transforms can be used to connect quantities in direct and reciprocal space.

Definition 8.1 (Direct discrete Fourier transform). *Given a field $f(\mathbf{r}) \in \mathbb{R}$ defined on the 3-dimensional grid in direct space of size $N_D = N^x N^y N^z$ with points $\{\mathbf{r}_i\}_{i=0}^{N_D}$ such that $f(\mathbf{r} = \mathbf{r}_i) \equiv f_i$, its discrete Fourier transform $\tilde{f} \equiv \text{FFT}[f]$ is defined as*

$$\begin{aligned} \tilde{f}(\mathbf{G}) &= \text{FFT}[f(\mathbf{r})] = \frac{1}{N_D} \sum_{\mathbf{r}} f(\mathbf{r}) \exp[-i\mathbf{G} \cdot \mathbf{r}] \\ &= \frac{1}{N_D} \sum_{i=0}^{N_D-1} f_i \exp\left[-i \frac{2\pi g^x q_i^x}{N^x}\right] \exp\left[-i \frac{2\pi g^y q_i^y}{N^y}\right] \exp\left[-i \frac{2\pi g^z q_i^z}{N^z}\right] \end{aligned} \quad (8.9)$$

The inverse operation is defined for a function in the discretized Fourier space $\tilde{f}(\mathbf{G} = \mathbf{G}_k) \equiv \tilde{f}_k$ where $\{\mathbf{G}_k\}_{k=0}^{N_R}$ are the reciprocal-grid points. In practice, the

inverse discrete Fourier $f = \text{iFFT}[\tilde{f}]$ is computed as

$$\begin{aligned} f(\mathbf{r}) &= \text{iFFT}[\tilde{f}(\mathbf{G})] = \tilde{f}(\mathbf{0}) + \sum_{\mathbf{G} > 0} \left[\tilde{f}(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] + \tilde{f}^*(\mathbf{G}) \exp[-i\mathbf{G} \cdot \mathbf{r}] \right] \\ &= \tilde{f}_0 + \sum_{k=0}^{N_R-1} \left\{ \tilde{f}_k \exp\left[i \frac{2\pi g_k^x q^x}{N^x}\right] \exp\left[i \frac{2\pi g_k^y q^y}{N^y}\right] \exp\left[i \frac{2\pi g_k^z q^z}{N^z}\right] \right. \\ &\quad \left. + \tilde{f}_k^* \exp\left[-i \frac{2\pi g_k^x q^x}{N^x}\right] \exp\left[-i \frac{2\pi g_k^y q^y}{N^y}\right] \exp\left[-i \frac{2\pi g_k^z q^z}{N^z}\right] \right\} \end{aligned} \quad (8.10)$$

where the number of reciprocal grid-points N_R is computed from N_D in such a way to exploit the fact that $\tilde{f}(-\mathbf{G}) = \tilde{f}^*(\mathbf{G})$, $\tilde{f}^*(\mathbf{G})$ being the complex conjugate of $\tilde{f}(\mathbf{G})$. This allows the reduction of the considered G -space, as instead of considering the interval $[-\mathbf{G}_{\max}, \mathbf{G}_{\max}]$ it is possible to just work in the interval $[0, \mathbf{G}_{\max}]$ with great benefits from a computational point of view. With this in mind, it is possible to express the electronic density in direct space as a linear combination of plane waves basis set, *i.e.*

$$n(\mathbf{r}) = \tilde{n}(\mathbf{0}) + \sum_{\mathbf{G} > 0} \left[\tilde{n}(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] + \tilde{n}^*(\mathbf{G}) \exp[-i\mathbf{G} \cdot \mathbf{r}] \right] \quad (8.11)$$

where the coefficient $\tilde{n}(\mathbf{G})$ are given by

$$\tilde{n}(\mathbf{G}) = \frac{1}{N_D} \sum_{\mathbf{r}} n(\mathbf{r}) \exp[-i\mathbf{G} \cdot \mathbf{r}] \quad (8.12)$$

8.2 Energies, Forces and Energy Derivatives

In orbital-free density functional theory, the potential energy of the system is expressed as a functional of the electronic density n and as a function of the nuclear coordinates $\mathbf{R}$:

$$E[n; \mathbf{R}] = E_K[n] + E_{\text{PS}}[n; \mathbf{R}] + E_{\text{ES}}[n; \mathbf{R}] + E_{\text{XC}}[n] \quad (8.13)$$

where the four contributions are presented in the following list:

E_K represents the kinetic energy of the electrons and it is usually written as some correction to the Thomas-Fermi energy of the free-electron gas.

E_{PS} represents the interaction energy between the electrons up to the last closed shell and the ions. Its form is usually given for a particular element and it is strictly connected with the choice of the pseudopotential.

E_{ES} represents the “classical” electrostatic energy of the outermost (valence) electrons and the nuclei. It is basically given by Coulomb interactions between valence electrons and between valence electrons and the ions, together with the ion-ion contribution

E_{XC} is the so-called exchange-correlation energy term. It is fully quantum and arises from the Pauli exclusion principle together with the asymmetry of the electronic wave function for particle exchange.

The kinetic and the exchange-correlation terms have highly nonlinear forms and their expression is usually obtained numerically from some external library. For these two terms, different approximations are possible, in what is called the “Jacob’s ladder to heaven” [169]. The easiest approximation is the *Local Density Approximation* (LDA) which considers $E_{\text{K}}[n]$ and $E_{\text{XC}}[n]$ to be functionals of the density alone. A more refined approximation considers the kinetic and exchange-correlation contributions to be functionals of the density $n(\mathbf{r})$ and of its spatial gradient $\nabla n(\mathbf{r})$. This is the so called *Generalized Gradient Approximation* (GGA). Going higher in the ladder we find the Meta-GGA and the hybrid-GGA approximations [169]. For most applications the GGA approximation is considered to be satisfactory and it is the case that will be discussed in this work, except when otherwise stated. We will now analyze the terms one after the other in view of the role they play in the mass-zero constrained dynamics.

8.2.1 The Electrostatic Energy

We start the discussion from the most common and well known term in the potential energy, the electrostatic energy. For a given electronic distribution $n(\mathbf{r})$ surrounding N_{I} ions at positions $\mathbf{R}_I$ with a charge Z_I , the electrostatic energy is written as

$$E_{\text{ES}} = \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \sum_{I=1}^{N_{\text{I}}} \int d^3r V_I^{\text{c}}(\mathbf{r})n(\mathbf{r}) + \frac{1}{2} \sum_{I \neq J}^{N_{\text{I}}} \frac{Z_I Z_J}{R_{IJ}} \quad (8.14)$$

where it is easy to recognize the electron-electron, electron-ion and ion-ion interactions. In particular, $V_I^c(\mathbf{r})$ is the potential associated to the core of the ion. Periodic boundary conditions allow to use the three-dimensional version of the Ewald summation technique. To do this in a convenient way for the treatment in plane waves, we associate to each core a Gaussian charge distribution, defined by

$$n_I^c(\mathbf{r}) = -\frac{Z_I}{(R_I^{\text{cut}})^3} \pi^{-\frac{3}{2}} \exp\left[-\left(\frac{\mathbf{r}-\mathbf{R}_I}{R_I^{\text{cut}}}\right)^2\right] \quad (8.15)$$

where R_I^{cut} is the Ewald cutoff radius of the ion I . To correctly account for the long-range interactions, the core potential can be defined to be the one corresponding to the Gaussian charge in Eq. (8.15), *i.e.*

$$V_I^c(\mathbf{r}) = \int d^3r' \frac{n_I^c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = -\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|} \text{erf}\left[\frac{|\mathbf{r}-\mathbf{R}_I|}{R_I^{\text{cut}}}\right] \quad (8.16)$$

Defining $n^c(\mathbf{r}) = \sum_I n_I^c(\mathbf{r})$, it is possible to add and subtract the interaction energy of the Gaussian distributions centered in the nuclei from the expression in Eq. (8.14) to obtain

$$\begin{aligned} E_{\text{ES}} = & \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2} \int d^3r d^3r' \frac{n^c(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2} \sum_{I \neq J}^{N_I} \frac{Z_I Z_J}{R_{IJ}} \\ & + \frac{1}{2} \int d^3r d^3r' \frac{n^c(\mathbf{r})n^c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{2} \int d^3r d^3r' \frac{n^c(\mathbf{r})n^c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \end{aligned} \quad (8.17)$$

Given the total density $n^t(\mathbf{r}) \equiv n^c(\mathbf{r}) + n(\mathbf{r})$ and solving the last integral of Eq. (8.17), it is possible to recast the electrostatic energy in the form

$$E_{\text{ES}} = \frac{1}{2} \int d^3r d^3r' \frac{n^t(\mathbf{r})n^t(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2} \sum_{I \neq J}^{N_I} \frac{Z_I Z_J}{R_{IJ}} \text{erfc}[\alpha_{IJ} R_{IJ}] - \sum_{I=1}^{N_I} \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^{\text{cut}}} \quad (8.18)$$

where $\alpha_{IJ} = (R_I^{\text{cut}2} + R_J^{\text{cut}2})^{-\frac{1}{2}}$. It is easy to recognize in this expression the short-range term and the self term of other treatments of the Ewald summation technique [7, 185], while in the the so-called Hartree term

$$E_{\text{H}} \equiv \frac{1}{2} \int d^3r d^3r' \frac{n^t(\mathbf{r})n^t(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (8.19)$$

it is encoded the long-range part of the ion-ion contribution to the electrostatic energy, together with the core-electrons and electron-electron contributions. The different contributions in E_H become evident once the periodicity of the box is used to write this expression in reciprocal space. Indeed, the total density $n^t(\mathbf{r})$ can be expanded in plane waves as

$$\tilde{n}^t(\mathbf{G}) = \tilde{n}(\mathbf{G}) + \sum_{I=1}^{N_I} \tilde{n}_I^c(\mathbf{G}) S_I(\mathbf{G}) \quad (8.20)$$

where $\tilde{n}(\mathbf{G})$ is given in Eq. (8.12), while the expression for the core density is given in reciprocal space by

$$\tilde{n}_I^c(\mathbf{G}) = -\frac{Z_I}{\Omega} \exp\left[-\left(\frac{GR_I^{\text{cut}}}{2}\right)^2\right] \quad (8.21)$$

where $G = |\mathbf{G}|$ and the structure factor $S_I(\mathbf{G})$ is given by

$$S_I(\mathbf{G}) = \exp[-i\mathbf{G} \cdot \mathbf{R}_I] \quad (8.22)$$

The expression of the Hartree energy in reciprocal space then yields the electrostatic energy of a periodic system of charges as

$$\begin{aligned} E_{\text{ES}} = & 4\pi\Omega \sum_{\mathbf{G}>0} \frac{|\tilde{n}^t(\mathbf{G})|^2}{G^2} - \sum_{I=1}^{N_I} \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^{\text{cut}}} \\ & + \sum_{I,J}' \sum_{\mathbf{L}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J + \mathbf{L}|} \text{erfc}[\alpha_{IJ} |\mathbf{R}_I - \mathbf{R}_J + \mathbf{L}|] \end{aligned} \quad (8.23)$$

where the prime on the summation in the ion-ion term means that for $\mathbf{L} = (0,0,0)$ the sum over the ions runs for $I < J$. In actual implementations, the sum over the replicated box is usually limited to the nearest one through the nearest image convention (NIC) as the complementary error function decays exponentially for $R_{IJ} > \alpha_{IJ}^{-1}$. While the short-range term and the correction for the self interaction have the standard form which can be found in every treatment of the Ewald summation technique, the long-range contribution to the ionic energy is hidden in the sum in reciprocal space of Eq. (8.23). In Section 8.7 it is shown how to obtain the standard Ewald summation expressions for the long-range contribution to the electrostatic energy from Eq. (8.23).

The forces on the ions due to the electrostatic interactions can be obtained from Eq. (8.23) taking the gradient with respect to ionic coordinates. Indeed we have that $\mathbf{F}_I = -\nabla_{\mathbf{R}_I} E_{\text{ES}}$. The self energy term is constant with respect to the ionic coordinates and therefore it does not give a contribution to the forces. Treating separately the two remaining terms yields a straightforward expression for the force due to short-range term, which can be written as

$$\mathbf{F}_I^{\text{SR}} = - \sum_{J \neq I}^{N_I} \frac{Z_I Z_J}{(R_{IJ}^{\text{NIC}})^2} \left[\frac{\text{erfc}[\alpha_{IJ} R_{IJ}^{\text{NIC}}]}{R_{IJ}^{\text{NIC}}} + \frac{2\alpha_{IJ}}{\sqrt{\pi}} \exp[-(\alpha_{IJ} R_{IJ}^{\text{NIC}})^2] \right] \mathbf{R}_{IJ}^{\text{NIC}} \quad (8.24)$$

where $\mathbf{R}_{IJ}^{\text{NIC}}$ represents the distance computed in the framework of the nearest image convention. The force due to the Hartree energy can be easily computed exploiting the chain rule for the gradient of a complex function on the first term of the RHS of Eq. (8.23)

$$\nabla_{\mathbf{R}_I} \frac{|\tilde{n}^t(\mathbf{G})|^2}{G^2} = \frac{\partial}{\partial \tilde{n}^t(\mathbf{G})} \frac{|\tilde{n}^t(\mathbf{G})|^2}{G^2} \nabla_{\mathbf{R}_I} \tilde{n}(\mathbf{G}) + \frac{\partial}{\partial (\tilde{n}^t(\mathbf{G}))^*} \frac{|\tilde{n}^t(\mathbf{G})|^2}{G^2} \nabla_{\mathbf{R}_I} (\tilde{n}^t(\mathbf{G}))^* \quad (8.25)$$

which yields for the forces

$$\mathbf{F}_I^{\text{H}} = -4\pi\Omega \sum_{\mathbf{G} > 0} \left[\frac{(\tilde{n}^t(\mathbf{G}))^*}{G^2} \nabla_{\mathbf{R}_I} \tilde{n}(\mathbf{G}) + \frac{\tilde{n}^t(\mathbf{G})}{G^2} \nabla_{\mathbf{R}_I} (\tilde{n}^t(\mathbf{G}))^* \right] \quad (8.26)$$

The gradient of the total electronic density in reciprocal space can be computed exploiting the definitions of the core density in reciprocal space (independent of the ionic positions) and of the structure factor given in Eqs. (8.21) and (8.22). This yields

$$\nabla_{\mathbf{R}_I} \tilde{n}^t(\mathbf{G}) = \nabla_{\mathbf{R}_I} \left[\tilde{n}(\mathbf{G}) + \sum_{J=1}^{N_I} \tilde{n}_J^c(\mathbf{G}) \exp[-i\mathbf{G} \cdot \mathbf{R}_J] \right] = -i\mathbf{G} \tilde{n}_I^c(\mathbf{G}) S_I(\mathbf{G}) \quad (8.27)$$

The final expression for the Hartree force is then given by

$$\begin{aligned} \mathbf{F}_I^{\text{H}} &= 4\pi\Omega \sum_{\mathbf{G} > 0} \frac{(\tilde{n}^t(\mathbf{G}))^*}{G^2} i\mathbf{G} \tilde{n}_I^c(\mathbf{G}) S_I(\mathbf{G}) - \frac{\tilde{n}^t(\mathbf{G})}{G^2} i\mathbf{G} (\tilde{n}_I^c(\mathbf{G}) S_I(\mathbf{G}))^* \\ &= -8\pi\Omega \sum_{\mathbf{G} > 0} \frac{\tilde{n}_I^c(\mathbf{G})}{G^2} \Im \left[(\tilde{n}^t(\mathbf{G}))^* S_I(\mathbf{G}) \right] \mathbf{G} \end{aligned} \quad (8.28)$$

where $\Im$ denotes the imaginary part (note that $\tilde{n}_I^c(\mathbf{G}) \in \mathbb{R}$).

Mass-zero constrained dynamics requires the computation of the first and second derivatives of the energy functional with respect to the additional degrees of freedom. For this system, the latter are represented by the coefficients of the density in reciprocal space, *i.e.* the $\tilde{n}(\mathbf{G})$ given in Eq. (8.12). This is straightforward for the electrostatic contribution written in the form of Eq. (8.23) as there is only a quadratic dependence in the Hartree energy term on these variables. The first derivative is taken with respect to the complex conjugate of the electronic density. Note that the absolute value squared is not differentiable anywhere in the complex plane and therefore the variables $\tilde{n}(\mathbf{G})$ and $\tilde{n}^*(\mathbf{G})$ have to be considered independent (real) variables.¹ In this way we get

$$\frac{\partial E_{\text{ES}}}{\partial \tilde{n}^*(\mathbf{G})} = 4\pi\Omega \sum_{\mathbf{G}' > 0} \frac{1}{G'^2} \frac{\partial |\tilde{n}^t(\mathbf{G}')|^2}{\partial \tilde{n}^*(\mathbf{G})} = \frac{8\pi\Omega}{G^2} \tilde{n}(\mathbf{G}) \quad (8.29)$$

for $\mathbf{G} > 0$ where the definition of $\tilde{n}^t(\mathbf{G})$ in Eq. (8.20) has been used for the derivative.

The second derivative is now computed with respect to the density $\tilde{n}(\mathbf{G})$ and it is straightforward to obtain

$$\frac{\partial E_{\text{ES}}}{\partial \tilde{n}(\mathbf{G}) \partial \tilde{n}^*(\mathbf{G}')} = \frac{8\pi\Omega}{G^2} \frac{\partial \tilde{n}(\mathbf{G}')}{\partial \tilde{n}(\mathbf{G})} = \frac{8\pi\Omega}{G^2} \delta^3(\mathbf{G} - \mathbf{G}') \quad \text{for } \mathbf{G}, \mathbf{G}' > 0 \quad (8.30)$$

which shows that the second derivative of the Hartree energy term (the Hartree Hessian) is diagonal in reciprocal space.

8.2.2 Pseudopotentials and Pseudopotential Energy

To reduce the number of plane waves necessary to represent the electronic density, pseudopotentials are often used to represent the potential generated by the core

¹The approach is the following: let us consider $z = x + iy$ and $z^* = x - iy$, which implies $|z|^2 = x^2 + y^2$. Then it is possible to write

$$\begin{aligned} \frac{\partial |z|^2}{\partial z^*} &= \frac{\partial (x^2 + y^2)}{\partial (x - iy)} = \frac{\partial x}{\partial (x - iy)} \frac{\partial (x^2 + y^2)}{\partial x} + \frac{\partial y}{\partial (x - iy)} \frac{\partial (x^2 + y^2)}{\partial y} \\ &= 2x \left(\frac{\partial (x - iy)}{\partial x} \right)^{-1} + 2y \left(\frac{\partial (x - iy)}{\partial y} \right)^{-1} = 2(x + iy) = 2z \end{aligned}$$

which yields the result in Eq. (8.29).

electrons of the ions. Indeed, the steepness of the electrostatic interactions close to the nucleus of the atom would require very high-energy plane waves to represent the density close to the core with a nonnegligible overhead in computational costs. To avoid this, the electronic density is used to represent only the valence electrons and the electrons up to the last closed shell are considered to be fixed and represented by a given functional form. The choice of the pseudopotential is delicate and there is an entire branch of theoretical chemistry dedicated to the design and construction of accurate pseudopotentials which are portable and which reflects the good physical properties of the materials. In this work we will adopt the easiest approximation for this term in modeling the interaction, which consists in the use of a local pseudopotential, *i.e.* a pseudopotential that depends only on the distance from the nucleus. More refined forms consider nonlocal, norm-conserving pseudopotentials which are angular-momentum dependent. Note that, for this reason, they cannot be used in orbital-free density functional theory as the information on the angular momentum of the state is lost when the density is computed from the orbitals. In local approximation, the energy term E_{PS} can be written, for a periodic system, as

$$E_{\text{PS}} = \Omega \sum_{I=1}^{N_I} \left\{ \tilde{V}_I^{\text{PS}}(0) \tilde{n}(0) + 2 \sum_{\mathbf{G} > 0} \Re \left[\tilde{V}_I^{\text{PS}}(\mathbf{G}) S_I(\mathbf{G}) \tilde{n}^*(\mathbf{G}) \right] \right\} \quad (8.31)$$

where $\Re$ denotes the real part. The issue of computing the pseudopotential in reciprocal space $\tilde{V}_I^{\text{PS}}(\mathbf{G})$ is delicate and should not be underestimated. It is indeed not sufficient to compute the Fourier transform of the expression in real space, as the cutoff chosen for the plane wave basis set could not be enough to represent it. The standard procedure consists then in computing $V_I^{\text{PS}}(\mathbf{r}')$ on a finer grid (indicated here by the prime) in real space, move to the reciprocal of the (finer) grid obtaining $\tilde{V}_I^{\text{PS}}(\mathbf{G}')$ and then interpolate the finer grid to the standard grid used for the regular MD run. Even if in principle this procedure is quite expensive it has the advantage to be necessary only once at the beginning of the simulation. Once the value of $\tilde{V}_I^{\text{PS}}(\mathbf{G})$ is computed with the procedure outlined above, it can be used to go back and forth from (standard) direct to reciprocal space without any loss of information.

The proper local form of the pseudopotential $\Delta V_I^{\text{loc}}(r')$ is usually given by literature, but the form computed on the finer grid has to compensate for the assumption we have done on the density of the core in computing the electrostatic energy (see

Eq. (8.15)), so that

$$V_I^{\text{PS}}(r') = -V_I^{\text{core}}(r') + \Delta V_I^{\text{loc}}(r') = \frac{Z_I}{r'} \text{erf}\left[\frac{r'}{R_I^{\text{cut}}}\right] + \Delta V_I^{\text{loc}}(r') \quad (8.32)$$

The presence of the term V_I^{core} is discussed at length in Section 8.7. Eq. (8.32) in Fourier space has a simple analytic form thanks to the properties of three-dimensional Fourier transforms of spherically symmetric functions. On the reciprocal finer grid, the expression of the local pseudopotential is given by

$$\tilde{V}_I^{\text{PS}}(G') = \frac{4\pi}{\Omega} \int_0^\infty dr r^2 V_I^{\text{PS}}(r') j_0(Gr) \quad (8.33)$$

where $j_0(x) = \frac{\sin(x)}{x}$ represents the spherical Bessel function of the first kind of order zero. It is now possible to interpolate the function $\tilde{V}_I^{\text{PS}}(G')$ on the standard grid. A linear interpolation is usually accurate enough for the majority of applications. The value of $\tilde{V}_I^{\text{PS}}(G)$ with $G' < G < G''$ is then given by

$$\tilde{V}_I^{\text{PS}}(G) = \frac{\tilde{V}_I^{\text{PS}}(G')(G'' - G) + \tilde{V}_I^{\text{PS}}(G'')(G - G')}{G'' - G'} \quad (8.34)$$

For the pseudopotential term of the electronic energy, ion forces are computed straightforwardly as the only dependence on the ionic position in Eq. (8.31) is given by the structure factor. Considering the expanded form of Eq. (8.31)

$$E_{\text{PS}} = \Omega \sum_{I=1}^{N_I} \left\{ \tilde{V}_I^{\text{PS}}(0) \tilde{n}(0) + \sum_{\mathbf{G} > 0} \left[\tilde{V}_I^{\text{PS}}(G) S_I(\mathbf{G}) \tilde{n}^*(\mathbf{G}) + (\tilde{V}_I^{\text{PS}}(G) S_I(\mathbf{G}))^* \tilde{n}(\mathbf{G}) \right] \right\} \quad (8.35)$$

taking the gradient with respect to the ionic positions yields

$$\begin{aligned} \mathbf{F}_I^{\text{PS}} &= -\nabla_{\mathbf{R}_I} E_{\text{PS}} \\ &= -\Omega \sum_{I=1}^{N_I} \sum_{\mathbf{G} > 0} \left[\tilde{V}_I^{\text{PS}}(G) \tilde{n}^*(\mathbf{G}) \nabla_{\mathbf{R}_I} S_I(\mathbf{G}) + (\tilde{V}_I^{\text{PS}}(G))^* \tilde{n}(\mathbf{G}) \nabla_{\mathbf{R}_I} S_I^*(\mathbf{G}) \right] \\ &= \Omega \sum_{I=1}^{N_I} \sum_{\mathbf{G} > 0} i\mathbf{G} \left[\tilde{V}_I^{\text{PS}}(G) S_I(\mathbf{G}) \tilde{n}^*(\mathbf{G}) - (\tilde{V}_I^{\text{PS}}(G))^* S_I^*(\mathbf{G}) \tilde{n}(\mathbf{G}) \right] \\ &= -2\Omega \sum_{I=1}^{N_I} \sum_{\mathbf{G} > 0} \Im \left[\tilde{V}_I^{\text{PS}}(G) S_I(\mathbf{G}) \tilde{n}^*(\mathbf{G}) \right] \mathbf{G} \end{aligned} \quad (8.36)$$

Being the pseudopotential energy linear in the density, it gives no contribution to the Hessian, while its contribution to the gradient with respect to electronic density is given by

$$\frac{\partial E_{\text{PS}}}{\partial \tilde{n}^*(\mathbf{G})} = \Omega_{\mathbf{G}} \sum_{I=1}^{N_I} \tilde{V}_I^{\text{PS}}(G) S_I(\mathbf{G}) \quad (8.37)$$

where the property that $\tilde{n}(-\mathbf{G}) = \tilde{n}^*(\mathbf{G})$ for $\mathbf{G} \neq 0$ has been taken into account in the prefactor $\Omega_{\mathbf{G}}$ defined by

$$\Omega_{\mathbf{G}} = \begin{cases} \Omega & \text{for } \mathbf{G} = 0 \\ 2\Omega & \text{for } \mathbf{G} > 0 \end{cases} \quad (8.38)$$

8.2.3 Kinetic and Exchange-Correlation Energy

Kinetic and Exchange-Correlation energy terms are usually complicated nonlinear functionals of the density and — for what concerns this work — of its gradient. Their analytical form cannot be computed from first principles, but approximations are known and the research and design of accurate functionals for these terms of the energy functional is an extremely active branch of theoretical chemistry. The kinetic functional, in particular, and the research for more accurate forms, is peculiar of the orbital-free DFT domain, since in the more common Kohn-Sham (orbital-based) version of DFT, the kinetic energy of the electrons is expressed as a quadratic functional of the orbitals. The easiest approximation for the kinetic energy functional is given by the Thomas-Fermi functional for the free-electron gas [186], which can be written as

$$E_{\text{K}}^{\text{TF}}[n] = \frac{3\pi^2}{10} \left(\frac{3}{\pi} \right)^{\frac{2}{3}} \int d^3r (n(\mathbf{r}))^{\frac{5}{3}} \quad (8.39)$$

and it is a functional of the density alone. More refined forms consider also the gradient of the electronic density and they are often based on corrections to the Thomas-Fermi expression. For example, of great importance for this work are the von Weizsäcker correction [187]

$$E_{\text{K}}^{\text{vW}}[n] = E_{\text{K}}^{\text{TF}}[n] + \frac{1}{8} \int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} \quad (8.40)$$

and the Perrot correction [188]

$$E_K^P[n] = E_K^{vW}[n] + \Omega \sum_{\mathbf{G} > 0} |\tilde{n}(\mathbf{G})|^2 \left(\frac{1}{\chi^{vW}(G)} - \frac{1}{\chi^0(G)} \right) \quad (8.41)$$

where $\chi^{vW}(G)$ and $\chi^0(G)$ are the von Weizsäcker and Lindhard screened susceptibilities, defined by

$$\chi^{vW}(G) = -\frac{k_F}{\pi^2} \left(\frac{1}{1+3q^2} \right) \quad (8.42a)$$

$$\chi^0(G) = -\frac{k_F}{\pi^2} \left(\frac{1}{2} + \frac{1-q^2}{4q} \ln \left| \frac{1+q}{1-q} \right| \right) \quad (8.42b)$$

with $q = \frac{G}{2k_F}$ and k_F the Fermi wavevector for a uniform system of N_{el} electrons, given by $k_F = (3\pi^2\rho)^{\frac{1}{3}}$ with $\rho = \frac{N_{el}}{\Omega}$. For the Perrot functional, the screened susceptibilities $\chi^{vW}(G)$ and $\chi^0(G)$ are tuned in such a way to obtain the correct linear response in the limit of large and low G [181].

In this work, the expressions for $E_K[n]$ and $E_{XC}[n]$ — except when differently stated — are derived from the library `lib_xc` [189], together with their first and second derivatives with respect to the electronic density and its gradient. Since they are handled in the same way by the library, they will be collectively expressed as $E_{KXC}[n] \equiv E_K[n] + E_{XC}[n]$. For a periodic system they can be expressed as

$$\begin{aligned} E_{KXC}[n] &= \int d^3r \epsilon_{KXC}(n(\mathbf{r}), \nabla n(\mathbf{r})) n(\mathbf{r}) \\ &= \Omega \left\{ \tilde{\epsilon}_{KXC}(0) \tilde{n}(0) + \sum_{\mathbf{G} > 0} \left[\tilde{\epsilon}_{KXC}(\mathbf{G}) \tilde{n}^*(\mathbf{G}) + \tilde{\epsilon}_{KXC}^*(\mathbf{G}) \tilde{n}(\mathbf{G}) \right] \right\} \end{aligned} \quad (8.43)$$

For the energy, the library `lib_xc` yields the integral kernel $\epsilon_{KXC}(n(\mathbf{r}), \nabla n(\mathbf{r}))$ so this expression is usually computed in direct space. Since this term does not depend on the nuclear coordinates, it gives no contribution to the ionic forces. On the other hand, the contribution coming from kinetic and exchange-correlation part is crucial in the computation of first and second derivatives of the energy functional with respect to the electronic density. `Lib_xc` provides these expressions — again in direct space — in a very straightforward way. For the GGA case, the library does not work directly with the gradient of the density $\nabla n(\mathbf{r})$ but with its modulus squared $\varsigma(\mathbf{r}) = |\nabla n(\mathbf{r})|^2$. Therefore, for the energy, the library yields $\epsilon_{KXC}(n(\mathbf{r}), \varsigma(\mathbf{r}))$ defined as the energy

per unit particle so that the expression for E_{KXC} is computed from $\epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r}))$ as

$$E_{\text{KXC}} = \frac{\Omega}{N_{\text{D}}} \sum_{\mathbf{r}} \epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r})) n(\mathbf{r}) \quad (8.44)$$

For the gradient of the energy, lib_xc yields $v_{\text{KXC}}^n(n(\mathbf{r}), \zeta(\mathbf{r}))$ and $v_{\text{KXC}}^\zeta(n(\mathbf{r}), \zeta(\mathbf{r}))$, defined

$$\begin{aligned} v_{\text{KXC}}^n(n(\mathbf{r}), \zeta(\mathbf{r})) &= \frac{\partial \epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r})) n(\mathbf{r})}{\partial n(\mathbf{r})} \\ v_{\text{KXC}}^\zeta(n(\mathbf{r}), \zeta(\mathbf{r})) &= \frac{\partial \epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r})) n(\mathbf{r})}{\partial \zeta(\mathbf{r})} \end{aligned} \quad (8.45)$$

respectively, and, for the Hessian of the energy, $f_{\text{KXC}}^{nn}(n(\mathbf{r}), \zeta(\mathbf{r}))$, $f_{\text{KXC}}^{n\zeta}(n(\mathbf{r}), \zeta(\mathbf{r}))$ and $f_{\text{KXC}}^{\zeta\zeta}(n(\mathbf{r}), \zeta(\mathbf{r}))$, defined

$$\begin{aligned} f_{\text{KXC}}^{nn}(n(\mathbf{r}), \zeta(\mathbf{r})) &= \frac{\partial^2 \epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r})) n(\mathbf{r})}{\partial^2 n(\mathbf{r})} \\ f_{\text{KXC}}^{n\zeta}(n(\mathbf{r}), \zeta(\mathbf{r})) &= \frac{\partial^2 \epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r})) n(\mathbf{r})}{\partial n(\mathbf{r}) \partial \zeta(\mathbf{r})} \\ f_{\text{KXC}}^{\zeta\zeta}(n(\mathbf{r}), \zeta(\mathbf{r})) &= \frac{\partial^2 \epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r})) n(\mathbf{r})}{\partial^2 \zeta(\mathbf{r})} \end{aligned} \quad (8.46)$$

respectively. The derivatives of ϵ_{KXC} are given per unit volume, at difference with ϵ_{KXC} itself which, we recall, is given per particle. For both the minimization algorithms described in this work the expressions for v_{KXC} and f_{KXC} have to be computed in reciprocal space and the way in which they will be obtained in practice from the output of lib_xc will be discussed in detail together with the algorithms.

8.3 Mass-Zero Constrained Dynamics in Complex Space

In accordance with the Born-Oppenheimer approximation for the dynamics, the “electrons” (here represented by the electronic density) relax instantaneously to the minimum of the potential generated by the ions which are considered fixed. The forces on the ions are then computed at each timestep using the density which minimize the energy functional discussed in the previous section.

In a plane-waves expansion, the natural framework to do this minimization is the reciprocal space. In particular the coefficients of the electronic density in reciprocal

space act now as the additional degrees of freedom over which the minimization has to be carried over. In mathematical terms, the motion of the ions has to be performed with the electronic density satisfying the condition

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} = 0 \quad (8.47)$$

which in reciprocal space is translated in the expression

$$\frac{\partial E}{\partial \tilde{n}^*(\mathbf{G})} = 0 \quad (8.48)$$

We are now in the same situation discussed in Section 6.1 when the mass-zero constrained algorithm was introduced. Eq. (8.48) can be considered a holonomic constraint (there is no dependence on the time-derivatives of the density coefficients) and mass-zero constrained dynamics can be performed on the system. The additional difficulty lies in the fact that the additional variables are now complex quantities. This does not add any conceptual difficulty, but it makes the calculations a bit more cumbersome. These calculations are the object of this section.

In the framework of the extended-Lagrangian methods, we consider the system composed by the ions and the additional degrees of freedom which, in this case, are represented by the coefficients of the electronic density in reciprocal space $\tilde{n}(\mathbf{G})$. The motion must also keep constant the number of electrons, a condition that can be expressed, in real space, as

$$\int d^3r n(\mathbf{r}) = N_{\text{el}} \quad (8.49)$$

where N_{el} is the number of electrons in the system. Eq. (8.49), once the electronic density is expanded in plane waves, reads

$$\tilde{n}(0)\Omega = N_{\text{el}} \quad (8.50)$$

Note that, adopting a plane-waves expansion for the density, the condition of constant number of electrons could be straightforwardly imposed by keeping fixed the $\tilde{n}(0)$ component of the electronic density. In the following, however, we have implemented the conditioned minimization described in Section 6.2 for illustrative purposes. Following the discussion in Section 6.2, we expand the phase space further to include the Lagrange multiplier v as an additional variable. The potential function then

becomes

$$\mathcal{E}(\mathbf{R}, \tilde{n}, \nu) = E(\mathbf{R}, \tilde{n}) + \nu(\tilde{n}(0)\Omega - N_{\text{el}}) \quad (8.51)$$

The Lagrangian of the extended system is then given by

$$L = \frac{1}{2} \sum_I^{N_I} M_I \dot{\mathbf{R}}_I^2 + \frac{1}{2} \sum_{\mathbf{G}} \mu_{\tilde{n}} |\dot{\tilde{n}}(\mathbf{G})|^2 + \frac{1}{2} \mu_{\nu} \dot{\nu}^2 - \mathcal{E}(\mathbf{R}, \tilde{n}, \nu) \quad (8.52)$$

where $\mu_{\tilde{n}}$ and μ_{ν} represent the two fictitious masses associated to the additional variables $\tilde{n}(\mathbf{G})$ and ν . Note also that, for the moment, the $\mathbf{G}$ index runs in the interval $\mathbf{G} \in [-\mathbf{G}_{\text{max}}, \mathbf{G}_{\text{max}}]$. The adiabatic condition can be rephrased in the holonomic constraint

$$\begin{aligned} \sigma(\mathbf{G}) &= \frac{\partial \mathcal{E}(\mathbf{R}, \tilde{n}, \nu)}{\partial \tilde{n}^*(\mathbf{G})} = 0 \quad \text{for } \mathbf{G} \in [-\mathbf{G}_{\text{max}}, \mathbf{G}_{\text{max}}] \\ \sigma_{\text{add}} &= \frac{\partial \mathcal{E}(\mathbf{R}, \tilde{n}, \nu)}{\partial \nu} = 0 \end{aligned} \quad (8.53)$$

and, therefore, the equations of motion for the constrained system are given by

$$\begin{aligned} M_I \ddot{\mathbf{R}}_I &= -\nabla_{\mathbf{R}_I} E(\mathbf{R}, \tilde{n}) \\ \ddot{\tilde{n}}(\mathbf{G}) &= -\sum_{\mathbf{G}'} \gamma(\mathbf{G}') \frac{\partial \sigma(\mathbf{G}')}{\partial \tilde{n}^*(\mathbf{G})} - \gamma_{\text{add}} \frac{\partial \sigma_{\text{add}}}{\partial \tilde{n}^*(\mathbf{G})} \\ \ddot{\nu} &= -\kappa \sum_{\mathbf{G}'} \gamma(\mathbf{G}') \frac{\partial \sigma(\mathbf{G}')}{\partial \nu} - \gamma_{\text{add}} \kappa \frac{\partial \sigma_{\text{add}}}{\partial \nu} \end{aligned} \quad (8.54)$$

where the limit for $\mu \rightarrow 0$ has been performed in a homogeneous way for all the additional degrees of freedom (with the consequent arise of the factor κ defined by $\mu_{\tilde{n}} = \kappa \mu_{\nu}$). In the actual implementation, the range considered is $[0, \mathbf{G}_{\text{max}}]$ and the conjugate of the complex quantities is used to replace the missing part of the interval. This is possible because all the quantities in reciprocal space ($\gamma(\mathbf{G})$ and $\sigma(\mathbf{G})$ in particular) are the Fourier transforms of real quantities in direct space for which the property $f(-\mathbf{G}) = f^*(\mathbf{G})$ holds. The equations of motion for the system can then be

written as

$$\begin{aligned}
M_I \ddot{\mathbf{R}}_I &= -\nabla_{\mathbf{R}_I} E(\mathbf{R}, \tilde{n}) \\
\ddot{\tilde{n}}(\mathbf{G}) &= - \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \frac{\partial \sigma(\mathbf{G}')}{\partial \tilde{n}^*(\mathbf{G})} + \gamma^*(\mathbf{G}') \frac{\partial \sigma^*(\mathbf{G}')}{\partial \tilde{n}^*(\mathbf{G})} \right] \\
&\quad - \gamma(0) \frac{\partial \sigma(0)}{\partial \tilde{n}^*(\mathbf{G})} - \gamma_{\text{add}} \frac{\partial \sigma_{\text{add}}}{\partial \tilde{n}^*(\mathbf{G})} \\
\ddot{\mathbf{v}} &= -\kappa \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \frac{\partial \sigma(\mathbf{G}')}{\partial \mathbf{v}} + \gamma^*(\mathbf{G}') \frac{\partial \sigma^*(\mathbf{G}')}{\partial \mathbf{v}} \right] \\
&\quad - \gamma(0) \kappa \frac{\partial \sigma(0)}{\partial \mathbf{v}} - \gamma_{\text{add}} \kappa \frac{\partial \sigma_{\text{add}}}{\partial \mathbf{v}}
\end{aligned} \tag{8.55}$$

It is also easy to show, for the complex conjugate of the constraint expression, the relation

$$\sigma^*(\mathbf{G}) = \frac{\partial \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}(\mathbf{G})} = 0 \tag{8.56}$$

so that Eq. (8.55) can be written making use of the explicit expression of the constraints in term of derivatives of the energy in Eqs. (8.53) and (8.56)

$$\begin{aligned}
M_I \ddot{\mathbf{R}}_I &= -\nabla_{\mathbf{R}_I} E(\mathbf{R}, \tilde{n}) \\
\ddot{\tilde{n}}(\mathbf{G}) &= - \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}^*(\mathbf{G}')} + \gamma^*(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}(\mathbf{G}')} \right] \\
&\quad - \gamma(0) \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}(0)} - \gamma_{\text{add}} \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \mathbf{v}} \\
\ddot{\mathbf{v}} &= -\kappa \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \mathbf{v} \partial \tilde{n}^*(\mathbf{G}')} + \gamma^*(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \mathbf{v} \partial \tilde{n}(\mathbf{G}')} \right] \\
&\quad - \gamma(0) \kappa \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \mathbf{v} \partial \tilde{n}(0)}
\end{aligned} \tag{8.57}$$

where it has been noticed that $\tilde{n}(0) \in \mathbb{R}$ and that the second derivative of $\mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})$ with respect to $\mathbf{v}$ trivially vanishes, in general, by its own definition in Eq. (8.51).

8.3.1 The Homogeneous Limit for Plane-Waves Expansion

The nature of the additional variables introduced to describe the electronic density in the previous section is profoundly different from other equivalent situations in classical force-field-based simulations. In fact, while in the case of polarizable systems or electrode charges it made sense to consider all the additional variables of

the same kind (with the obvious exception of the Lagrange multiplier associated to the additional conditions), the plane-waves expansion used to describe the electronic density in reciprocal space implies a different approach. In analogy with the theory of scattering [190], it is possible to think of each wavevector of the plane waves to be associated to a “particle” of different mass, here represented by the plane-waves expansion coefficient. In view of this, we are closer to the case of simultaneous presence of polarizable particles and fluctuating charges introduced in Section 7.3, with the difference that here, each additional variable represents a particle of different mass. This property has to be taken into account in the definition of the equations of motion of the system, where the fictitious mass associated to the additional variables should be considered a function of the $\mathbf{G}$ -vector, *i.e.* $\mu_{\tilde{n}}(\mathbf{G})$ for $\mathbf{G} \in [0, \mathbf{G}_{\max}]$, instead of the single $\mu_{\tilde{n}}$ introduced in Eq. (8.52). Note that it is safe to assume $\mu_{\tilde{n}}(\mathbf{G}) = \mu_{\tilde{n}}^*(\mathbf{G})$, *i.e.* $\mu_{\tilde{n}}(\mathbf{G}) \in \mathbb{R}$.

The approach in taking the adiabatic limit is analogous the the one used for the additional conditions: We define $\mu_{\tilde{n}}(\mathbf{G}) = \mu_{\tilde{n}} \xi^{-1}(\mathbf{G})$ and then we take the limit $\mu_{\tilde{n}} \rightarrow 0$. The definition of μ_v does not change. The equations of motion for the extended dynamical system then take the form

$$\begin{aligned}
M_I \ddot{\mathbf{R}}_I &= -\nabla_{\mathbf{R}_I} E(\mathbf{R}, \tilde{n}) \\
\ddot{\tilde{n}}(\mathbf{G}) &= -\xi(\mathbf{G}) \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, v)}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}^*(\mathbf{G}')} + \gamma^*(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, v)}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}(\mathbf{G}')} \right] \\
&\quad - \gamma(0) \xi(\mathbf{G}) \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, v)}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}(0)} - \gamma_{\text{add}} \xi(\mathbf{G}) \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, v)}{\partial \tilde{n}^*(\mathbf{G}) \partial v} \\
\dot{v} &= -\kappa \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, v)}{\partial v \partial \tilde{n}^*(\mathbf{G}')} + \gamma^*(\mathbf{G}') \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, v)}{\partial v \partial \tilde{n}(\mathbf{G}')} \right] \\
&\quad - \gamma(0) \kappa \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, v)}{\partial v \partial \tilde{n}(0)}
\end{aligned} \tag{8.58}$$

Eq. (8.58) represents the dynamical system to be integrated numerically.

8.4 Numerical Implementation

Once again the combination of Verlet algorithm and SHAKE can be used to evolve the additional degrees of freedom and to compute the Lagrange multipliers. Assuming

the knowledge of the values of the density coefficients for two different steps, say $\tilde{n}(\mathbf{G}; t)$ and $\tilde{n}(\mathbf{G}; t - \delta t)$ (same for the additional variable $\mathbf{v}$) the Verlet algorithm yields the value of the coefficients at time $t + \delta t$ as a function of the Lagrange multipliers $\gamma(\mathbf{G}), \gamma^*(\mathbf{G})$

$$\begin{aligned}
\tilde{n}(\mathbf{G}; t + \delta t) &= 2\tilde{n}(\mathbf{G}; t) - \tilde{n}(\mathbf{G}; t - \delta t) \\
&\quad - \delta t^2 \gamma(0) \xi(\mathbf{G}) \left. \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}(0)} \right|_{\tilde{n}(t), \mathbf{v}(t)} - \delta t^2 \gamma_{\text{add}} \xi(\mathbf{G}) \left. \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \mathbf{v}} \right|_{\tilde{n}(t), \mathbf{v}(t)} \\
&\quad - \delta t^2 \xi(\mathbf{G}) \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \left. \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}^*(\mathbf{G}')} \right|_{\tilde{n}(t), \mathbf{v}(t)} + \gamma^*(\mathbf{G}') \left. \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \tilde{n}^*(\mathbf{G}) \partial \tilde{n}(\mathbf{G}')} \right|_{\tilde{n}(t), \mathbf{v}(t)} \right] \\
\mathbf{v}(t + \delta t) &= 2\mathbf{v}(t) - \mathbf{v}(t - \delta t) - \delta t^2 \gamma(0) \kappa \left. \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \mathbf{v} \partial \tilde{n}(0)} \right|_{\tilde{n}(t), \mathbf{v}(t)} \\
&\quad - \delta t^2 \kappa \sum_{\mathbf{G}' > 0} \left[\gamma(\mathbf{G}') \left. \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \mathbf{v} \partial \tilde{n}^*(\mathbf{G}')} \right|_{\tilde{n}(t), \mathbf{v}(t)} + \gamma^*(\mathbf{G}') \left. \frac{\partial^2 \mathcal{E}(\mathbf{R}, \tilde{n}, \mathbf{v})}{\partial \mathbf{v} \partial \tilde{n}(\mathbf{G}')} \right|_{\tilde{n}(t), \mathbf{v}(t)} \right]
\end{aligned} \tag{8.59}$$

As the notation will increase in complexity let us simplify it: we will denote the derivative of a function $\mathcal{F}$ with respect to the variable x with index i computed at $x_i = x_i(t) \forall i$ by $\partial_x \mathcal{F}_i^t$. A second derivative with respect to the variable y with index j will be denoted by $\partial_{xy}^2 \mathcal{F}_{ij}^t$. Note that, in this particular case, the function is the energy $\mathcal{E}$, the variables with respect to which we take the derivative are $\tilde{n}$ and $\mathbf{v}$ and the indexes are given by $\mathbf{G}$ and “add”. This notation, together with the definitions $\tilde{n}_{\mathbf{G}}^t \equiv \tilde{n}(\mathbf{G}; t)$, $\mathbf{v}^t \equiv \mathbf{v}(t)$, $\gamma(\mathbf{G}) \equiv \gamma_{\mathbf{G}}$ and $\xi(\mathbf{G}) \equiv \xi_{\mathbf{G}}$, allows Eq. (8.59) to be recast in the simpler form

$$\begin{aligned}
\tilde{n}_{\mathbf{G}}^{t+\delta t} &= 2\tilde{n}_{\mathbf{G}}^t - \tilde{n}_{\mathbf{G}}^{t-\delta t} - \delta t^2 \gamma_0 \xi_{\mathbf{G}} \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}0}^t - \delta t^2 \gamma_{\text{add}} \xi_{\mathbf{G}} \partial_{\tilde{n}^* \mathbf{v}}^2 \mathcal{E}_{\mathbf{G}\text{add}}^t \\
&\quad - \delta t^2 \xi_{\mathbf{G}} \sum_{\mathbf{G}' > 0} [\gamma_{\mathbf{G}'} \partial_{\tilde{n}^* \tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}\mathbf{G}'}^t] \\
\mathbf{v}^{t+\delta t} &= 2\mathbf{v}^t - \mathbf{v}^{t-\delta t} - \delta t^2 \gamma_0 \kappa \partial_{\mathbf{v} \tilde{n}}^2 \mathcal{E}_{\text{add}0}^t \\
&\quad - \delta t^2 \kappa \sum_{\mathbf{G}' > 0} [\gamma_{\mathbf{G}'} \partial_{\mathbf{v} \tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\mathbf{v} \tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t]
\end{aligned} \tag{8.60}$$

The values of the Lagrange multipliers that satisfy Eqs. (8.53) and (8.56) at time $t + \delta t$ can be found by solving the equation of the constraints at time $t + \delta t$. This means solving $\sigma_{\mathbf{G}}(\tilde{n}^{t+\delta t}, \mathbf{v}^{t+\delta t}) \equiv \sigma(\tilde{n}(t + \delta t), \mathbf{v}(t + \delta t); \mathbf{G}) = 0$ for all the $\mathbf{G} \geq 0$ together with the additional condition. This is a system of nonlinear equations which

has to be solved iteratively. Let us write $\tilde{n}^{t+\delta t} = \tilde{n}^P + \delta\tilde{n}$ and $\mathbf{v}^{t+\delta t} = \mathbf{v}^P + \delta\mathbf{v}$ where $\tilde{n}^P = 2\tilde{n}^t - \tilde{n}^{t-\delta t}$ and $\mathbf{v}^P = 2\mathbf{v}^t - \mathbf{v}^{t-\delta t}$ and

$$\begin{aligned}\delta\tilde{n}_{\mathbf{G}} &= -\gamma_0 \xi_{\mathbf{G}} \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}0}^t - \gamma_{\text{add}} \xi_{\mathbf{G}} \partial_{\tilde{n}^* \mathbf{v}}^2 \mathcal{E}_{\mathbf{G}\text{add}}^t - \xi_{\mathbf{G}} \sum_{\mathbf{G}' > 0} [\gamma_{\mathbf{G}'} \partial_{\tilde{n}^* \tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}\mathbf{G}'}^t] \\ \delta\mathbf{v} &= -\gamma_0 \kappa \partial_{\mathbf{v} \tilde{n}}^2 \mathcal{E}_{\text{add}0}^t - \kappa \sum_{\mathbf{G}' > 0} [\gamma_{\mathbf{G}'} \partial_{\mathbf{v} \tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\mathbf{v} \tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t]\end{aligned}\quad (8.61)$$

where the Lagrange multipliers have been redefined to include the factors δt^2 . The equation of the constraints as a function of the unknown γ can then be written as $\sigma(\tilde{n}^P + \delta\tilde{n}, \mathbf{v}^P + \delta\mathbf{v}) = 0$ where the dependence on the Lagrange multipliers is enclosed in the $\delta\tilde{n}$ and $\delta\mathbf{v}$ terms. Taylor expanding this expression around $\gamma = 0$ yields, to the first order in γ

$$\begin{aligned}0 &= \sigma_{\mathbf{G}}(\tilde{n}^P + \delta\tilde{n}, \mathbf{v}^P + \delta\mathbf{v}) \\ &\approx \sigma_{\mathbf{G}}(\tilde{n}^P, \mathbf{v}^P) + \frac{\partial \sigma_{\mathbf{G}}}{\partial \mathbf{v}} \bigg|_{\tilde{n}^P, \mathbf{v}^P} \delta\mathbf{v} + \frac{\partial \sigma_{\mathbf{G}}}{\partial \tilde{n}_0} \bigg|_{\tilde{n}^P, \mathbf{v}^P} \delta\tilde{n}_0 + \sum_{\mathbf{G}'' > 0} \left[\frac{\partial \sigma_{\mathbf{G}}}{\partial \tilde{n}_{\mathbf{G}''}} \bigg|_{\tilde{n}^P, \mathbf{v}^P} \delta\tilde{n}_{\mathbf{G}''} + \frac{\partial \sigma_{\mathbf{G}}}{\partial \tilde{n}_{\mathbf{G}''}^*} \bigg|_{\tilde{n}^P, \mathbf{v}^P} \delta\tilde{n}_{\mathbf{G}''}^* \right]\end{aligned}\quad (8.62)$$

for $\mathbf{G} \in [0, \mathbf{G}_{\text{max}}]$ and

$$\begin{aligned}0 &= \sigma_{\text{add}}(\tilde{n}^P + \delta\tilde{n}, \mathbf{v}^P + \delta\mathbf{v}) \\ &\approx \sigma_{\text{add}}(\tilde{n}^P, \mathbf{v}^P) + \frac{\partial \sigma_{\text{add}}}{\partial \tilde{n}_0} \bigg|_{\tilde{n}^P, \mathbf{v}^P} \delta\tilde{n}_0 + \sum_{\mathbf{G}'' > 0} \left[\frac{\partial \sigma_{\text{add}}}{\partial \tilde{n}_{\mathbf{G}''}} \bigg|_{\tilde{n}^P, \mathbf{v}^P} \delta\tilde{n}_{\mathbf{G}''} + \frac{\partial \sigma_{\text{add}}}{\partial \tilde{n}_{\mathbf{G}''}^*} \bigg|_{\tilde{n}^P, \mathbf{v}^P} \delta\tilde{n}_{\mathbf{G}''}^* \right]\end{aligned}\quad (8.63)$$

for the constraint on the number of electrons. In Eq. (8.63) it has again been recognized that the derivative of the additional constraint with respect to $\mathbf{v}$ (the second derivative of the energy functional) vanishes. It is now possible to substitute the explicit expressions for $\delta\tilde{n}$ and for $\delta\mathbf{v}$ given in Eq. (8.61). In doing that, we also introduce the notation $\sigma^P \equiv \sigma(\tilde{n}^P, \mathbf{v}^P)$ and the same for the second derivative of the

energy. Using also the explicit expression for the constraint we obtain

$$\begin{aligned}
0 \approx & \sigma_{\mathbf{G}}^{\text{P}} - \gamma_0 \kappa \partial_{\mathbf{v}\tilde{n}^*}^2 \mathcal{E}_{\text{add}}^{\text{P}} \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}0}^t \\
& - \kappa \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'} \partial_{\mathbf{v}\tilde{n}^*}^2 \mathcal{E}_{\text{add}}^{\text{P}} \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\mathbf{v}\tilde{n}^*}^2 \mathcal{E}_{\text{add}}^{\text{P}} \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t \right] \\
& - \gamma_0 \xi_0 \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^t - \gamma_{\text{add}} \xi_0 \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^t \\
& - \xi_0 \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}'}^t \right] \\
& - \sum_{\mathbf{G}'' > 0} \left\{ \gamma_0 \xi_{\mathbf{G}''} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t + \gamma_{\text{add}} \xi_{\mathbf{G}''} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t \right. \\
& - \xi_{\mathbf{G}''} \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right] \\
& - \gamma_0 \xi_{\mathbf{G}''} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t - \gamma_{\text{add}} \xi_{\mathbf{G}''} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t \\
& \left. - \xi_{\mathbf{G}''} \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'}^* \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \gamma_{\mathbf{G}'} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right] \right\} \quad (8.64)
\end{aligned}$$

for $\mathbf{G} \in [0, \mathbf{G}_{\text{max}}]$ and

$$\begin{aligned}
0 \approx & \sigma_{\text{add}}^{\text{P}} - \gamma_0 \xi_0 \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^t - \gamma_{\text{add}} \xi_0 \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^t \\
& - \xi_0 \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}'}^t \right] \\
& - \sum_{\mathbf{G}'' > 0} \left\{ \gamma_0 \xi_{\mathbf{G}''} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t + \gamma_{\text{add}} \xi_{\mathbf{G}''} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t \right. \\
& - \xi_{\mathbf{G}''} \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right] \\
& - \gamma_0 \xi_{\mathbf{G}''} \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t - \gamma_{\text{add}} \xi_{\mathbf{G}''} \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t \\
& \left. - \xi_{\mathbf{G}''} \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'}^* \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \gamma_{\mathbf{G}'} \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right] \right\} \quad (8.65)
\end{aligned}$$

It is now possible to recognize in Eqs. (8.64) and (8.65) the form of the linearized system $\sigma - \mathbb{S}\gamma = 0$ already encountered in Section 6.6. To help the reader visualize

this, let us define the vectors

$$\begin{aligned}\sigma &= \left\{ \sigma_0, \sigma_{\mathbf{G}_1}, \sigma_{\mathbf{G}_1}^*, \dots, \sigma_{\mathbf{G}_{N_R}}, \sigma_{\mathbf{G}_{N_R}}^*, \sigma_{\text{add}} \right\} \\ \gamma &= \left\{ \gamma_0, \gamma_{\mathbf{G}_1}, \gamma_{\mathbf{G}_1}^*, \dots, \gamma_{\mathbf{G}_{N_R}}, \gamma_{\mathbf{G}_{N_R}}^*, \gamma_{\text{add}} \right\}\end{aligned}\quad (8.66)$$

of dimensions $2N_R$ and the matrix $\mathbb{S}$, of dimension $2N_R \times 2N_R$, which has the following structure:

$$\begin{bmatrix} \mathbb{S}_{00} & \mathbb{S}_{0\mathbf{G}_1} & \mathbb{S}_{0\mathbf{G}_1}^* & \dots & \mathbb{S}_{0\mathbf{G}_{N_R}} & \mathbb{S}_{0\mathbf{G}_{N_R}}^* & \mathbb{S}_{\text{add}0} \\ \mathbb{S}_{\mathbf{G}_1 0} & [\mathbb{S}_{\mathbf{G}_1 \mathbf{G}_1}] & & & & & \mathbb{S}_{\mathbf{G}_1 \text{add}} \\ \mathbb{S}_{\mathbf{G}_1 0}^* & & & & & & \mathbb{S}_{\mathbf{G}_1 \text{add}}^* \\ \vdots & & & \ddots & & & \vdots \\ \mathbb{S}_{\mathbf{G}_{N_R} 0} & & & & [\mathbb{S}_{\mathbf{G}_{N_R} \mathbf{G}_{N_R}}] & & \mathbb{S}_{\mathbf{G}_{N_R} \text{add}} \\ \mathbb{S}_{\mathbf{G}_{N_R} 0}^* & & & & & & \mathbb{S}_{\mathbf{G}_{N_R} \text{add}}^* \\ \mathbb{S}_{\text{add}0} & \mathbb{S}_{\text{add}\mathbf{G}_1} & \mathbb{S}_{\text{add}\mathbf{G}_1}^* & \dots & \mathbb{S}_{\text{add}\mathbf{G}_{N_R}} & \mathbb{S}_{\text{add}\mathbf{G}_{N_R}}^* & \mathbb{S}_{\text{addadd}} \end{bmatrix} \quad (8.67)$$

where the submatrixes $[\mathbb{S}_{\mathbf{G}\mathbf{G}}]$, defined for $\mathbf{G} > 0$, have the form:

$$[\mathbb{S}_{\mathbf{G}\mathbf{G}}] = \begin{bmatrix} \mathbb{S}_{\mathbf{G}\mathbf{G}} & \mathbb{S}_{\mathbf{G}\mathbf{G}}^* \\ (\mathbb{S}^*)_{\mathbf{G}\mathbf{G}}^* & \mathbb{S}_{\mathbf{G}\mathbf{G}}^* \end{bmatrix} \quad (8.68)$$

Note that $\mathbb{S}_{\mathbf{G}\mathbf{G}}^*$ is not $\mathbb{S}_{\mathbf{G}\mathbf{G}}^*$. The elements of the matrix in Eq. (8.67) are given by

$$\begin{aligned}\mathbb{S}_{00} &= \kappa \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}0}^{\text{P}} \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}0}^t + \xi_0 \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^t \\ &\quad + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t + \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t] \\ \mathbb{S}_{0\mathbf{G}'} &= \kappa \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}0}^{\text{P}} \partial_{\mathbf{v}\tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t + \xi_0 \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^{\text{P}} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}'}^t \\ &\quad + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t] \\ \mathbb{S}_{0\mathbf{G}'}^* &= \kappa \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}0}^{\text{P}} \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t + \xi_0 \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}'}^t \\ &\quad + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t] \\ \mathbb{S}_{0\text{add}} &= \xi_0 \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^t \\ &\quad + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}^* \mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t + \partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t]\end{aligned}\quad (8.69)$$

for the first row

$$\begin{aligned}
\mathbb{S}_{\text{add}\mathbf{G}'} &= \xi_0 \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}'}^t \\
&+ \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} \left[\partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right] \\
\mathbb{S}_{\text{add}\mathbf{G}'}^* &= \xi_0 \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}'}^t \\
&+ \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} \left[\partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right] \\
\mathbb{S}_{\text{addadd}} &= \xi_0 \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{0\text{add}}^t \\
&+ \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} \left[\partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t + \partial_{\tilde{n}^*\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t \right]
\end{aligned} \tag{8.70}$$

for the last row, and

$$\begin{aligned}
\mathbb{S}_{\mathbf{G}\mathbf{G}'} &= \kappa \partial_{\mathbf{v}\tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}}^{\text{P}} \partial_{\mathbf{v}\tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t + \xi_0 \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}'}^t \\
&+ \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} \left[\partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \partial_{\tilde{n}^*\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right] \\
\mathbb{S}_{\mathbf{G}\mathbf{G}'}^* &= \kappa \partial_{\mathbf{v}\tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}}^{\text{P}} \partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}'}^t + \xi_0 \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}'}^t \\
&+ \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} \left[\partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t + \partial_{\tilde{n}^*\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}'}^t \right]
\end{aligned} \tag{8.71}$$

for the central block, *i.e.* $\mathbf{G} > 0$.

With the notation just introduced, Eqs. (8.64) and (8.65) can be written compactly in the form of the linearized system

$$\sigma - \mathbb{S}\gamma \approx 0 \tag{8.72}$$

Eq. (8.72) represents a linear system of $2N_{\text{R}}$ equations in $2N_{\text{R}}$ unknowns, which is clearly redundant, as N_{R} equations (and consequently N_{R} unknowns) are the complex conjugate of the other N_{R} . It is therefore possible to reduce the system to half its original size and to solve only the equations stemming from the relations for σ , disregarding in this way the ones obtained by the σ^* . With the exception of γ_0 and γ_{add} we have freedom also in the choice of the unknowns. This means that it is possible to solve the system in γ or in γ^* . We arbitrarily chose to solve the linear system in the unknowns γ^* leaving us with just the $\mathbb{S}^*$ terms of the matrix defined in Eqs. (8.69)-(8.71).

The linear system, even in its reduced form, is a formidable problem to solve numerically. Indeed, in most situations the matrix is of high dimension and cannot be inverted efficiently. Moreover, the second order terms in the expansions Eqs. (8.62) and (8.63) are expected to play an important role considered the nonquadratic nature of the exchange-correlation and kinetic terms in the energy functional so that the solution has to be found iteratively even solving the full linear system. To further reduce the computational cost of the problem, the matrix will be approximated by its diagonal, as commonly done in numerical algorithms for constrained problems. In this way we are left with only three terms of the matrix $\mathbb{S}$ which are given by

$$\begin{aligned}
\mathbb{S}_{00} &= \kappa \partial_{v\tilde{n}}^2 \mathcal{E}_{\text{add}0}^{\text{P}} \partial_{v\tilde{n}}^2 \mathcal{E}_{\text{add}0}^t + \xi_0 \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{00}^t \\
&\quad + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t + \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''0}^t] \\
\mathbb{S}_{\mathbf{GG}}^* &= \kappa \partial_{v\tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}}^{\text{P}} \partial_{v\tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}}^t + \xi_0 \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{0\mathbf{G}}^t \\
&\quad + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^t + \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''\mathbf{G}}^t] \\
\mathbb{S}_{\text{addadd}} &= \xi_0 \partial_{\tilde{n}v}^2 \mathcal{E}_{0\text{add}}^{\text{P}} \partial_{\tilde{n}v}^2 \mathcal{E}_{0\text{add}}^t \\
&\quad + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}v}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}^*v}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t + \partial_{\tilde{n}^*v}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^{\text{P}} \partial_{\tilde{n}v}^2 \mathcal{E}_{\mathbf{G}''\text{add}}^t]
\end{aligned} \tag{8.73}$$

This equation represents the denominator of SHAKE which has been introduced in Section 6.6.1. Once the particular expression taken by Eq. (8.73) has been specified, together with the expression of the constraints, Eq. (8.72) with $\mathbb{S}^* \approx \text{diag } \mathbb{S}^*$ yields an approximation for the Lagrange multipliers as

$$\gamma^* = \frac{\sigma^{\text{P}}}{\text{diag } \mathbb{S}^*} \tag{8.74}$$

The particular form taken by the constraints and their gradient in the diagonal expression of the SHAKE matrix is the subject of the next section.

8.4.1 Explicit Expressions for Constraints and Gradients of the Constraints

We will now specify the form of the energy functional to the particular expression given in Eq. (8.51). This allows, in particular, to derive simple forms for the derivatives involving the additional constraint and it will contribute to simplify the

equations for the constraints and their gradients. Let us consider at first the form of $\mathbb{S}_{\text{addadd}}$ given in Eq. (8.73). This is expressed as a sum of the derivatives with respect to the wavevectors of the additional constraint, the latter being given by

$$\sigma_{\text{add}} = \frac{\partial \mathcal{E}(\mathbf{R}, \tilde{n}, \nu)}{\partial \nu} = \frac{\partial}{\partial \nu} \left(E(\mathbf{R}, \tilde{n}) + \nu(\tilde{n}(0)\Omega - N_{\text{el}}) \right) = \tilde{n}(0)\Omega - N_{\text{el}} \quad (8.75)$$

It is therefore clear that all the derivatives of σ_{add} computed for $\mathbf{G} \neq 0$ vanish, while the derivative for $\mathbf{G} = 0$ yields

$$\frac{\partial \sigma_{\text{add}}}{\partial \tilde{n}(0)} = \Omega \quad (8.76)$$

We then have $\mathbb{S}_{\text{addadd}} = \xi_0 \Omega^2$. In the same fashion, in the expression for $\mathbb{S}_{00}$ in Eq. (8.73) we have $\kappa \partial_{\tilde{n}}^2 \mathcal{E}_{\text{add}0}^{\text{P}} \partial_{\tilde{n}}^2 \mathcal{E}_{\text{add}0}^{\text{t}} = \kappa \Omega^2$. Moreover, as the term $\mathbf{G} = 0$ is not considered in $\mathbb{S}_{\mathbf{G}\mathbf{G}}^*$ we have simply that $\kappa \partial_{\tilde{n}^*}^2 \mathcal{E}_{\text{add}\mathbf{G}}^{\text{P}} \partial_{\tilde{n}}^2 \mathcal{E}_{\text{add}\mathbf{G}}^{\text{t}} = 0$ in Eq. (8.73). Finally, for the generic constraint $\sigma_{\mathbf{G}}$ with $\mathbf{G} \in [0, \mathbf{G}_{\text{max}}]$ we have $\partial_{\tilde{n}^* \tilde{n}}^2 \mathcal{E}_{\mathbf{G}'\mathbf{G}} = \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}'\mathbf{G}} \forall \mathbf{G}' \in [0, \mathbf{G}_{\text{max}}]$. Therefore, once the additional condition of the problem has been specified to be the one in Eq. (8.75), the new expression for the components of the shake denominator is given by

$$\begin{aligned} \mathbb{S}_{00} &= \kappa \Omega^2 + \xi_0 \partial_{\tilde{n}\tilde{n}}^2 E_{00}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 E_{00}^{\text{t}} + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}}^2 E_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}''0}^{\text{t}} + \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}''0}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 E_{\mathbf{G}''0}^{\text{t}}] \\ \mathbb{S}_{\mathbf{G}\mathbf{G}}^* &= \xi_0 \partial_{\tilde{n}\tilde{n}^*}^2 E_{0\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 E_{0\mathbf{G}}^{\text{t}} + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}^*}^2 E_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}''\mathbf{G}}^{\text{t}} + \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}''\mathbf{G}}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 E_{\mathbf{G}''\mathbf{G}}^{\text{t}}] \\ \mathbb{S}_{\text{addadd}} &= \xi_0 \Omega^2 \end{aligned} \quad (8.77)$$

Let us now focus the discussion on the “adiabatic” constraints, *i.e.* $\sigma_{\mathbf{G}}$ for $\mathbf{G} \in [0, \mathbf{G}_{\text{max}}]$. We have that

$$\frac{\partial E(\mathbf{R}, \tilde{n})}{\partial \tilde{n}_{\mathbf{G}}^*} = \frac{\partial}{\partial \tilde{n}_{\mathbf{G}}^*} [E_{\text{KXC}} + E_{\text{PS}} + E_{\text{H}}] \quad (8.78)$$

where the Hartree energy E_{H} is defined by Eq. (8.19) in direct space and $E_{\text{KXC}} = E_{\text{K}} + E_{\text{XC}}$. The contribution to the expression $\sigma_{\mathbf{G}}$ arising from E_{PS} and E_{H} are given in Section 8.2 in reciprocal space (the gradient of the Hartree term with respect to the density coefficient in reciprocal space is given in Eq. (8.29); Eq. (8.37) yields the same quantity for the pseudopotential energy), so no further development of these terms is necessary. We also assume that the expression for the kinetic and exchange-correlation terms of the energy functional are provided by the library `lib_xc` in direct

space and in GGA approximation, so that we have

$$E_{\text{KXC}} = \frac{\Omega}{N_D} \sum_{\mathbf{r}} \epsilon_{\text{KXC}}(n(\mathbf{r}), \zeta(\mathbf{r})) n(\mathbf{r}) = \frac{\Omega}{N_D} \sum_{\mathbf{r}} \epsilon_{\text{KXC}}(\mathbf{r}) \quad (8.79)$$

where $\zeta(\mathbf{r}) = |\nabla n(\mathbf{r})|^2$ and $\epsilon_{\text{KXC}}(\mathbf{r})$ represents the energy per unit volume.² The contribution coming from E_{KXC} can be computed as

$$\begin{aligned} \frac{\partial E_{\text{KXC}}}{\partial \tilde{n}_{\mathbf{G}}^*} &= \delta \Omega_{\mathbf{G}} \sum_{\mathbf{r}} \frac{\partial \epsilon_{\text{KXC}}(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} = \delta \Omega_{\mathbf{G}} \sum_{\mathbf{r}} \left[\frac{\partial \epsilon_{\text{KXC}}(\mathbf{r})}{\partial n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} + \frac{\partial \epsilon_{\text{KXC}}(\mathbf{r})}{\partial \zeta(\mathbf{r})} \frac{\partial \zeta(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} \right] \\ &= \delta \Omega_{\mathbf{G}} \sum_{\mathbf{r}} \left[\frac{\partial n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} v_{\text{KXC}}^n(\mathbf{r}) + \frac{\partial \zeta(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} v_{\text{KXC}}^\zeta(\mathbf{r}) \right] \end{aligned} \quad (8.80)$$

where the derivatives of the kinetic-exchange-correlation kernel have been defined in Eqs. (8.45) and $\delta \Omega_{\mathbf{G}} = \Omega_{\mathbf{G}}/N_D$ (Eq. (8.38) defines $\Omega_{\mathbf{G}}$). The derivatives of $n(\mathbf{r})$ and $\zeta(\mathbf{r})$ with respect to the coefficients of the electronic density in reciprocal space can be computed easily using their definitions. From Eq. (8.11), we have for $n(\mathbf{r})$

$$\frac{\partial}{\partial \tilde{n}_{\mathbf{G}}^*} \left[\tilde{n}_0 + \sum_{\mathbf{G}' > 0} \left[\tilde{n}_{\mathbf{G}'} \exp[i\mathbf{G}' \cdot \mathbf{r}] + \tilde{n}_{\mathbf{G}'}^* \exp[-i\mathbf{G}' \cdot \mathbf{r}] \right] \right] = \exp[-i\mathbf{G} \cdot \mathbf{r}] \quad (8.81)$$

The derivative over the reduced gradient $\zeta(\mathbf{r})$ can be computed once again using the chain rule so that

$$\frac{\partial \zeta(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} = \frac{\partial \zeta(\mathbf{r})}{\partial \nabla n(\mathbf{r})} \cdot \frac{\partial \nabla n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} \quad (8.82)$$

where the gradient of the density can be computed in reciprocal space as

$$\nabla n(\mathbf{r}) = \sum_{\mathbf{G}' > 0} \left[\tilde{n}_{\mathbf{G}'} \exp[i\mathbf{G}' \cdot \mathbf{r}] i\mathbf{G}' - \tilde{n}_{\mathbf{G}'}^* \exp[-i\mathbf{G}' \cdot \mathbf{r}] i\mathbf{G}' \right] \quad (8.83)$$

Recalling the definition of $\zeta(\mathbf{r}) = |\nabla n(\mathbf{r})|^2$, Eq. (8.82) can be computed easily to give

$$\frac{\partial \zeta(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}}^*} = -2 \nabla n(\mathbf{r}) \cdot i\mathbf{G} \exp[-i\mathbf{G} \cdot \mathbf{r}] \quad (8.84)$$

²Note that lib_xc yields the energy *per particle* while its derivatives *per volume*. Introducing the energy *per volume* simplifies the following discussion.

Combining the two terms in Eqs. (8.81) and (8.84) we get

$$\begin{aligned} \frac{\partial E_{\text{KXC}}}{\partial \tilde{n}_{\mathbf{G}}^*} &= \delta \Omega_{\mathbf{G}} \sum_{\mathbf{r}} v_{\text{KXC}}^n(\mathbf{r}) \exp[-i\mathbf{G} \cdot \mathbf{r}] \\ &\quad - \delta \Omega_{\mathbf{G}} \left[2 \sum_{\mathbf{r}} v_{\text{KXC}}^{\zeta}(\mathbf{r}) \nabla n(\mathbf{r}) \exp[-i\mathbf{G} \cdot \mathbf{r}] \right] \cdot i\mathbf{G} \end{aligned} \quad (8.85)$$

Note that it is possible to recognize in the sums over direct space multiplied by the exponentials, the definition of the Fast Fourier Transform given in Eq. (8.9). The contribution to the “adiabatic” constraints arising from the kinetic-exchange-correlation energy term are given by

$$\frac{\partial E_{\text{KXC}}}{\partial \tilde{n}_{\mathbf{G}}^*} = \Omega_{\mathbf{G}} \left[\text{FFT} \left[v_{\text{KXC}}^n(\mathbf{r}) \right] - 2 \text{FFT} \left[v_{\text{KXC}}^{\zeta}(\mathbf{r}) \nabla n(\mathbf{r}) \right] \cdot i\mathbf{G} \right] \quad (8.86)$$

This expression, together with the expression obtained from the additional constraint (that applies only to the term $\mathbf{G} = 0$) and with the terms arising from E_{PS} and E_{H} , yields the expression for the constraints of the system in reciprocal space.

Let us now move to the expression of the second derivatives of the energy functional. Again, the contribution arising from the Hartree term has been discussed in Section 8.2 in reciprocal space (see in particular Eq. (8.30)) and does not need further development. The only other term which gives a contribution to the Hessian of the energy functional with respect to the electronic density is the kinetic-exchange-correlation term. Considering the expressions in Eq. (8.77) we need to compute the four possible combinations $\partial_{\tilde{n}^* \tilde{n}^*}^2 E_{\mathbf{G}' \mathbf{G}}$, $\partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}' \mathbf{G}}$, $\partial_{\tilde{n} \tilde{n}^*}^2 E_{\mathbf{G}' \mathbf{G}}$ and $\partial_{\tilde{n} \tilde{n}}^2 E_{\mathbf{G}' \mathbf{G}}$. We will focus on the first of these in what follows, as the other can be trivially deduced by it using complex conjugation rules. This is given by

$$\frac{\partial^2 E_{\text{KXC}}}{\partial \tilde{n}_{\mathbf{G}'}^* \partial \tilde{n}_{\mathbf{G}}^*} = \delta \Omega_{\mathbf{G}} \sum_{\mathbf{r}} \exp[-i\mathbf{G} \cdot \mathbf{r}] \left[\frac{\partial v_{\text{KXC}}^n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}'}^*} - 2i\mathbf{G} \cdot \frac{\partial (v_{\text{KXC}}^{\zeta}(\mathbf{r}) \nabla n(\mathbf{r}))}{\partial \tilde{n}_{\mathbf{G}'}^*} \right] \quad (8.87)$$

Let us compute separately the two derivatives appearing in the RHS of this last equation. The first term yields

$$\frac{\partial v_{\text{KXC}}^n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}'}^*} = \frac{\partial v_{\text{KXC}}^n(\mathbf{r})}{\partial n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}'}^*} + \frac{\partial v_{\text{KXC}}^n(\mathbf{r})}{\partial \zeta(\mathbf{r})} \frac{\partial \zeta(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}'}^*} \quad (8.88)$$

The same calculations performed for the first derivative of the energy functional, in particular Eqs. (8.81) and (8.84), and the definition of the second derivative of the kinetic-exchange-correlation kernel in Eq. (8.46) yield, in this case,

$$\frac{\partial v_{\text{KXC}}^n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}'}^*} = \left[f_{\text{KXC}}^{nn}(\mathbf{r}) - 2f_{\text{KXC}}^{n\zeta}(\mathbf{r}) \nabla n(\mathbf{r}) \cdot i\mathbf{G}' \right] \exp[-i\mathbf{G}' \cdot \mathbf{r}] \quad (8.89)$$

The second term of the RHS of Eq. (8.87) is computed component by component. Indicating by $\partial_\alpha n(\mathbf{r})$ with $\alpha \in \{x, y, z\}$ a cartesian component of the vector $\nabla n(\mathbf{r})$, the second term in Eq. (8.87) can be expanded as

$$\frac{\partial (v_{\text{KXC}}^\zeta(\mathbf{r}) \partial_\alpha n(\mathbf{r}))}{\partial \tilde{n}_{\mathbf{G}'}^*} = \frac{\partial \partial_\alpha n(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}'}^*} v_{\text{KXC}}^\zeta(\mathbf{r}) + \frac{\partial v_{\text{KXC}}^\zeta(\mathbf{r})}{\partial \tilde{n}_{\mathbf{G}'}^*} \partial_\alpha n(\mathbf{r}) \quad (8.90)$$

The derivative of $v_{\text{KXC}}^\zeta(\mathbf{r})$ takes the same form of Eq. (8.89) with ζ in place of the first superscript n . The derivative of the gradient can be computed from the definition in Eq. (8.83). Together, the two substitutions yield

$$\begin{aligned} \frac{\partial (v_{\text{KXC}}^\zeta(\mathbf{r}) \partial_\alpha n(\mathbf{r}))}{\partial \tilde{n}_{\mathbf{G}'}^*} = \exp[-i\mathbf{G}' \cdot \mathbf{r}] & \left[-iG'_\alpha v_{\text{KXC}}^\zeta(\mathbf{r}) \right. \\ & \left. + \partial_\alpha n(\mathbf{r}) \left[f_{\text{KXC}}^{\zeta n}(\mathbf{r}) - 2f_{\text{KXC}}^{\zeta\zeta}(\mathbf{r}) \partial_\beta n(\mathbf{r}) iG'_\beta \right] \right] \end{aligned} \quad (8.91)$$

where summation is assumed on multiplied repeated greek indexes. Eqs. (8.89) and (8.91) can now be substituted in Eq. (8.87) to obtain the expression of the second derivative of the energy with respect to the (conjugate) coefficients of the density. This is given by

$$\begin{aligned} \frac{\partial^2 E_{\text{KXC}}}{\partial \tilde{n}_{\mathbf{G}'}^* \partial \tilde{n}_{\mathbf{G}}^*} = \delta \Omega_{\mathbf{G}} \sum_{\mathbf{r}} \exp[-i\mathbf{G}' \cdot \mathbf{r}] \exp[-i\mathbf{G} \cdot \mathbf{r}] \\ \times \left[f_{\text{KXC}}^{nn}(\mathbf{r}) - 2i\partial_\alpha n(\mathbf{r}) (G'_\alpha + G_\alpha) f_{\text{KXC}}^{n\zeta}(\mathbf{r}) \right. \\ \left. - 2G'_\alpha G_\beta (v_{\text{KXC}}^\zeta(\mathbf{r}) \delta_{\alpha\beta} + 2\partial_\alpha n(\mathbf{r}) \partial_\beta n(\mathbf{r}) f_{\text{KXC}}^{\zeta\zeta}(\mathbf{r})) \right] \end{aligned} \quad (8.92)$$

The other three terms can be trivially derived from the one in Eq. (8.92) exploiting the complex conjugacy in the derivatives with respect to plane-waves.

Let us now introduce the functions

$$\begin{aligned}\Xi(\mathbf{r}) &\equiv f_{\text{KXC}}^{mn}(\mathbf{r}) \\ \Phi_\alpha(\mathbf{r}) &\equiv 2\partial_\alpha n(\mathbf{r})f_{\text{KXC}}^{n\zeta}(\mathbf{r}) \\ \Psi_{\alpha\beta}(\mathbf{r}) &\equiv 2(v_{\text{KXC}}^\zeta(\mathbf{r})\delta_{\alpha\beta} + 2\partial_\alpha n(\mathbf{r})\partial_\beta n(\mathbf{r})f_{\text{KXC}}^{\zeta\zeta}(\mathbf{r}))\end{aligned}\quad (8.93)$$

in terms of which the components $\mathbf{G} \neq 0$ of the SHAKE denominator in Eq. (8.77) take the form

$$\begin{aligned}&\xi_0 \partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_0^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_0^{\text{t}} + \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} [\partial_{\tilde{n}\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''}^{\text{P}} \partial_{\tilde{n}^*\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''}^{\text{t}} + \partial_{\tilde{n}^*\tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}''}^{\text{P}} \partial_{\tilde{n}\tilde{n}}^2 \mathcal{E}_{\mathbf{G}''}^{\text{t}}] \\ &= \delta\Omega^2 \xi_0 \sum_{\mathbf{r}, \mathbf{r}'} e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}'} [\Xi^{\text{P}}(\mathbf{r}) - iG_\alpha \Phi_\alpha^{\text{P}}(\mathbf{r})] [\Xi^{\text{t}}(\mathbf{r}') + iG_\alpha \Phi_\alpha^{\text{t}}(\mathbf{r}')] \\ &+ \delta\Omega^2 \sum_{\mathbf{r}, \mathbf{r}'} e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}'} \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} e^{i\mathbf{G}''\cdot\mathbf{r}} e^{-i\mathbf{G}''\cdot\mathbf{r}'} \\ &\quad \times [\Xi^{\text{P}}(\mathbf{r}) + i(G_\alpha'' - G_\alpha) \Phi_\alpha^{\text{P}}(\mathbf{r}) + G_\alpha'' G_\beta \Psi_{\alpha\beta}^{\text{P}}(\mathbf{r})] \\ &\quad \times [\Xi^{\text{t}}(\mathbf{r}') - i(G_\alpha'' - G_\alpha) \Phi_\alpha^{\text{t}}(\mathbf{r}') + G_\alpha'' G_\beta \Psi_{\alpha\beta}^{\text{t}}(\mathbf{r}')] \\ &+ \delta\Omega^2 \sum_{\mathbf{r}, \mathbf{r}'} e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}'} \sum_{\mathbf{G}'' > 0} \xi_{\mathbf{G}''} e^{-i\mathbf{G}''\cdot\mathbf{r}} e^{i\mathbf{G}''\cdot\mathbf{r}'} \\ &\quad \times [\Xi^{\text{P}}(\mathbf{r}) - i(G_\alpha'' + G_\alpha) \Phi_\alpha^{\text{P}}(\mathbf{r}) - G_\alpha'' G_\beta \Psi_{\alpha\beta}^{\text{P}}(\mathbf{r})] \\ &\quad \times [\Xi^{\text{t}}(\mathbf{r}') + i(G_\alpha'' + G_\alpha) \Phi_\alpha^{\text{t}}(\mathbf{r}') - G_\alpha'' G_\beta \Psi_{\alpha\beta}^{\text{t}}(\mathbf{r}')] \end{aligned}\quad (8.94)$$

It is possible to simplify the numerical calculation of this complicated expression exploiting periodicity in direct space. In this way, the numerical complexity for computing the SHAKE denominator can be made to scale linearly with N_{R} . Let us consider the first summation over $\mathbf{G}''$ of Eq. (8.94). Each term derived from the multiplication between the expressions in square brackets can be written in the form

$$h_1^{mn}(\mathbf{G}) = \sum_{\mathbf{r}, \mathbf{r}'} \sum_{\mathbf{G}'' > 0} \xi(\mathbf{G}'') e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}''\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}'} e^{-i\mathbf{G}''\cdot\mathbf{r}'} (iG_\alpha'')^m (iG_\beta'')^n f(\mathbf{r}) g(\mathbf{r}') \quad (8.95)$$

where $m, n = 0, 1$. The function $f(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}e^{i\mathbf{G}''\cdot\mathbf{r}}$ is periodic in $\mathbf{r}$ with period $\mathbf{L}$. It is therefore possible to reorder the sum so to have

$$\begin{aligned} h_1^{mn}(\mathbf{G}) &= \sum_{\mathbf{r}=0}^{\mathbf{L}} \sum_{\mathbf{r}'=0}^{\mathbf{L}} \sum_{\mathbf{G}''>0} \xi(\mathbf{G}'') e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}''\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}'} e^{-i\mathbf{G}''\cdot\mathbf{r}'} (iG''_{\alpha})^m (iG''_{\beta})^n f(\mathbf{r}) g(\mathbf{r}') \\ &= \sum_{\mathbf{r}=\mathbf{r}'}^{\mathbf{L}+\mathbf{r}'} \sum_{\mathbf{r}'=0}^{\mathbf{L}} \sum_{\mathbf{G}''>0} \xi(\mathbf{G}'') e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}''\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}'} e^{-i\mathbf{G}''\cdot\mathbf{r}'} (iG''_{\alpha})^m (iG''_{\beta})^n f(\mathbf{r}) g(\mathbf{r}') \end{aligned} \quad (8.96)$$

The substitution $\mathbf{r} = \mathbf{r}' + \mathbf{r}''$ yields

$$\begin{aligned} h_1^{mn}(\mathbf{G}) &= \sum_{\mathbf{r}''=0}^{\mathbf{L}} \sum_{\mathbf{r}'=0}^{\mathbf{L}} \sum_{\mathbf{G}''>0} \xi(\mathbf{G}'') e^{-i\mathbf{G}\cdot(\mathbf{r}'+\mathbf{r}'')} e^{i\mathbf{G}''\cdot(\mathbf{r}'+\mathbf{r}'')} e^{i\mathbf{G}\cdot\mathbf{r}'} e^{-i\mathbf{G}''\cdot\mathbf{r}'} \\ &\quad \times (iG''_{\alpha})^m (iG''_{\beta})^n f(\mathbf{r}' + \mathbf{r}'') g(\mathbf{r}') \\ &= \sum_{\mathbf{r}, \mathbf{r}''} \sum_{\mathbf{G}''>0} \xi(\mathbf{G}'') e^{-i\mathbf{G}\cdot\mathbf{r}''} e^{i\mathbf{G}''\cdot\mathbf{r}''} (iG''_{\alpha})^m (iG''_{\beta})^n f(\mathbf{r}' + \mathbf{r}'') g(\mathbf{r}') \end{aligned} \quad (8.97)$$

The terms in Eq. (8.97) can now be rearranged to obtain

$$h_1^{mn}(\mathbf{G}) = \sum_{\mathbf{r}''} e^{-i\mathbf{G}\cdot\mathbf{r}''} \left[\left(\sum_{\mathbf{G}''>0} e^{i\mathbf{G}''\cdot\mathbf{r}''} \xi(\mathbf{G}'') (iG''_{\alpha})^m (iG''_{\beta})^n \right) \left(\sum_{\mathbf{r}'} g(\mathbf{r}') f(\mathbf{r}' + \mathbf{r}'') \right) \right] \quad (8.98)$$

where it is possible to recognize in the last term of Eq. (8.98) the spatial correlation function $C_{gf}(\mathbf{r}'')$.

Let us now take into account the second summation over $\mathbf{G}''$ of Eq. (8.94). Retracing the same steps it is possible to obtain, for the corresponding terms in the sum

$$h_2^{mn}(\mathbf{G}) = \sum_{\mathbf{r}''} e^{-i\mathbf{G}\cdot\mathbf{r}''} \left[\left(\sum_{\mathbf{G}''>0} e^{-i\mathbf{G}''\cdot\mathbf{r}''} \xi(\mathbf{G}'') (-iG''_{\alpha})^m (-iG''_{\beta})^n \right) C_{gf}(\mathbf{r}'') \right] \quad (8.99)$$

Finally, the term $\mathbf{G}'' = 0$ is of the form

$$h_0^{mn}(\mathbf{G}) = \xi(0) \sum_{\mathbf{r}, \mathbf{r}'} e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}'} f(\mathbf{r}) g(\mathbf{r}') = \xi(0) \sum_{\mathbf{r}''} e^{-i\mathbf{G}\cdot\mathbf{r}''} C_{gf}(\mathbf{r}'') \delta_{m0} \delta_{n0} \quad (8.100)$$

Therefore, each term of Eq. (8.94) can be written as

$$h_0^{mn}(\mathbf{G}) + h_1^{mn}(\mathbf{G}) + h_2^{mn}(\mathbf{G}) = \sum_{\mathbf{r}''} C_{gf}(\mathbf{r}'') e^{-i\mathbf{G} \cdot \mathbf{r}''} \left[\xi(0) \delta_{m0} \delta_{n0} + \sum_{\mathbf{G}'' > 0} \xi(\mathbf{G}'') \left((iG''_\alpha)^m (iG''_\beta)^n e^{i\mathbf{G}'' \cdot \mathbf{r}''} + (-iG''_\alpha)^m (-iG''_\beta)^n e^{-i\mathbf{G}'' \cdot \mathbf{r}''} \right) \right] \quad (8.101)$$

It is now possible to rewrite the expression using the operation of Fast Fourier Transforms. First it is possible to recognize in the term in square brackets the definition of the inverse FFT given in Eq. (8.10). Moreover, the convolution theorem yields an expression for the correlation function in terms of direct and inverse Fourier transforms. With the definitions for the FFT and its inverse given in Eqs. (8.9) and (8.10) we obtain

$$C_{gf}(\mathbf{r}'') = \sum_{\mathbf{r}'} g(\mathbf{r}') f(\mathbf{r}' + \mathbf{r}'') = N_D \text{iFFT} [\text{FFT}[g]^* \text{FFT}[f]] \quad (8.102)$$

Finally the sum over $\mathbf{r}''$ times the exponential can be recognized as another direct FFT times the size of the direct grid. Each term can then be written as

$$h_0^{mn}(\mathbf{G}) + h_1^{mn}(\mathbf{G}) + h_2^{mn}(\mathbf{G}) = N_D^2 \text{FFT} \left[\left(\text{iFFT} [\xi(\mathbf{G}'') (iG''_\alpha)^m (iG''_\beta)^n] \right) \left(\text{iFFT} [\text{FFT}[g]^* \text{FFT}[f]] \right) \right] \quad (8.103)$$

Note that Eq. (8.103) yields already the whole function in reciprocal space, not just the single element. This means that the computation is reduced to a number of $O(N_D \log N_D)$ operations equal to the number of terms of the form of the LHS of Eq. (8.103).

Once the denominator is computed, the Lagrange multipliers γ can be obtained and the updated coefficients of the density in reciprocal space are calculated through Eq. (8.60). This operation is, in principle, a matrix vector multiplication with a cost in terms of operations of order N_D^2 . However, in the next section it will be proved how Fast Fourier Transforms can once again be exploited to obtain the result with $O(N_D \log N_D)$ operations and $O(N_R)$ memory resources.

8.4.2 Linear-Scaling Computation of Updated Density Coefficients

The starting point for the discussion on the computation of the updated coefficients of the density are Eqs. (8.61). First, let us consider the additional constraint term, specifying the discussion to the particular form in Eq. (8.75). Just like the computation of the SHAKE denominator, all the derivatives of the additional constraint with respect to $\mathbf{G} \neq 0$ vanish, while the derivative with respect to $\mathbf{G} = 0$ yields $\partial_{\tilde{n}\mathbf{v}}^2 \mathcal{E}_{\text{add}} = \Omega$. For the same reason, the derivatives of the “adiabatic” constraints $\sigma_{\mathbf{G}}$ with respect to the additional Lagrange multipliers $\mathbf{v}$ vanish for $\mathbf{G} \neq 0$, while $\partial_{\mathbf{v}\tilde{n}}^2 \mathcal{E}_{\text{add}} = \Omega$. For all the other terms, we have the relation $\partial_{\tilde{n}^* \tilde{n}^*}^2 \mathcal{E}_{\mathbf{G}\mathbf{G}'} = \partial_{\tilde{n}^* \tilde{n}^*}^2 E_{\mathbf{G}\mathbf{G}'}$. With this in mind, it is easy to see that the equations for the update of the additional degrees of freedom $\tilde{n}, \mathbf{v}$ are given by

$$\begin{aligned} \delta \tilde{n}_0 &= -\gamma_0 \xi_0 \partial_{\tilde{n}\tilde{n}}^2 E_{00}^t - \gamma_{\text{add}} \xi_0 \Omega - \xi_0 \sum_{\mathbf{G}' > 0} [\gamma_{\mathbf{G}'} \partial_{\tilde{n}\tilde{n}^*}^2 E_{0\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}\tilde{n}}^2 E_{0\mathbf{G}'}^t] \\ \delta \tilde{n}_{\mathbf{G}} &= \gamma_0 \xi_{\mathbf{G}} \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}0}^t + \xi_{\mathbf{G}} \sum_{\mathbf{G}' > 0} [\gamma_{\mathbf{G}'} \partial_{\tilde{n}^* \tilde{n}^*}^2 E_{\mathbf{G}\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}\mathbf{G}'}^t] \\ \delta \mathbf{v} &= \gamma_0 \kappa \Omega \end{aligned} \quad (8.104)$$

where $\mathbf{G} > 0$. Let us consider the generic term $\delta \tilde{n}_{\mathbf{G}}$ for $\mathbf{G} \in [0, \mathbf{G}_{\text{max}}]$ without the terms arising from the additional constraint and from the Hartree energy which are both diagonal and will be trivially taken into account later. The only nondiagonal term in reciprocal space is the one derived from E_{KXC} and therefore we will focus on this one. Exploiting the results for the second derivative of E_{KXC} with respect to the electronic density together with the definitions in Eq. (8.93) we get

$$\begin{aligned} \delta \tilde{n}_{\mathbf{G}} &= \gamma_0 \xi_{\mathbf{G}} \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}0}^t + \xi_{\mathbf{G}} \sum_{\mathbf{G}' > 0} [\gamma_{\mathbf{G}'} \partial_{\tilde{n}^* \tilde{n}^*}^2 E_{\mathbf{G}\mathbf{G}'}^t + \gamma_{\mathbf{G}'}^* \partial_{\tilde{n}^* \tilde{n}}^2 E_{\mathbf{G}\mathbf{G}'}^t] \\ &= \delta \Omega \gamma_0 \xi_{\mathbf{G}} \sum_{\mathbf{r}} e^{-i\mathbf{G} \cdot \mathbf{r}} [\Xi(\mathbf{r}) - iG_{\alpha} \Phi_{\alpha}(\mathbf{r})] + \delta \Omega \xi_{\mathbf{G}} \\ &\quad \times \sum_{\mathbf{G}' > 0} \left[\gamma_{\mathbf{G}'} \sum_{\mathbf{r}} e^{-i\mathbf{G} \cdot \mathbf{r}} e^{-i\mathbf{G}' \cdot \mathbf{r}} [\Xi(\mathbf{r}) - i(G_{\alpha} + G'_{\alpha}) \Phi_{\alpha}(\mathbf{r}) - G_{\alpha} G'_{\beta} \Psi_{\alpha\beta}(\mathbf{r})] \right. \\ &\quad \left. + \gamma_{\mathbf{G}'}^* \sum_{\mathbf{r}} e^{-i\mathbf{G} \cdot \mathbf{r}} e^{i\mathbf{G}' \cdot \mathbf{r}} [\Xi(\mathbf{r}) - i(G_{\alpha} - G'_{\alpha}) \Phi_{\alpha}(\mathbf{r}) + G_{\alpha} G'_{\beta} \Psi_{\alpha\beta}(\mathbf{r})] \right] \end{aligned} \quad (8.105)$$

Rearranging terms and summations we have that

$$\begin{aligned}
\delta \tilde{n}_{\mathbf{G}} = & \delta \Omega \xi_{\mathbf{G}} \left\{ \sum_{\mathbf{r}} \Xi(\mathbf{r}) \sum_{\mathbf{G}' > 0} \left[\gamma_0 + \gamma_{\mathbf{G}'} e^{-i\mathbf{G}' \cdot \mathbf{r}} + \gamma_{\mathbf{G}'}^* e^{i\mathbf{G}' \cdot \mathbf{r}} \right] e^{-i\mathbf{G} \cdot \mathbf{r}} \right. \\
& - iG_{\alpha} \sum_{\mathbf{r}} \Phi_{\alpha}(\mathbf{r}) \sum_{\mathbf{G}' > 0} \left[\gamma_0 + \gamma_{\mathbf{G}'} e^{-i\mathbf{G}' \cdot \mathbf{r}} + \gamma_{\mathbf{G}'}^* e^{i\mathbf{G}' \cdot \mathbf{r}} \right] e^{-i\mathbf{G} \cdot \mathbf{r}} \\
& + \sum_{\mathbf{r}} \Phi_{\alpha}(\mathbf{r}) \sum_{\mathbf{G}' > 0} \left[(-iG'_{\alpha}) \gamma_{\mathbf{G}'} e^{-i\mathbf{G}' \cdot \mathbf{r}} + (iG'_{\alpha}) \gamma_{\mathbf{G}'}^* e^{i\mathbf{G}' \cdot \mathbf{r}} \right] e^{-i\mathbf{G} \cdot \mathbf{r}} \\
& \left. - iG_{\alpha} \sum_{\mathbf{r}} \Psi_{\alpha\beta}(\mathbf{r}) \sum_{\mathbf{G}' > 0} \left[(-iG'_{\beta}) \gamma_{\mathbf{G}'} e^{-i\mathbf{G}' \cdot \mathbf{r}} + (iG'_{\beta}) \gamma_{\mathbf{G}'}^* e^{i\mathbf{G}' \cdot \mathbf{r}} \right] e^{-i\mathbf{G} \cdot \mathbf{r}} \right\}
\end{aligned} \tag{8.106}$$

Fast Fourier Transforms can once again be exploited to obtain

$$\begin{aligned}
\delta \tilde{n}_{\mathbf{G}} = & \delta \Omega \xi_{\mathbf{G}} \left\{ \text{FFT} \left[\Xi(\mathbf{r}) \text{iFFT}[\gamma^*] + \Phi_{\alpha}(\mathbf{r}) \text{iFFT}[iG'_{\alpha} \gamma^*] \right] \right. \\
& \left. - iG_{\alpha} \text{FFT} \left[\Phi_{\alpha}(\mathbf{r}) \text{iFFT}[\gamma^*] + \Psi_{\alpha\beta}(\mathbf{r}) \text{iFFT}[iG'_{\beta} \gamma^*] \right] \right\}
\end{aligned} \tag{8.107}$$

Again, just like the SHAKE denominator case, this relation yields the whole vector $\delta \tilde{n}$, not just the single elements, so that the computational burden is of order $N_D \log N_D$.

8.5 Simulation Results

The accuracy and efficiency of the mass-zero constrained dynamics in the framework of orbital-free DFT are demonstrated in this section in a proof-of-principle calculation of a Sodium crystal. The equations derived in the previous section have been implemented in a specifically-designed in-house, nonparallel code. The software is written in C and adheres to best practices such as modularization, basic optimization, clear documentation. The code is publicly available on the [E-CAM software repository](#) and it has been used to produce the simulations discussed in this section. The results presented here considerably extend the tests discussed in Chapter 7 on classical force-field-based simulations in terms of system size, with the number of the auxiliary variables now ranging between 10^4 and 10^5 and with up to 2000 ions.

The calculations discussed in the following are inspired by the numerical experiments performed by Pearson *et al.* in [181] when they first proposed orbital-free

DFT. However, since our goal is to present a case study to assess the potential of mass-zero constrained dynamics for *ab initio* simulations and not to provide an accurate description of solid Sodium, we consider a simpler model, sufficient for our purposes, that adopts the Thomas-Fermi approximation for the kinetic energy [186] together with Slater functional for the exchange energy [191]. We also consider explicitly only the valence electrons so that their interaction energy with the Na^+ ions is effectively defined through a local pseudopotential. This pseudopotential is chosen to be a Gaussian function within a core radius r_c and the exact Coulomb potential outside this core region

$$v_{PP}(r) = \begin{cases} -V_0 \exp(-\frac{r^2}{2\sigma^2}) & \text{for } r \leq r_c \\ -\frac{1}{r} & \text{for } r > r_c. \end{cases} \quad (8.108)$$

V_0 and σ were adjusted such that $v_{PP}(r)$ and its first derivative are continuous at $r = r_c$. This pseudopotential thus depends on the single parameter r_c that was set to the value indicated by Topp and Hopfield to represent Na atoms [192], $r_c = 1.58 \text{ \AA}$. This choice of pseudopotential is less refined than more recent proposals for orbital-free DFT [193, 194], mainly because it lacks a repulsive core. However, such feature would lead to pathologies when used with the simple Thomas-Fermi kinetic energy functional adopted here and its absence is not significant for testing the effectiveness of the mass-zero constrained method.

The mass-zero constrained method was implemented using the SHAKE algorithm as described in Sections 6.4 and 6.6 in general and in Section 8.4 in the context of orbital-free DFT. To provide a reference, in the following we compare the performance and the results attained *via* the mass-zero constrained algorithm with those obtained using minimization *via* a line-search nonlinear conjugate-gradient algorithm [112, 119]. Conjugate-gradient minimizations were performed at fixed $\tilde{n}(0)$. Convergence, for both algorithms, was monitored calculating $\|\sigma\|_\infty$ at each iteration. Note that, due to the different way of treating the additional condition, the vectors σ have different dimensions for the two methods. For the mass-zero constrained dynamics, in fact, $\sigma \in \mathbb{R}^{N_R+1}$, the Lagrange multiplier v being an additional dynamical variable for the system, while for the conjugate-gradient minimizations $\sigma \in \mathbb{R}^{N_R-1}$ as $\tilde{n}(0)$ is not part of the dynamics. In the following, we indicate by tolerance the maximum value of $\|\sigma\|_\infty$ allowed in the different runs. Timings in

the comparisons are reported for single core computation on a AMD Opteron 6376 CPU.

To begin with, we consider a system of $N = 250$ Na atoms in a cubic supercell of side $L = 15.88 \text{ \AA}$ evolved for about 1 ps (2500 steps with a timestep of 0.4 fs) at constant energy and volume. A typical snapshot of the simulated system is reported in Figure 8.1. The cutoff for the plane-waves expansion was set to $\frac{G_c^2}{2} = 5 E_h$. Electrostatic interactions were treated using Ewald sums, with a cutoff for the Sodium atoms equal to $R_c = 1.06 \text{ \AA}$. In the comparative runs, the mass-zero constrained algorithm and the conjugate gradient used the same initial conditions for all degrees of freedom. The ions were placed on the sites of a BCC lattice, with initial velocities sampled from a Maxwell-Boltzmann distribution at temperature $T = 50 \text{ K}$. Initial values for the auxiliary variables were determined as follows. A set of $\tilde{n}_{\mathbf{G}}$ was calculated *via* analytic Fourier transform from a first guess for the electronic density in real space as a superposition of Gaussians of charge $-e$ centered at the ionic positions and with variance equal to the pseudopotential cutoff radius. The initial value of $v = 0$ was also assigned. These values were used as the input for a highly converged minimization of the energy functional yielding the values for $\tilde{n}(\mathbf{G})$ and v at $t = 0$.

The free scaling parameter $\kappa = \mu_v / \mu_n$, introduced in the dynamical system to enforce a homogeneous adiabatic limit on all degrees of freedom, $\tilde{n}(\mathbf{G})$ and v , was chosen by dimensional analysis and by the requirement of being independent of the system size, as $\tilde{n}(\mathbf{G})$ and v are intensive variables (density and chemical potential). This leads to the observation that $\sqrt{\kappa}$ has to be the product of a typical energy times a typical volume, which suggests a typical value for $\sqrt{\kappa}$ given by $\sqrt{\kappa} = \frac{E\Omega}{N_{\text{el}}^2}$ where E is the typical energy of the system. The factor N_{el}^{-2} is used to enforce the intensivity of this quantity. We explored different values for κ using the typical energy per electron and typical volume per electron as initial guess, which, for our simulation set up, leads to $\sqrt{\kappa} \approx 200$. Our tests show that, while small values of this parameter lead to a loss in efficiency, all results presented below are nearly insensitive to the specific choice for $\sqrt{\kappa}$ in a broad range of values, typically $\sqrt{\kappa} > 100$, and independent of the system size.

We start by demonstrating, looking at two basic quantities, that the two methods employed generate the same observables. In these calculations, tolerance was set to 10^{-10} for both the mass-zero and conjugate-gradient runs. In Figure 8.2 the

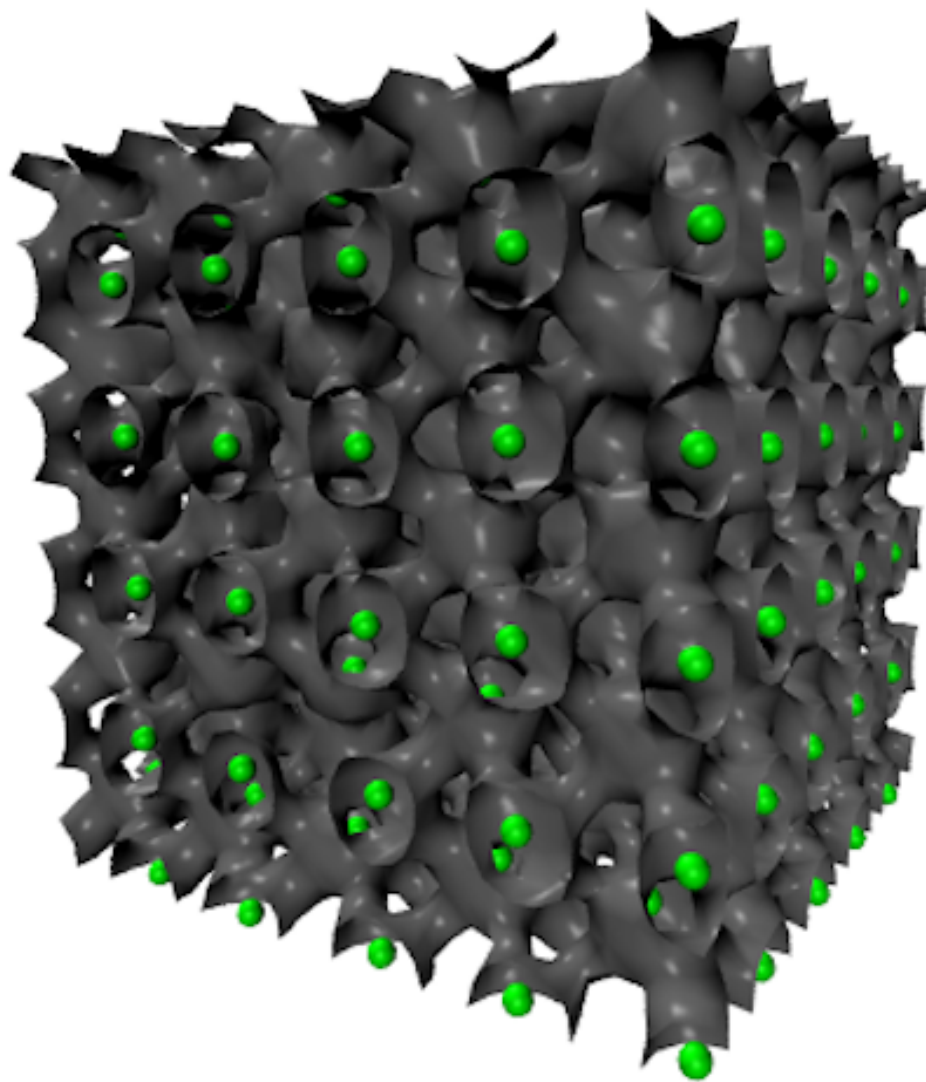


Fig. 8.1 Typical snapshot of solid Sodium with orbital-free DFT.

instantaneous kinetic energy, or temperature, of the system during the simulation is shown for the nonlinear conjugate-gradient algorithm (blue curve) and the mass-zero constraints algorithm (red curve). The curves are exactly superposed strongly

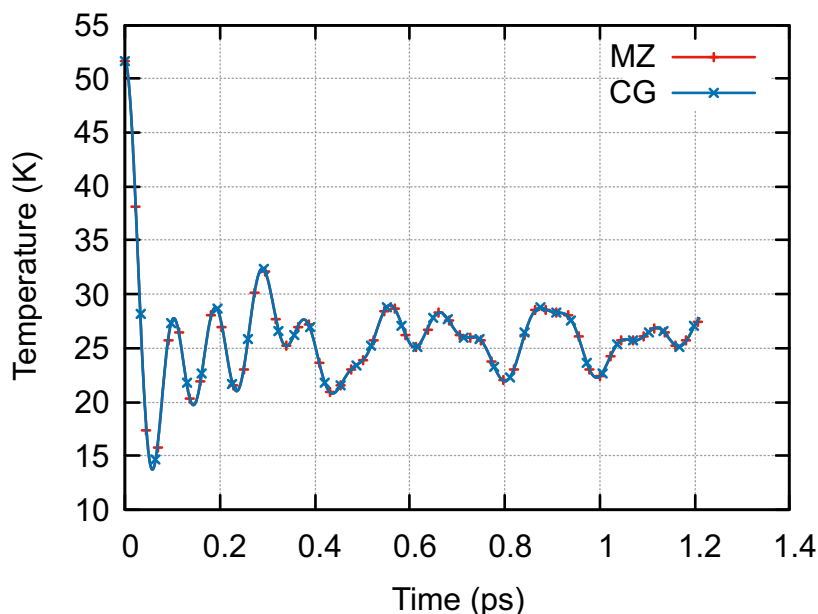


Fig. 8.2 Temperature of the system for nonlinear conjugate gradient (CG, blue curve with symbols) and mass-zero constrained (MZ, red curve with symbols) molecular dynamics runs of orbital-free DFT solid sodium. The tolerance was set to 10^{-10} in both runs of (equal) length of 2500 steps.

suggesting not only that the samplings performed *via* the two trajectories are fully compatible, but also that the generated dynamics are identical. Figure 8.3, on the other hand, displays the difference between the energy and its mean value along the run for both methods (same color code as in the previous figure). Also in this case the mass-zero results are superimposed to the conjugate-gradient reference and the very small fluctuations are dominated by the propagation error of the Verlet algorithm. The fluctuations of the total energy with respect to the ones of the electronic ground state energy $\Delta E_{\text{tot}}/\Delta \mathcal{E}$, where $\Delta X = \sqrt{\langle X^2 \rangle - \langle X \rangle^2}$, are of the order of 10^{-5} .

While the results obtained *via* the two algorithms are essentially indistinguishable, the mass-zero constrained algorithm is more efficient than its counterpart. In Table 8.1, we report data for different values of the tolerance for the two algorithms. The mass-zero constrained algorithm performs better for all tolerances both in terms of average number of iterations for convergence and of time of a single iteration.

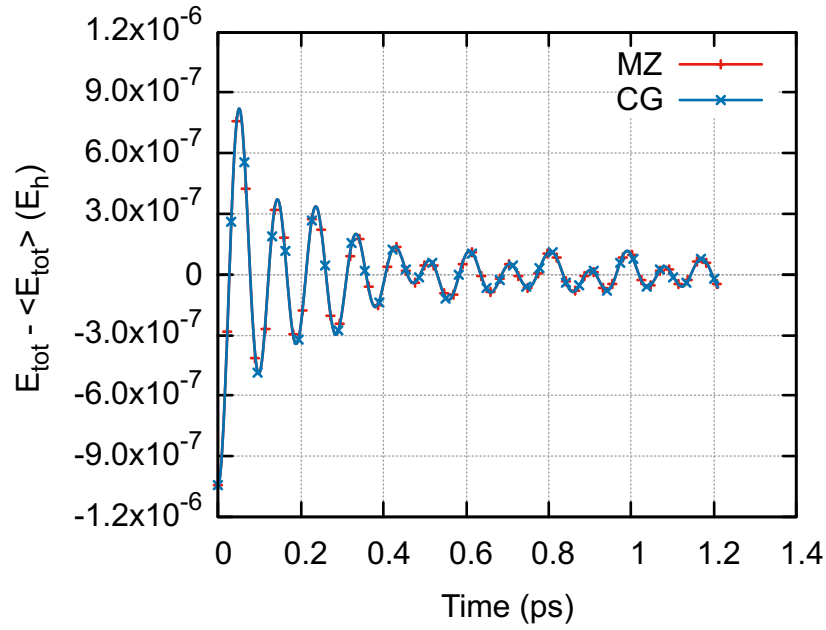


Fig. 8.3 Difference between the instantaneous energy estimator and the average value of the energy as a function of time for the nonlinear conjugate gradient (CG) and the mass-zero constrained (MZ) dynamics algorithms. Color coding and tolerance as in Figure 8.2.

Table 8.1 Comparison between the performances of the two algorithms to compute the electronic density. The nonlinear conjugate gradient is labeled with CG and the mass zero constrained dynamics with MZ. The first column indicates the different values of the tolerance tested. In the third and fourth column the average number of iterations and the average time to converge per timestep are reported, respectively. The CG method implemented in the code did not converge for tolerance smaller than 10^{-10} as indicated by the symbol “/”.

Tolerance	Algorithm	Average Iterations	Time to Converge (s)
10^{-4}	CG	16.9	4.51
10^{-4}	MZ	1.01	0.0941
10^{-6}	CG	24.7	6.49
10^{-6}	MZ	1.16	0.100
10^{-8}	CG	33.0	8.66
10^{-8}	MZ	2.17	0.161
10^{-10}	CG	40.5	10.6
10^{-10}	MZ	3.25	0.193
10^{-12}	CG	/	/
10^{-12}	MZ	6.21	0.325

For example, the tolerance 10^{-8} , which is often considered satisfactory in applications, is achieved with only two iterations with respect to the about 30 needed by the conjugate gradient. Furthermore, the SHAKE based algorithm is able to reach tighter convergence parameters maintaining, in particular, a very good speed of convergence even for the 10^{-12} tolerance which essentially coincides with the attainable numerical precision and where conjugate gradient fails to converge.

To further validate the efficiency of the mass-zero constrained algorithm, we show in Figure 8.4 some randomly picked paths to convergence for the two methods. The figure shows in red (blue) the maximum of the residue as a function of the

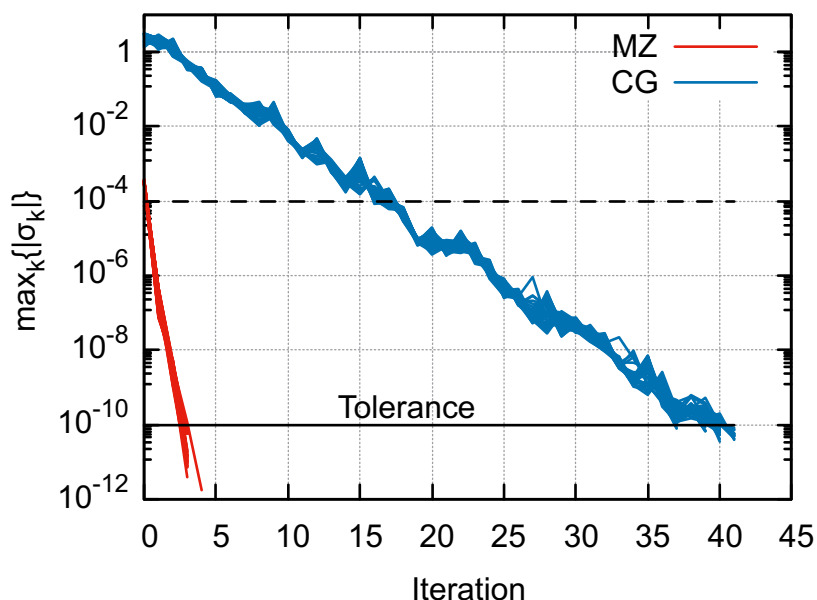


Fig. 8.4 Tolerance vs. number of iteration for convergence paths at randomly chosen steps during the simulations adopting the two methods used to compute the electronic density. The solid blue line shows the path to convergence for nonlinear conjugate-gradient procedure (CG). In solid red lines the mass zero constrained algorithm (MZ). The dashed line indicates a typical value of $\max_k |\sigma_k(R, \tilde{n}, v)|$ at the beginning of the iterative process for MZ.

iteration step for mass-zero (conjugate gradient) for the same ionic configuration. The mass-zero constrained method efficiently approaches convergence *via* an essentially exponential convergence, as visible from the slopes of the curves in Figure 8.4, and reaches the 10^{-10} threshold in about 3 or 4 iterations. In contrast, the convergence of the conjugate gradient method is nonmonotonous and the algorithm needs up to 40 iterations to reach the same tight tolerance. Note also that for the mass-zero constrained method, already the initial point (no iterations) is closer to convergence

compared to the conjugate gradient. In fact, the SHAKE algorithm includes a dynamical step that generates a first guess for the iterative loop using values of the auxiliary variables and Lagrange multipliers computed at previous steps [195]. The conjugate-gradient method, on the other hand, uses as initial guess simply the value of the auxiliary variables at the previous step. The structure of this first guess is an important feature of the SHAKE algorithm whose advantages are clear from Figure 8.4. Strikingly, however, the figure also suggests that even if we were to improve the conjugate-gradient method by extrapolating an initial guess to the same accuracy as SHAKE, *i.e.* starting at the threshold identified by the dashed line, conjugate gradient would still need about 20 iterations to reach convergence against the 3 (on average) required by the mass-zero constrained algorithm.

To provide a demonstration of the conditioned minimization within the mass-zero constrained algorithm, a convergence path for the additional condition to be enforced — fixed number of electrons — is shown in Figure 8.5. The total number of electrons

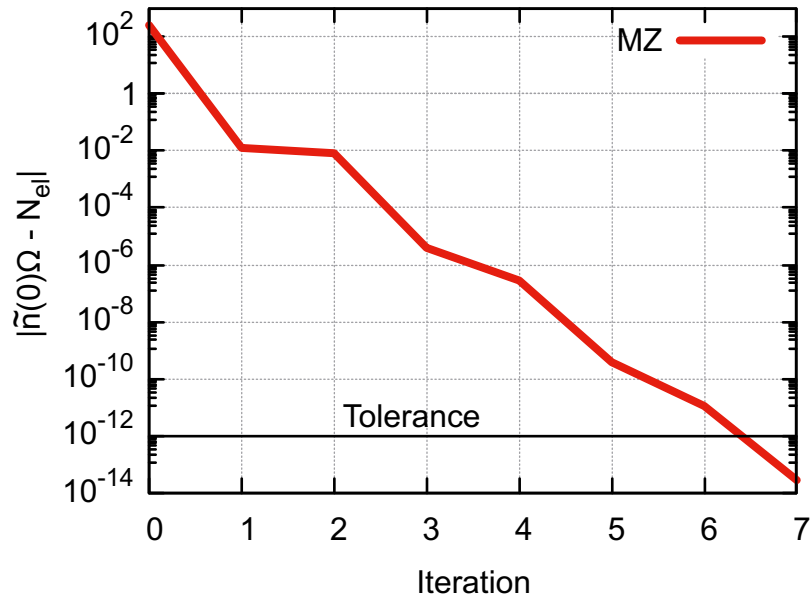


Fig. 8.5 Absolute value of the difference between the number of electrons computed at each step in the iterative procedure and the target value of $N_{el} = 250$. The path to convergence is shown for a single constrained dynamics minimization in the run, tolerance is set to 10^{-12} .

is kept free in this approach but is seen to evolve rapidly during the minimization procedure to converge to the correct value.

We conclude by illustrating the scaling properties of the mass-zero constrained algorithm for orbital-free DFT dynamics with respect to the number of degrees of freedom. In particular, we have tested the performances of the algorithm at fixed basis expansion cutoff $\frac{G_c^2}{2} = 5 E_h$ but varying the number of particles, N_I , and adjusting the size of the box so as to keep the density constant. Figure 8.6 shows the total time employed for calculating the electronic density in a set of runs of equal length (2500 steps) with $N_I = 16, 54, 128, 250, 432, 1024, 2000$. The algorithm

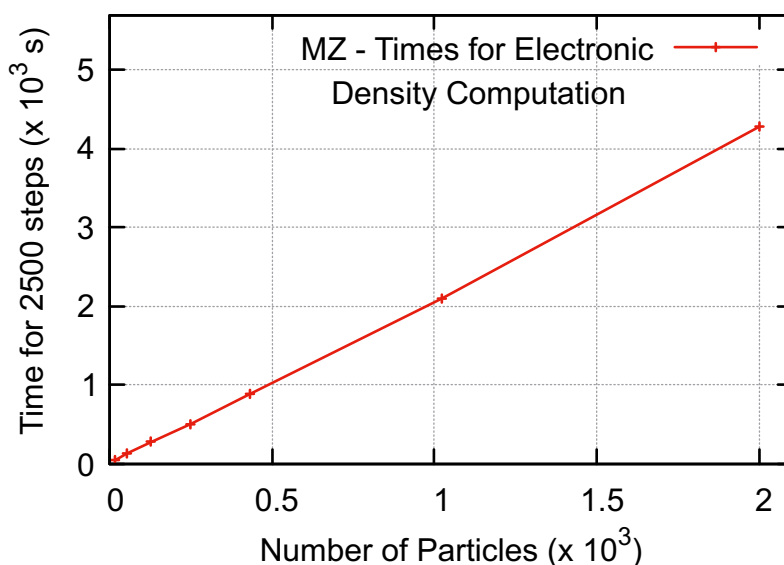


Fig. 8.6 The total time (walltime) spent in the computation of the electronic density for a simulation of 2500 steps of a system of $N_I = 16, 54, 128, 250, 432, 1024, 2000$ particles.

shows an essentially linear scaling with the dimensionality of the system and the average number of iterations per timestep is basically constant for all system sizes analyzed. A similar performance is observed, at fixed number of ions $N_I = 250$ and box length $L = 15.88 \text{ \AA}$, when varying the expansion cutoff G_c . Table 8.2 reports the total time of the simulation spent in the computation of the electronic density for a run of 2500 steps as a function of the cutoff and the number of grid points in reciprocal space. The scaling with respect to the number of grid points is linear, leading to a $\frac{3}{2}$ power law as a function of cutoff. Here again the number of iterations to reach convergence is constant and independent on the reciprocal grid cutoff. These results further demonstrate the robustness of the mass-zero constrained approach and its potential for large scale calculations.

Table 8.2 Scaling of the mass-zero constrained algorithm. Column one (two) reports different energy cutoffs for the plane waves (number of reciprocal grid points). In column three we show the average number of iterations to convergence in a run of 2500 steps, while in the fourth column the total time needed to compute the electronic density is indicated.

Energy cutoff (E_h)	Reciprocal grid points	Average iterations to convergence	Time to converge (s)
5	17969	3.25	486.03
10	45563	3.26	1178.2
15	83188	3.20	2149.6
20	125024	3.23	3366.9

8.6 Summary

In this chapter, we have shown how the mass-zero constrained dynamics can be adapted to the interesting case of Born-Oppenheimer *first principles* molecular dynamics for the so-called orbital-free approach to DFT. The model was used to derive the equations of the system in the complex field and to show that, notwithstanding some complexity, the algorithm can be made to scale linearly with the system size. The model was also used to illustrate in some detail the extension of the approach for these systems when a single additional condition must be fulfilled. The procedure can be easily extended to the case of multiple additional conditions, thus enabling to tackle also Kohn-Sham DFT propagation.

A proof-of-principles calculation of the usefulness of the mass-zero constrained approach for *first principles* molecular dynamics in the orbital-free DFT approximation is presented. The method is shown to be very efficient and a promising alternative to existing schemes. The algorithms have been extensively tested for a simple form of the energy functional employing the Thomas-Fermi kinetic energy, LDA exchange-correlation, and a simple pseudopotential for Sodium with excellent results with up to 2000 atoms. This gives us confidence that orbital-free DFT MD simulations using MaZe with 1000's of particles are possible, paving the way to challenging applications. To achieve this, some optimisation of the code used is needed together with more fundamental developments to implement modern kinetic energy functionals leading to a state-of-the-art level of accuracy. The code now enables use of any functional in the lib_xc library, including GGA kinetic energy functionals such as the von Weizsäcker functional. The nonlocal Perrot kinetic energy functional

has also been implemented. Future work will address the issue, of both analytical and implementative nature, of including more general, nonlocal functionals, *e.g.* Wang-Teter [196, 197] and Huang-Carter [198], keeping the linear scalability of the method. Preliminary tests on GGAs are encouraging but a complete assessment of the efficiency for this more general class of functionals will be necessary.

8.7 Appendix: Standard Ewald Summation for Nuclei

It is interesting to derive the standard expressions for the long-range term arising from nuclear interactions in the electrostatic energy treated through the Ewald summation technique. The starting point of the derivation is the sum over the reciprocal vectors in Eq. (8.23), the definition of total and core density in reciprocal space given in Eqs. (8.20) and (8.21) and the expression of the structure factor specified in Eq. (8.22). Using Eq. (8.20) it is possible to expand the summation over reciprocal space of the electrostatic energy of a periodic system as

$$E_{\text{ES}}^{\text{lr}} = 4\pi\Omega \sum_{\mathbf{G}>0} \frac{|\tilde{n}^{\text{t}}(\mathbf{G})|^2}{G^2} = 4\pi\Omega \sum_{\mathbf{G}>0} \frac{|\tilde{n}(\mathbf{G}) + \sum_{I=1}^{N_I} \tilde{n}_I^{\text{c}}(\mathbf{G}) S_I(\mathbf{G})|^2}{G^2} \quad (8.109)$$

which can be written developing the modulus squared as

$$E_{\text{ES}}^{\text{lr}} = 4\pi\Omega \sum_{\mathbf{G}>0} \frac{1}{G^2} \left\{ |\tilde{n}(\mathbf{G})|^2 + \left| \sum_{I=1}^{N_I} \tilde{n}_I^{\text{c}}(\mathbf{G}) S_I(\mathbf{G}) \right|^2 + \tilde{n}^*(\mathbf{G}) \sum_{I=1}^{N_I} \tilde{n}_I^{\text{c}}(\mathbf{G}) S_I(\mathbf{G}) + \tilde{n}(\mathbf{G}) \left[\sum_{I=1}^{N_I} \tilde{n}_I^{\text{c}}(\mathbf{G}) S_I(\mathbf{G}) \right]^* \right\} \quad (8.110)$$

Substituting the expression for the core density in reciprocal space, Eq. (8.21), one gets

$$E_{\text{ES}}^{\text{lr}} = 4\pi\Omega \sum_{\mathbf{G}>0} \frac{1}{G^2} \left\{ |\tilde{n}(\mathbf{G})|^2 + \frac{e^{-\frac{G^2}{4\alpha_{\text{IJ}}^2}}}{\Omega^2} |\rho(\mathbf{G})|^2 - \frac{2}{\Omega} \sum_{I=1}^{N_I} Z_I \exp \left[-\frac{G^2 R_I^{\text{cut}2}}{4} \right] \Re \left[\tilde{n}^*(\mathbf{G}) S_I(\mathbf{G}) \right] \right\} \quad (8.111)$$

where $\rho(\mathbf{G}) = \sum_{I=1}^{N_I} Z_I S_I(\mathbf{G})$ and the factor $\alpha_{IJ} = \sqrt{R_I^{\text{cut}2} + R_J^{\text{cut}2}}$ has been introduced in Section 8.2. The long-range contribution to the electrostatic energy can then be recast in the form

$$E_{\text{ES}}^{\text{lr}} = 4\pi\Omega \sum_{\mathbf{G}>0} \frac{|\tilde{n}(\mathbf{G})|^2}{G^2} + \frac{4\pi}{\Omega} \sum_{\mathbf{G}>0} \frac{e^{-\frac{G^2}{4\alpha_{IJ}^2}}}{G^2} |\rho(\mathbf{G})|^2 - 8\pi \sum_{\mathbf{G}>0} \sum_{I=1}^{N_I} Z_I \frac{e^{-\frac{G^2 R_I^{\text{cut}2}}{4}}}{G^2} \Re \left[\tilde{n}^*(\mathbf{G}) S_I(\mathbf{G}) \right] \} \quad (8.112)$$

It is now also clear why we need to include the contribution from the assumption made on the core potential in the pseudopotential term (see, in particular, Eq. (8.32)). To obtain the correct expression for the interactions between nuclei and electrons — computed in the pseudopotential term — it is necessary to compensate for the assumption made in the Ewald treatment of the ionic electrostatic interactions. Comparing the last term of Eq. (8.112) with Eq. (8.31) a term

$$\tilde{V}_I^{\text{core}}(G) = \frac{4\pi Z_I}{G^2} \exp \left[-\frac{G^2 R_I^{\text{cut}2}}{4} \right] \quad (8.113)$$

has to be added to the expression of the pseudopotential in reciprocal space. Using again the properties of the Bessel function to compute the spherically symmetric 3D Fourier Transform we obtain an expression for the core potential in direct space given by

$$V_I^{\text{core}}(r) = \frac{1}{2\pi^2} \int_0^\infty dG V_I^{\text{core}}(G) G^2 j_0(Gr) = \frac{Z_I}{r} \text{erf} \left[\frac{r}{R_I^{\text{cut}}} \right] \quad (8.114)$$

which is the expression used in Eq. (8.32).

Chapter 9

Conclusion

The work presented in this thesis covers multiple topics, which can be basically framed in two macroareas: The study of the behaviour of different systems under the action of time-reversal operations and the developments of a new technique for the simulation of adiabatically separated systems based on molecular dynamics with constraints.

Building on previous work [1, 19] we have shown not only that the invariance of a system of particles under the action of the standard time-reversal phase-space transformation is a sufficient but not necessary condition for the system to be defined time-reversal invariant, but also that the transformations that allow such definitions are more than what is usually assumed in the literature [20]. Under rather common hypotheses for the interaction potential, it has been shown that a system of interacting particles can admit up to eight independent time-reversal transformations, with the addition of the ones derived by the composition with the geometrical symmetries of the system [59]. The number of such time-reversal symmetries is reduced by the applications of external fields. The presence of an external magnetic field reduces by half the number of available symmetries, but the system remains time-reversal invariant under the action of the remaining four. The same thing happens with the application of an external electric field. In this case, the broken symmetries are different from the magnetic-field case, an obvious example being the standard time-reversal transformation, which remains valid contrarily to the case when a magnetic field is present. Simultaneous action of external electric and magnetic field further

reduces the number of available symmetries, but at least one transformation survives, leaving the definition of time-reversible system valid for these systems.

Using these new transformations, it has been possible to reinstate statistical mechanics results which were not believed to be true for systems under the action of constant external electromagnetic fields or other isomorphic situations (*e.g.* systems under shear or rotating with constant angular velocity). In Refs. [1, 19, 20] it has been proven that the Kubo relations for time-correlation functions can be derived for systems of particles under the action of a single external magnetic field. This completely bypasses the state-of-the-art approach, where the additional hypothesis on the inversion of the field is considered necessary in order to recover the standard time-reversal transformation. Using the symmetries introduced in Refs. [19, 20] this additional hypothesis was avoided and standard relations have been reinstated for systems under the action of the same magnetic field. An immediate corollary of this result is that it is possible to theoretically predict the cancellation of some of the off-diagonal components of transport tensors such as diffusion and conductivity in different situations. Moreover, it is now clear that systems of isotropically interacting particles under external magnetic fields do not need the modification of the Onsager reciprocal relations *à la* Casimir.

The same strategy developed for Kubo and Onsager relations has been used for another set of statistical mechanics formulae which are usually believed to behave differently when magnetic fields are present, the fluctuation theorems. The presence of valid time-reversal symmetries made it possible to derive transient and steady-state fluctuation relations for system under the action of magnetic fields. In Ref. [21] a theoretical discussion has been presented for isokinetic and canonical ensemble. In Ref. [22] simulations have been performed for a realistic NVT system of NaCl, in order to show the validity of the transient fluctuation relation. The results obtained are in very good agreement with the theoretical predictions.

The second part of the thesis focuses on the development of a new method for the simulation of adiabatically separated systems using the method of massless constraints. The mass-zero constrained algorithm (MaZe) originated from the necessity of including the polarization effects in the simulations of Calcium Fluoride [67], but the algorithm turned out to be applicable to more general problems which include two sets of adiabatically separated variables. Many methods are available in the literature to deal with these kinds of problems, but they all suffer from stability and efficiency

issues, justifying and highlighting our effort for methodological development in this area.

The idea at the roots of MaZe is to recognize that the adiabatic condition — the condition for which the dynamics of the massive variables of the system is performed at the minimum of the energy function(al) with respect to some additional variables — can be expressed as a holonomic constraint. This allows the dynamical system to be written in terms of an extended Lagrangian and to derive the equations of motion using the method of undetermined Lagrange multipliers. Thanks to a rigorous zero-mass limit, the dynamics of the additional variables is proven to be governed only by constraint forces, while the equations of motion for the massive degrees of freedom only depend on the additional variables through the interaction potential. The adiabatic separation is enforced rigorously in this method and it has been proven that the dynamics samples the correct Born-Oppenheimer probability distribution. The method can also include in a natural way additional kinematic conditions on the auxiliary variables of arbitrary number and form, such as orthonormality conditions or electroneutrality constraints. The dynamical system can be numerically solved using a combination of Verlet algorithm and SHAKE or velocity-Verlet and RATTLE. The algorithm is proven to be symplectic and time reversible and is consequently expected to be stable regardless the length of the simulation.

The efficiency and versatility of the algorithm was demonstrated in different fields of molecular dynamics simulations. A shell-model of Sodium Chloride is simulated [23] and compared with available alternatives for Born-Oppenheimer simulations (conjugate-gradient minimization). As expected, phase-space trajectories and observables computed with the two methods are exactly equal up to numerical precision. MaZe, on the other hand, proved to be more efficient than the alternatives for this particular model. The same qualitative results are also obtained for simulations of supercapacitors using the so-called fluctuating charge model [25]. For this particular application, the enforcement of additional conditions has also been tested for the electroneutrality constraint of the metallic double layer. In this case too, the MaZe algorithm proved to be more efficient of state-of-the-art iterative alternatives like the conjugate-gradient procedure and as fast as other minimization methods such as the matrix-inversion method. Finally, the field of *ab initio* simulations has been probed through the implementation of the MaZe algorithm for an orbital-free DFT simulation [24, 115] of solid Na. The good results obtained for the other applications are confirmed also in this case. The MaZe algorithm performs much better than the

brute-force conjugate-gradient in all the tests examined. Again, the enforcement of additional conditions, in this application represented by the conservation of the number of electrons, is accomplished in a natural and efficient way by the algorithm.

The work presented here paves the way to several developments that will be pursued in the future. The numerical study of fluctuation relations in the presence of magnetic fields has to be completed by the calculations of the steady-state relation and by an analysis of the correlation term (Eq. (2.36) of Section 2.2) as done in previous studies without magnetic field [70]. This is not expected to present any formal or technical difficulty with the exception of the high computational time demanded by the numerical experiment. Indeed, for these kinds of simulations the choice of the intensity of the dissipative field is delicate and can strongly affect the time needed to get a good statistics: Choosing a high value for the field would reduce the time necessary for reaching the steady state but it would make very hard the accumulation of statistics for negative value of the dissipation, which will spend most of the time oscillating closely around its mean value. Preferring a low value of the intensity of the field, on the other hand, would improve the statistics of negative values of the dissipation once the steady state is reached, but reaching the steady state could take a very long time. Moreover, the brute-force computation of conditional averages like the one in Eq. (2.36) are known to be very demanding and inefficient from a computational point of view. For this reason it would be interesting to tackle the problem under the perspective of biased dynamics, such as the blue-moon ensemble [104].

The results discussed in the area of simulations of adiabatically separated systems also leave room for future developments. From a computational point of view, MaZe currently employs the SHAKE iterative scheme, essentially equivalent to the Newton-Raphson algorithm, to determine the values of the Lagrange multipliers necessary for the propagation of the dynamics of the additional variables. This approach has proved accurate and efficient in a vast set of applications, but experience shows that convergence can be slower when the constraint matrix is not diagonally dominant. Furthermore, the evaluation of this matrix requires computing first derivatives of the constraint that correspond to the second derivatives of the potential (or the energy functional) with respect to the auxiliary variables. Even though our preliminary tests have shown that this can be compensated by faster convergence with the number of iterations, this introduces a nonnegligible computational overhead with respect to alternative schemes that only require first derivative evaluations. Future work

should be directed to the reduction of the computational cost of MaZe. This could be achieved, for example, by exploring quasi-Newton methods, *e.g.* the L-BFGS approach [199–201], that estimate the derivative of the constraints based on the values of the constraints at previous steps while, at the same time, reducing the number of iterations by improving the choice of the starting point in each iteration *via* predictor methods [96, 171, 174, 202] and/or adapting preconditioning-like techniques to enhance diagonal dominance of the problem.

From the point of view of technological applications, the natural continuation of Chapter 7 is the simulation of polarizable electrolytes within constant potential electrodes. The theoretical basis for such an extension has been laid already in Section 7.3 through the definition of the interaction potential and of the equations of motion to be numerically integrated. The application of MaZe to these systems not only does not seem to present any formal difficulties, but it also represent a very promising alternative to other iterative schemes which have been tried in the past and which proved slow in converging and unstable. The MaZe approach provides a unified framework in which all variables are subject to holonomic constraints of the same nature. The techniques developed for orbital-free density functional theory (such as the homogeneous limit or the over-relaxation scheme) would represent useful tools aimed at improving the efficiency and stability of the iterations for these applications too.

In the framework of first principle molecular dynamics, orbital-free DFT have proven to be a very promising, cost-effective alternative to other more accurate and widespread methods like the Kohn-Sham method. Nonetheless, developing reliable and transferable kinetic-energy functionals for general systems (and for different phases of matter) is an open challenge that prevents universal use of the method. For this reason, the so-called Kohn-Sham method has been developed to overcome the difficult issue of the kinetic energy functional. This approach replaces the exact kinetic energy functional with the one corresponding to a noninteracting electron gas with the same density as the system of interest. A set of N orthonormal orbitals is then introduced and the density defined as the sum of the square of their modulus. Following this approach, it is possible to express the energy as a functional of these orbitals and it can be shown that minimisation with respect to the orbitals leads to the correct ground state. Additional holonomic constraints are imposed to enforce orthonormality of the orbitals along the trajectory. Kohn-Sham is the most used method for first principles molecular dynamics and it is implemented in the vast

majority of community codes. MaZe is perfectly suited for this framework. There are different issues that should be tackled for this task. As the Kohn-Sham orbitals are now the auxiliary variables, the kinetic energy takes a simple bilinear form, but the corresponding Coulomb, pseudopotential and exchange-correlation energy second derivatives (necessary to compute the SHAKE matrix in MaZe) must be expressed in a form suitable for MaZe. Particular attention should be taken in keeping the same scaling properties as the Car-Parrinello MD, for example by avoiding the explicit calculation of matrices of second-derivatives using only matrix-vector products. A second important difference with orbital-free DFT is the presence of orthonormality constraints. In Section 6.2 it has been shown how such auxiliary constraints can be naturally incorporated in MaZe. There remains however a gauge freedom, since any unitary transformation of the Kohn-Sham orbitals is permitted. Fixing this gauge is not necessary in Car-Parrinello MD, but tests will be necessary to understand whether this is the case also with MaZe. If not, the gauge can anyway be fixed by enlarging the set of auxiliary constraints. In fact, this can be turned in an advantage by exploring the possibility to fix the gauge propagating Maximally Localized Wannier Functions (MLWFs). These functions have proved very useful for interpreting the electronic structure of simulated systems [203–205] or in the framework of vibrational spectroscopy [206]. However, they usually require a computationally expensive optimisation step along the dynamics. A tentative dynamical approach to compute them was proposed by M. Tuckerman some time ago [207]. The formalism of MaZe can in principle naturally include such auxiliary constraint on the orbital gauge.

Finally, the two parts of this thesis should be connected by extending the mass-zero constrained dynamics to system in external magnetic field. This generalization leads, however, to a new challenge. The evolution equations for these systems, in fact, contain a force term proportional to the time-derivative of the auxiliary variables. For charge-based models, like the shell model, this term is the analogous of the Lorentz force, and a similar term is found in models involving dipoles [208, 209]. As a consequence, the constraints now contain an explicit dependence on the velocity and are nonholonomic, *i.e.* outside the scope of current constrained molecular dynamics. These constraints are, however, affine in the velocity, indicating that a Lagrange multiplier formalism can still be applied to solve the dynamics [210, 211]. Indeed, a similar approach has already been tried in the context of the molecular dynamics sampling of the isokinetic ensemble [212] and more in general for numerically

solving problems with nonholonomic constraints [213–215]. Among other things, this generalization would also allow to tackle the problem of the simulation of superionic conductors in magnetic field beyond the rigid ion model.

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